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### **Review**

# Single-molecule nano-optoelectronics: insights from physics

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#### Abstract

Single-molecule optoelectronic devices promise a potential solution for miniaturization and functionalization of silicon-based microelectronic circuits in the future. For decades of its fast development, this field has made significant progress in the synthesis of optoelectronic materials, the fabrication of single-molecule devices and the realization of optoelectronic functions. On the other hand, single-molecule optoelectronic devices offer a reliable platform to investigate the intrinsic physical phenomena and regulation rules of matters at the single-molecule level. To further realize and regulate the optoelectronic functions toward practical applications, it is necessary to clarify the intrinsic physical mechanisms of single-molecule optoelectronic nanodevices. Here, we provide a timely review to survey the physical phenomena and laws involved in single-molecule optoelectronic materials and devices, including charge effects, spin effects, exciton effects, vibronic effects, structural and orbital effects. In particular, we will systematically summarize the basics of molecular optoelectronic materials, and the physical effects and manipulations of single-molecule optoelectronic nanodevices. In addition, fundamentals of single-molecule electronics, which are basic of single-molecule optoelectronics, can also be found in this review. At last, we tend to focus the discussion on the opportunities and challenges arising in the field of single-molecule optoelectronics, and propose further potential breakthroughs.

Keywords: single-molecule optoelectronics, spin effect, exciton effect, vibronic effect, structural and orbital effect

(Some figures may appear in colour only in the online journal)

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#### 1. Introduction

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Single-molecule optoelectronic devices, using a single molecule as a functional unit between two electrodes, are expected to become a potential solution to overcome the

72 increasing difficulties and fundamental limitations faced by further miniaturization of traditional semiconductor devices 73 and promote a higher optoelectronic performance [1-9]. 73 For decades, single-molecule optoelectronic devices have been constructed to achieve various device functions, such 74 as photovoltaics [10], electroluminescence [11], switching [12], rectification [13, 14] and field-effect transistor [15]. In 74 addition to satisfying the requirements for functional realization, single-molecule optoelectronic devices also provide a 74 platform for exploring basic chemical and physical laws at the single-molecule level, including charge effects, spin effects, exciton effects, and vibronic effects, etc. Furthermore, it is 76 possible to study the interactions between single molecules 78 and external fields, as well as the regulation of single-molecule 78 properties.

Organic optoelectronic materials, especially smallmolecule optoelectronic materials, such as semiconductor molecules [16], photo-isomeric molecules [7, 12], redox 80 molecules [14, 17, 18] and magnetic molecules [19, 20], are generally opto- or electro-active. Because of their rich optoelectronic properties, these materials can be used to fabricate various optoelectronic devices. According to their electrical conductivity and optical behavior, they are applied for many applications in optoelectronics, including photodetectors [21, 22], rectifiers [23, 24], field-effect transistors [15, 16], light-emitting diodes [25], photovoltaic devices [10], and so on. Therefore, understanding the intrinsic electrical, optical and mechanical properties of optoelectronic materials, and the interaction between optoelectronic materials and external fields is the basis for further improving device performances. Since the single-molecule behavior reflects the intrinsic physical mechanism, it is of great significance to study the properties of optoelectronic materials at the single-molecule 90 level. Through single-molecule investigations, a series of significant electronic, photonic, phononic and magnetic behaviors of optoelectronic materials can be obtained, and the related charge effects [26], spin effects [27], vibration 92 effects, photoelectric effects and quantum effects [28] can be revealed. 93

Here, we provide a comprehensive and timely review of the physical phenomena and mechanisms involved in singlemolecule optoelectronic materials and devices. Firstly, we briefly introduce the fundamentals of single-molecule devices, including their design, fabrication, and inherent charge transport mechanisms. Then, from the perspective of charge effects, spin effects, exciton effects, vibration effects, structural and orbital effects, we systematically summarize the molecular material basis, physical mechanism, manipulation and application of single-molecule optoelectronic nanodevices. Finally, we tend to focus the discussion on the opportunities and challenges in the field of single-molecule optoelectronics, and propose further potential breakthroughs.

#### 2. Fundamentals of single-molecule devices

Single-molecule devices refer to devices that use single molecules as active electronic components to fabricate electronic circuits, especially optoelectronic devices. Generally, a single molecule is connected to two electrodes by anchor groups, realizing charge transport in the devices. Based on this concept, various single-molecule devices have been developed to satisfy the functional requirements of different scenes. In a single-molecule device, lots of key factors can affect the electrical properties, such as the electrode, anchor group, utilized molecule, and fabrication method. Here, the properties of these components and their impact on the single-molecule devices will be discussed.

#### 2.1. Design of single-molecule devices

The electrical properties of single-molecule optoelectronic devices depend on the well-defined optoelectronic structure. Each component can provide a variety of possible options in the construction of devices, resulting in different functions and applications. In this section, the structure of single-molecule devices, the role of electrode materials, anchor groups, and bridge components are explained.

2.1.1. Structure of single-molecule devices. The device stability is a necessary prerequisite for realizing its properties in a single-molecule device. Here, we introduce three components in the device architecture: the electrodes, the anchor groups and the bridge molecules (figure 1) [2]. The electrodes in single-molecule devices include a source electrode and a drain electrode in a two-terminal device, while in a three-terminal system, an additional gate electrode ie needed. The whole bridge can be used as a conductive channel. In some cases, the ends of the bridge may be used to adjust the molecule/electrode coupling, and the central group usually serves as the functional center. The bridge is connected to electrodes by anchor groups to form a single-molecule device. During the charge transport process, the charge transfers (CT) from the source electrode to the drain electrode through the bridge, and the gate electrode can be used to manipulate the charge transport properties by shifting the energy level alignment between the molecule and the Fermi level of the electrode.

2.1.2. Electrode materials. The basic principle of singlemolecule devices is to fabricate electrode-molecule-electrode junctions, in which electrodes have a significant effect on charge transport through the devices. The suitable electrodes should have the good chemical stability in ambient environments and compatibility with various molecules. According to the electrode materials, the widely used electrodes include metal electrodes and carbon-based electrodes. In single-molecule devices formed by mechanically controllable break junction (MCBJ), scanning tunneling microscopy break junction (STM-BJ), electromigration break junction and conductive atomic force microscopy break junction (AFM-BJ), gold (Au) is the mostly used electrode material due to its high chemical stability and electrical conductivity. Au electrodes can connect with a broad range of anchor groups, providing the extraordinary reproducibility for single-molecule devices. The single Au–Au bridge has a quantum conductance of  $1G_0$  $(G_0 = 2e^2/h)$  with a value of  $\sim 77 \ \mu$ S. The Fermi energy  $(E_F)$  of Au is  $\sim$  -5.1 eV in vacuum and shifts by 0.6 eV to  $\sim$  -4.5 eV in water because water possesses a permanent dipole moment,

which will be strongly oriented when approaching the metal surface [29]. In addition, other metals have also been used to fabricate single-molecule devices, including Ag, Pt, Pb and Pd, which all have special characteristics. For example, Pt has stronger *d*-orbital characteristics and a larger local density of states (DOS) near the Fermi level, resulting in a strong substrate–molecule coupling [30, 31]. In comparison with Au electrodes, these metals may have a stronger bond strength for some anchor groups. For example, the conductance for alkanedithiols on Pt electrodes is  $\sim$ 3.5 times higher than that on Au electrodes [29]; the conductance for acetylene-terminated oligophenylenes on Ag electrodes is  $\sim$ 10 times higher than that on Au electrodes [32]. However, the higher chemical reactivity with oxygen, especially for Ag, limits its use.

Although there are lots of single-molecule devices based on metal electrodes, some inevitable disadvantages still exist, including the poor biocompatibility, the low stability of the connection and the formation of multiple covalent or dative bonds on the electrodes. In addition, the relatively high atom mobility, especially for Au, leads to the thermodynamical instability of metal electrodes or wires at several nanometers at room temperature. Furthermore, an electric field can accelerate the migration of atoms, which greatly limits the further miniaturization of metallic electrodes, especially for Au.

In these aspects, carbon-based electrodes, including carbon nanotube and graphene, have attracted large attention in single-molecule devices because of their extraordinary electronic properties, providing the complementary materials to metals. Specifically, single-walled carbon nanotubes (SWC-NTs) can be classified into metallic and semiconducting types, which have exceptional electrical, physical, and thermal properties. The conductance of semiconducting SWCNTs has a high on/off ratio and can be easily regulated, while metallic SWCNTs are suitable for the connection of molecular bridges in electrical devices [33–35]. In particular, the transport current capability of carbon nanotube can reach  $\sim 10^9$  A cm<sup>-2</sup>, while that of copper cannot reach because when the current capability is above  $10^6$  A cm<sup>-2</sup>, electromigration happens [36].

Graphene, another typical carbon material, possesses zerobandgap semimetal characteristics, has received significant attention because of its special molecular structure, electronic structure and high-temperature stability. Specifically, the charge carriers in graphene behave like massless Dirac fermions and can move freely in graphene. Furthermore, they are independent on temperature, indicating that they are limited by defect scattering. Therefore, in general graphene has linear current–voltage (I-V) characteristics. Similar to SWC-NTs, the current capability of graphene is high, which can reach ~10<sup>8</sup> A cm<sup>-2</sup> [37].

In a word, both graphene and SWCNTs show some advantages in single-molecule devices. The extremely thin electrodes can be prepared by single-layer graphene or SWCNT on the sub-nanometer scale, which provides an effective method for further miniaturization of single-molecule devices. Especially in a field-effect device, in comparison with thicker metallic electrodes, thin carbon-based electrodes can reduce the screening of the applied gate-field, thereby improving the gate regulation efficiency in the transistor. Furthermore, the



Figure 1. Schematic diagram of a single-molecule device with three components: electrodes, anchor groups and bridge. Reproduced from [2], with permission from Springer Nature.

well-defined covalent bond connection between carbon-based electrodes and anchor groups of the bridge can present the high compatibility with different substrates, such as hard and soft substrates.

2.1.3. Anchor groups. The anchor group of single molecules is the key to connecting them to electrodes in single-molecule devices through chemisorption or physisorption, which determines the stability, formation probability and charge transport characteristics of the devices. For carbon-based electrodes prepared by oxygen plasma etching, carbon nanotube and graphene electrodes can be modified with carboxyl groups and connected with amine end groups of the molecules through covalent amide bonds [38]. In addition,  $\pi-\pi$  stacking is also an effective way to connect the molecular bridge and carbon electrodes, such as pyrene and phenanthrene [39, 40]. Here, we mainly introduce the terminal groups that can be bonded with gold electrodes (figure 2), since Au is widely used as metal electrodes.

In general, desirable anchor groups should provide relatively high conductance and high stability in ambient environments. Thiols (-SH) are the most widely used anchor groups in single-molecule devices because of their convenience and high probability of junction formation. Thiols can form -RS-Au covalent bonds in solution with a conductance peak at  $\sim$  3.3  $\times$  $10^{-6}G_0$  for 1,12-dodecanedithiol with a binding energy of  $\sim$ 40 kcal mol<sup>-1</sup>, while –RSH–Au dative bonds are formed in the air with a lower conductance peak at  $\sim 9.0 \times 10^{-7} G_0$ . This difference is attributed to the different binding energies between sulfur and gold. In solution measurements, the thiol hydrogen is lost during bond formation and the covalent bond is formed. In contrast, the thiol hydrogen remains intact in the air, so there is no significant chemical change when the molecule interacts with gold. This implies that the excess molecules around high-energy, under-coordinated surface gold sites are a prerequisite for the cleavage of thiol sulfur-hydrogen bond [41]. Meanwhile, thiols have some disadvantages as well. In specific, thiols can readily react with oxidants and electrophiles especially bonded to the aromatic backbone, which leads to the poor stability of sulfhydrylcontaining molecules. Due to different contact geometries (i.e., top-hollow and top-top geometries) of thiols and gold, there may be a five-times difference in conductance [42]. In addition to thiol, methyl sulfide (-SMe) can form a stable dative bond with Au through the delocalization of the lone pair electrons to under-coordinated gold atoms in single-molecule devices. Similarly, methyl selenide (-SeMe) can also form a dative bond with Au [43]. Carboxylic acid (–COOH) can be also bonded to Au electrodes with Au–O bond strength of  $\sim$ 2 kcal mol<sup>-1</sup>. Due to protonation or deprotonation, the binding strength between –COOH and Au is sensitive to the pH. In addition, the deprotonated –COOH with a negative charge will enhance the binding strength with Au [44].

Nitrogen terminated molecules are also popular to be bonded to Au, including amines (-NH<sub>2</sub>), pyridine (-Py), nitrile (-CN) and isonitrile (-NC). The amines can be bonded to metals as two-electron donors to fabricate the singlemolecule devices by dative bonds. The binding strength and ability between NH<sub>2</sub> and Au are also sensitive to the pH. At low pH, the protonated NH<sub>2</sub> has a weak ability to bind Au because the N atoms donate their lone pairs of electrons to H ions. Pyridine also presents relatively high conductance, high formation probability and stability in single-molecule devices due to the higher binding energy. NH<sub>2</sub> and Py terminated diphenylacetylenes have a similar conductance [45, 46]. In addition, nitrile can form the dative bond with Au as well. By comparing these nitrogen terminal groups, the binding strength follows the sequence of  $Py > CN > NH_2$ , while the stability and formation probability follow the sequence of Py > $NH_2 > CN$  [47]. Generally, Py and CN have well chemical stability in solution in comparison with NH<sub>2</sub>. When a double layer is present around the tip, as the tip bias increases, the dative bond between NH<sub>2</sub> and Au can be converted to a covalent bond by removing an electron and a proton [48]. In addition, dimethyl phosphines (-PMe<sub>2</sub>) can bind Au with higher strength and lower contact resistance than NH<sub>2</sub>. Specifically, the contact resistance of PMe<sub>2</sub> and NH<sub>2</sub> are  $\sim$ 130 k $\Omega$ and  $\sim 370 \text{ k}\Omega$ , and the binding strengths of PMe<sub>2</sub> and NH<sub>2</sub> are  $\sim 0.6 \text{ eV}$  and  $\sim 1.2 \text{ eV}$ , respectively [49]. In particular, in comparison with the -SH, the contact geometry of Au-NH<sub>2</sub> dative bond has a weaker influence on conductance due to the isotropic coupling of the N lone pair to Au electrodes [50]. The NH<sub>2</sub>-Au connection has a larger connection resistance, measured in oligophenylene as  $\sim 189 \text{ k}\Omega$ , while the contact resistance of S–Au interfaces is  $\sim 40 \text{ k}\Omega$  [32].

Furthermore, some weak interactions between anchor groups and electrodes can form a stable connection in singlemolecule devices. For example, the Coulombic interaction between Au and the positively charged pyridinium terminal groups serves as an efficient electrostatic way to form singlemolecule devices [51]. Fullerene and oligoacenes can also be used as anchor groups for Au electrodes [52, 53].



Figure 2. Molecular structures of common anchors.

However, the above-mentioned anchor groups present some disadvantages as well, including non-uniform binding geometries, and the poor chemical and mechanical stability. The direct metal-C covalent bond provides a promising solution to realize a well-defined and stable connection in singlemolecule devices with the lower contact resistance. Specifically, trimethyl tin (SnMe<sub>3</sub>) terminal groups can form a covalent Au–C  $\sigma$  bond by replacing SnMe<sub>3</sub> with Au atom at the electrode. The conductance of SnMe3 terminated alkanes is  $\sim 100$  times larger than that of analogous alkanes with most other terminations, such as NH<sub>2</sub> [54]. The trimethylsilyl (TMS) terminated alkynyl moiety can also form covalent Au-C bonds in situ to create a single-molecule device by cleaving the TMS protecting groups in an alkaline solution. The conductance is about 10 times higher than that of dithiol analogs. Meanwhile, this connection route presents a high junction formation probability of  $\sim 90\%$  and the mechanical stability [55]. However, SnMe<sub>3</sub> and TMS assisted Au-C bond formation presents some unavoidable shortcomings, including the use of toxic or deprotecting reagents and significant in situ dimerization. Therefore, the formation of Au-C bond without protecting groups and additional reagents is desirable for the fabrication of single-molecule devices. By depositing molecules on Au electrodes, the alkynyl terminated oligophenylenes can spontaneously form covalent Au-C bonds through in situ deprotonation of the acidic C-H proton of alkynyl groups [56]. When silver (Ag) electrodes are used, alkynyl anchor groups can also form a covalent Ag-C bond through deprotonation. Importantly, the conductance of Ag-based devices is nearly 10 times higher than that of the devices formed with Au electrodes for acetylene-terminated oligophenylenes, because the contact resistance of the acetylene–Ag interface (6 k $\Omega$ ) is significantly smaller than that of the acetylene–Au interface [50, 57].

In addition, both aryl and alkyl iodine atoms can bind Au electrodes to fabricate single-molecule devices, because the iodide group has a higher ability to form halogen bonding with Au. 1,4-diiodobenzene can be attached to Au electrodes to form the molecular device with the conductance of  $\sim$ 3.6  $\times$  $10^{-4}G_0$ , which is smaller than that of 1,4-benzenediamine device  $(\sim 1 \times 10^{-4}G_0)$  [58, 59]. When an electric field is introduced into the system through the supporting electrolyte, two conductance values can be observed. The lower conductance is attributed to the dative Au-I contact and the higher conductance is attributed to the covalent Au-C bond contact, which indicates that the connection changes from dative Au-I contact to covalent Au-C bond by an in situ oxidative addition reaction. In addition, the reaction can be controlled by the applied tip bias. Specifically, the negative tip bias is favorable to the formation of Au-C bond. This generated electric field provides a feasible method to form metal-C bonds [60].

2.1.4. Bridge components. Bridge molecules significantly determine the properties and applications of single-molecule devices. The relative energy position between the bridge molecular orbital and the Fermi level of electrodes will significantly affect the conductance. The bridge is responsible for connecting the electrodes to form a complete single-molecule device, in which the whole bridge may be a conducting channel, while in some cases, the aimed functional group is a part of the bridge. Charge transport through the bridge can be affected by many factors, such as the bridge length, molecular structure of the main chain and side groups. The functionalized bridges with two anchor groups are used in most cases. When a bridge is connected to the electrodes with two anchor groups, the CT mainly through an intramolecular path. In addition to the intramolecular charge transport, the intermolecular charge transport is also an important phenomenon. Some bridges with one or more anchor groups can be used to create special singlemolecule devices, where the charge is transported through an

#### **Table 1.** Representative $\beta$ values for different bridges.

Backbone	Structure	$\beta$ (Å <sup>-1</sup> )	References	
Vacuum		5.5	[63]	
Alkane		0.76 <sup>a</sup>	[54]	
Silane	Si ,	0.39 <sup>b</sup>	[62]	
Germane	Ge	0.36 <sup>b</sup>	[64]	
Alkene		0.22 <sup>c</sup>	[65]	
Alkyne		0.32 <sup>c</sup>	[66]	
<i>p</i> -phenylene		0.43 <sup>a</sup>	[67]	
Thiophene		0.3 <sup>b</sup>	[68]	
Peptide		0.87 <sup>c</sup>	[69]	

 $\beta$  values of oligomeric materials with conductance dominated by coherent-tunneling mechanisms

<sup>a</sup>Anchor group is -SnMe<sub>3</sub>.

<sup>b</sup>Anchor group is –SMe.

<sup>c</sup>Anchor group is –SH.

intermolecular path. In this process, the molecules may present the twisted or stacked features [61]. In addition to the relative energy position between the bridge molecular orbital and the Fermi level of electrodes, the molecule–electrode interface coupling strength also has a significant effect on charge transport. Specifically, a strong coupling may result in the loss of intrinsic functionalities of single molecules and poor gating effects in three-terminal structural devices. Therefore, short segments (i.e., methylene groups) can be introduced into the bridge to change the coupling strength between the functional center and electrodes.

When the whole bridge is the aimed molecule, the effect of the bridge length on charge transport of single molecules have been extensively studied. In the coherent off-resonant regime, the decay value ( $\beta$ ) is an important character to evaluate its conductivity. In brief, higher  $\beta$  means the greater decrease with the increase of per unit length. The more the degree of conjugation in bridges is, the higher the charge transport efficiency will be, therefore leading to a lower  $\beta$  value. Representative  $\beta$  values for different bridges are listed in table 1. Typically, alkanes have a greater  $\beta$  value than aromatic molecules because alkanes are more insulating than aromatic molecules. Conjugated but non-aromatic molecules have lower  $\beta$  values than purely aromatic molecules, such as alkene and alkyne. For example,  $\beta$  values of alkanes, p-phenylene molecules and alkene are ~0.84 Å<sup>-1</sup>, ~0.43 Å<sup>-1</sup>, ~0.22 Å<sup>-1</sup>, respectively. In addition, the  $\beta$  value is closely related to the molecular backbone. Oligosilanes present a more effective transport charge, and the  $\beta$  value of isostructural permethyloligogermanes is ~0.36 Å<sup>-1</sup>, which is much smaller than alkanes [62]. The molecular energy level also has a significant effect on charge transport in single-molecule devices. Changing side groups is an effective way to adjust the CT by changing molecular energy levels. For instance, the electron-donating groups will increase the conductance of 1,4-diamin-obenzene analogs, while electron-withdrawing groups will decrease conductance.

#### 2.2. Fabrication of single-molecule devices

Appropriate electrode materials, interface connections and device configurations are important factors in the construction of single-molecule optoelectronic devices. To date, different fabrication methods have been developed, including mechanical break junctions, electrical breakdown and lithographydefined cutting. These different fabrication methods make it possible to fabricate single-molecule optoelectronic devices using different electrode materials. Generally, metal electrodes are suitable for mechanical break junctions and electrical

Single-molecule junctions	Schematics	Advantages	Reference
STM-BJ	v_ 😴 🕻	Repeatable	[49]
AFM-BJ		Convenient preparation Repeatable	[70]
МСВЈ		Information for mechanics Repeatable	[61]
Electromigration break junction	v <sub>s</sub>	Precise preparation Device configuration	[75]
Carbon nanotube-based junction		Fine compatibility High stability	[91]
Graphene-based junction		Size matching High stability	[92]
	· v	High success rate	

breakdown, while carbon-based electrodes are suitable for lithography-defined cutting and electrical breakdown. Here, different fabrication processes of single-molecule devices are introduced, along with their specific advantages for their applications in nano-optoelectronics (table 2).

2.2.1. Mechanical break junctions. Scanning probe microscopes, typically including scanning tunneling microscopy (STM) and atomic force microscopy (AFM), play a significant role in surface imaging due to their high spatial and temporal resolution. The difference between these two methods is that the tunneling current is used to control the tip position in STM, while the force is used in AFM. STM and conductive AFM-based break junctions have been developed to become a powerful method for the fabrication of singlemolecule devices in situ (figures 3(a) and (b)) [47, 70]. The basic working principle is to form a molecular bridge between two electrodes, meanwhile record the current through the junctions in real time. In one cycle, the tip is precisely manipulated to approach and then move away from the substrate. When the tip approaches the substrate, two contact modes (i.e., soft contact and hard contact) have been applied. Hard contact means that the tip will contact and connect to the substrate, and the rupture of atomic contacts at quantum conductance will be obtained during the stretching of the tip. Soft contact means that when the current increases to the threshold conductance, the tip will withdraw. During the separation process, the target

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molecules can be inserted into the nanogap formed between the tip and the substrate electrode. By changing the distance between the tip and substrate, the bridged molecules can be reduced until only one molecule remains in the nanogap. In this case, a single-molecule device based on STM-BJ or AFM-BJ is formed.

MCBJ is another efficient method to fabricate singlemolecule devices (figure 3(c)), which is firstly used to measure the conductance of a single benzene-1,4-dithiol molecule in 1997 [71]. In brief, the MCBJ instrument includes three parts: a notched metal nanowire-electrode material glued onto the flexible substrate (also named as MCBJ chip), a push rod to fracture the nanowire driven by the piezoelectric actuator and a counter used to bend and support the substrate. The notched metal nanowire can be fabricated by mechanically cutting, electrochemically deposition and nanofabrication. When the push rod moves toward the substrate in the vertical plane, the substrate will bend due to the three-point counter support structure, causing the nanowire to stretch and break at the notch point to form two-point electrodes. Then, the target molecule with specific anchor groups can bridge two electrodes to form a single-molecule device until the whole device breaks during continuous elongation. In the MCBJ setting, a large reduction factor between the piezo elongation and the electrode separation provides a relatively slow loading speed for a molecule with high mechanical stability, which ensures an inherently stable contact of the molecules in



**Figure 3.** Three kinds of mechanical break junctions. (a) Schematic of STM-BJ. Reprinted with permission from [49]. Copyright (2007) American Chemical Society. (b) Schematic of AFM-BJ. Reproduced from [70], with permission from Springer Nature. (c) Schematic of MCBJ. Reproduced with permission from [61]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC 4.0.

single-molecule devices [70]. In addition, a fresh break cross-section will be formed during the connection process in MCBJ experiments, leading to the minimized contaminants involved in the system.

The STM-BJ, AFM-BJ and MCBJ mentioned above can rapidly create amounts of single-molecule junctions, which have been proved to be effective statistical analysis methods for charge transport measurements at the single-molecule level. As the distance between the two electrodes increases, when the nanogap distance is larger than the molecular length, the molecular junction breaks. It should be noted that the breaking process is also related to the binding strength between molecules and electrodes. The greater the binding strength is, the greater the stretched length of the molecule is. Furthermore, these platforms can also be used to study forceinduced conformational transition through the single-molecule electrical characterization, because a force will be applied to the molecule during the stretching process, which is different from the traditional temperature-changing nuclear magnetic resonance (NMR). Specifically, NMR can be used to identify the different isomers, but it reflects the ensemble signal contributed by all the possible isomers from amounts of molecules, while the break junction can identify the different isomers at the single-molecule level. For instance, the conformational isomers of cyclohexane have been identified at room temperature through STM-BJ, while such identification is only feasible at low temperatures by ensemble characterization [72].

Furthermore, break junction platforms also manifest some different characteristics. The electric field can be conveniently integrated into STM-BJ and AFM-BJ [73]. Because of the asymmetrical point-plane electrode configuration of STM-BJ and AFM-BJ, when supporting electrolyte with ions is introduced into the experiments, a dense charge double layer builds up around the small area of the coated tip, and a sparse double layer is formed on the bottom, large-area, uncoated substrate. This resultant asymmetric electronic coupling of molecules at two electrodes will bring about the unique properties of single-molecule devices, such as charge-induced rectification [43, 60, 74].

2.2.2. Electrical breakdown. Electrical breakdown is an important physical phenomenon in the electronic field, which

may result in the failure of materials. One dominant phenomenon of electrical breakdown is the electromigration, which refers to the movement of metallic atoms along the electron flow direction. Specifically, when an electric field is applied, the gradual movement of the atoms in the metal may occur, since the momentum of the moving electrons can be transferred to the metal atom. Traditionally, electromigration has been regarded as a frequently damage in electronic devices. However, this phenomenon can be utilized as a controlled menthod to create a nanogap for single-molecule devices. In comparison with MCBJ, the advantage of the feedback control electromigration is the potential combination with the conventional Si wafer fabrication. Moreover, the formation of the multiple channels on the single-molecule device is available. In particular, when the current is too small to induce significant Joule heating, which is proportional to the square of the current, the metal wires tend to fail at the cathode end. Therefore, the local higher temperature also plays an important role in the breakdown of metal wires because local Joule heating will increase Au mobility and trigger electromigration at a critical temperature [75]. In other words, electrical breakdown through electromigration relies on the combination of high current density and high local temperature, which eventually induces the movement of atoms from their previously fixed position. Generally, the breakdown occurs at the center of the metal wire, where the temperature is highest due to the different thermal expansion coefficients of the wire and the substrate. When constriction occurs, that is, the bow-tie shape, the current and the temperature will be higher than that in other regions. Consequently, this constriction in the nanowire is beneficial to the breakdown.

It is reported that the breaking of the Au wire starts when the local temperature reaches 400 K by Joule heating, which depends on the surrounding temperature (4.2 K, 77 K or 295 K). This threshold temperature is related to the activated behavior of metal atom migration [76]. In addition to Au nanowire, the similar role of Joule heating is observed in the breaking of aluminum (Al) nanowires with a constriction in the central part. When the applied voltage linearly increases of few hundreds of mV every 100 ms, the resistance evolution during the first electromigration process is showed in figure 4(a). Initially, due to the inhomogeneous heating and the temperature dependent resistance, the resistance increases



**Figure 4.** Electrical breakdown for metal and carbon electrodes, and lithography-defined cutting for carbon-based electrodes. (a) The resistance evolution during the first electromigration process for Al wire. Reproduced from [77]. CC BY 4.0. (b) I-V curves during the feedback controlled electromigration process at DC. Reprinted from [79], with the permission of AIP Publishing. (c) Schematic of feedback electromigration at alternative voltage. Reprinted with permission from [80]. Copyright (2020) American Chemical Society. (d) Schematic of the feedback-controlled electroburning process, and the I-V traces of the evolution (green arrow) of the feedback-controlled electroburning. Reprinted with permission from [84]. Copyright (2011) American Chemical Society. (e) The calculated current density profile after bottom electroburning. Reproduced from [86]. CC BY 4.0. (f) Fabrication of SWCNT electrodes by oxygen plasma cutting. From [91]. Reprinted with permission from AAAS. (g) Fabrication of graphene point contact electrodes. Reproduced with permission from [92]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC 4.0.

in the parabolic. In this regime, when the current is reduced from any point, the reversible response is observed, which indicates that the initial geometry is constant and no electromigration will occur. When the voltage further increases, the current decreases with the resistance increase and the curve becomes irreversible, which indicates that the electromigration occurs from point B [77].

The above mentioned verifies the importance of Joule heating in electromigration, but it also presents some drawbacks. Once the constriction is formed, the increased current density and the increased heating will accelerate the atom migration. Excessive heating will also result in the melting of metal wires. Both these effects can result in larger nanogap and metal island. Therefore, in the electromigration breakdown process, the challenge is to precisely control the size and position of the nanogap. To solve this problem, the electromigration breaking is initially carried out in an ultra-low temperature environment by two steps to control the heating. When the metal wire partially breaks as indicated by the increased resistance, the devices is put into the liquid helium to eventually complete the breaking procedure. In this way, a nanogap less than 2 nm can be created between the thin Au film electrodes [78]. In order to create the nanogap with the molecular scale at room temperature, feedback-controlled methods are developed to break the metal wire by precise control of the voltage applied on the devices. Specifically, the current initially increases with the increase of the applied voltage. When a decrease in current is observed, the applied voltage ramps down immediately and then increases again (figure 4(b)). For example, in one cycle, the voltage applied on an Au electrode-device increases at 4 mV s<sup>-1</sup> at the initial stage, and the local heating in the neck will result in the electromigration of Au atoms. When the conductance decreases by a certain threshold percentage, the voltage is sharply reduced at 40 mV s<sup>-1</sup> to present further breaking. Then, repeating this procedure until the metal wire is completely broken, forming a nanogap [79].

In the above electromigration breaking processes, direct current (DC) is used. However, the main driving force of electromigration is closely related to the current direction, which results in tensile stress at the cathode end and compressive stress at the anode end [75]. When the alternate current (AC) is used in feedback control of the electromigration procedure, the high crystallinity electrodes with 1 nm nanogap are created under low temperature in H<sub>2</sub> atmosphere. These created electrodes are large and smooth grains with sharp facets, while the electrodes created by DC are composed of small grains. In addition, the nanogap is approximately in the center between the cathode and the anode (figure 4(c)) [80].

In addition to feedback control electromigration, electromigration assisted self-breaking can also create a nanogap. In this case, a constriction with a few atoms is firstly formed in the metal wire by electromigration. Then, due to the high mobility of Au atoms, the constriction tends to be unstable, gradually forming a nanogap at room temperature without applied voltage. This nanogap created by self-breaking is less likely to form metal islands [81]. Similarly, self-breaking of platinum (Pt) electrodes are observed at temperature above 420 K due to the higher activation barrier, which also indicates that Pt electrodes are more stable than Au electrodes at room temperature [82].

While metal electrode-based single-molecule devices have been widely used, nonmetal materials also present good prospects and variable properties, which may lead to new possibilities for single-molecule devices. Among these nonmetal materials, carbon materials are desirable, including carbon nanotube and graphene. The electrical breakdown of carbon materials has been developed to create a precise and controllable nanogap for the single-molecule devices with carbonbased electrodes [37, 83]. Though these carbon-based electrodes present high current capability, they will ultimately fail at high currents due to the defect formation. As an attractive carbon material, graphene is likely to be more convenient to fabricate single-molecule devices due to its regular planar structure. Similar to the electrical breakdown of metal wires, feedback control electroburning can be used to created graphene electrodes with 1-2 nm gap in atmosphere at room temperature. The feedback control electroburning is similar to electromigration above mentioned [84, 85]. In brief, an applied voltage on the device increases at 1 V  $s^{-1}$ , and the conductance evolution is recorded. When the conductance drops >10% in the past 200 mV, the voltage immediately returns to zero. Then, the voltage increases from zero again until the occurrence of next conductance drops (figure 4(d)). At the end of each cycle, both the conductance and the voltage decrease with the repetition, and graphene is gradually narrowed. The critical current densities of first electroburning are comparable for studied devices, which is independent on the layer number of graphene and near to the breakdown current of single layer graphene. Furthermore, it has been found that the electroburning is a thermal activation process and is related to the oxygen pressure. Due to its higher reactivity with oxygen resulting from the incomplete  $sp^2$ -hybridization at the edge of graphene, the electroburning begins at the edge carbon atoms, predominantly at one side. After the first carbon atom has been removed, the electroburning tends to propagate from there because the temperature—a result of Joule heating—is the highest near this point. When a nanogap is finally created, the resistance of devices increases from 200  $\Omega$ -3 k $\Omega$  to 500 Ω-10 GΩ [84].

Although feedback control electroburning has presented high yield (>95%) for the nanogap formation, it is difficult to precisely control the position of the formed nanogap. Therefore, a constriction is created on the graphene to fabricate the nanogap with both precise position and high yield because the higher current density and consequently the higher temperature at this point [86, 87]. Specifically, single layer graphene is firstly transferred onto the substrate and processed by electron beam lithography (EBL) and oxygen plasma etching to fabricate a bow-tie structure. Then, the feedback control electroburning is carried out to produce a nanogap at the constriction (figure 4(e)). Statistical analysis shows that the combined method can fabricate 0.5-2.5 nm nanogaps with a high fabrication yield of ~71% [84].

2.2.3. Lithography-defined cutting. In order to connect molecular bridges and electrodes with well-defined structure through covalent bonds, lithography-defined oxidative cutting of SWCNTs and dash-line lithography (DLL) of graphene have been developed. In brief, SWCNTs and graphene devices fixed on the substrate is firstly coated by a spin-cast polymethylmethacrylate (PMMA) layer. Then, ultrahigh-resolution EBL combined with a designed CAD file is used to eliminate the PMMA at the specific position to open the exposed window. Finally, the electrodes are locally

cut through the open window by oxygen plasma to create the molecular scale nanogap. During the process, the oxidation in plasma is a controlled and non-equilibrium oxidation process, and the carboxylic acid functionalized ends are created with the well-defined structure [88–90].

For single-molecule devices based on SWCNT electrodes, SWCNTs with a diameter of 1-2 nm are firstly grown by the chemical vapor deposition (CVD) process. The source electrode and drain electrode separated by  $\sim 20 \ \mu m$  are deposited by thermal evaporation. Then, the devices are coated by a spin-cast PMMA layer and treated by EBL to create the windows with the size less than 10 nm by eliminating the PMMA. Finally, the exposed SWCNTs are locally cut through the open window by oxygen plasma ion etching with carboxylic acid groups on the new formed ends (figure 4(f)). In this scenario, the size of nanogap is 2-10 nm, which is dependent on the etching time. Specifically, the longer etching time results in a larger gap but a lower connection probability of single-molecule devices. The controllable gap size means that the molecules with different length can be investigated in this platform. Under optimized conditions, 20%–25% of carbon nanotubes are completely cut, and the connection yield for the 2.1 nm long molecule reaches  $\sim 10\%$ . When a mixture of three analogous oligomers with length between 2 to 6 nm are used, the connection yield can reach  $\sim 20\%$  [91].

Furthermore, a similar procedure has been developed for effectively creating molecular scale nanogap with point contacts electrodes, named as DLL. In brief, the CVD-grown graphene is transferred to silicon substrate and a protected graphene sheet with 250  $\mu$ m length and 40  $\mu$ m width is formed by selective oxygen plasma etching. The metal electrodes separated with 7  $\mu$ m are deposited onto this sheet through thermal evaporation. Then, a PMMA mask with indented windows with 5 nm width are created by electron-beam lithography. Graphene is locally cut through the open windows by oxygen plasma etching. By gradual etching and undercutting of PMMA and exposed graphene, the point contact graphene electrodes with carboxylic acid group will be formed (figure 4(g)). The formed nanogaps present good efficiency and universality for different length molecules (i.e., 2.2, 2.7, and 3.1 nm) with higher connection values in comparison with SWCNT electrodes [92]. The point electrodes effectively prevent the molecular aggregation and oligomerization between electrodes. Therefore, DLL-created graphene-based devices provide a pathway to capture and study single molecules.

Both lithography-defined cutting for SWCNTs and graphene are carried out under ambient environments, which can largely reduce the difficulty and complexity of fabricating single-molecule devices. Since the operations are compatible with conventional micro- and nanofabrication techniques, these methods present great potential for mass production. For the covalent connection of molecular bridges, by immersing the devices into a pyridine solution containing the diamines-terminated molecules and carbodiimide dehydrating/activating agent EDCI, single-molecule devices can be formed. The moderate reaction condition and robust covalent connection provides more opportunities to explore the single-molecule properties in varied environments [93, 94].

#### 2.3. Charge transport of single-molecule devices

The charge transport properties of single-molecule optoelectronic devices are the basis for realizing device functions. It is determined by the molecular structure and is affected by the arrangement of the molecular energy level relative to the Fermi level ( $E_F$ ) of the electrode. Here, the charge transport properties of single-molecule optoelectronic devices are systematically summarized in terms of their electronic structures, which are the basis of optoelectronic structures.

2.3.1. Electronic structure of single-molecule devices. The electronic structure determines charge transport of singlemolecule devices. Charge transport of single-molecule devices can be extremely affected by the alignment of the molecular energy levels with respect to the Fermi levels  $(E_{\rm F})$  of the electrodes. Generally, the molecular energy level refers to the frontier molecular orbitals (MO), such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). According to the relative position between the HOMO–LUMO energy level and  $E_{\rm F}$  of the electrodes, two mechanisms can be manifested for charge transport: 'resonant tunneling' and 'off-resonant tunneling'. In specific, when HOMO or LUMO falls inside the conduction window under a certain bias voltage, the  $E_{\rm F}$  of the electrodes are resonant with the molecular energy levels. In this case, resonant tunneling dominates the charge transport with higher conductance, so the conductance depends on the contact resistance. In this scenario, the mechanism can be divided into HOMO-dominated transport and LUMO-dominated transport. HOMO-dominated transport means that the  $E_{\rm F}$  of electrodes is closer to the HOMO of the molecule, and the converse case is defined as LUMO-dominated transport. When a gate voltage  $(V_{\rm g})$  is introduced into the system, a negative (or positive)  $V_{\rm g}$ can raise (or lower) the molecular orbital energies relative to the  $E_{\rm F}$  of electrodes [95]. Therefore, in the HOMO-dominated regime, the energy of HOMO will decrease and stay away from the  $E_{\rm F}$  at the positive  $V_{\rm g}$ , which will weaken the charge transport probability. Meanwhile, the converse result is obtained in the LUMO-dominated regime [73]. When HOMO and LUMO fall outside the conductive window, the mechanism of charge transport is off-resonant tunneling. In other words, there is a large energy difference between the LUMO or HOMO and the  $E_{\rm F}$  of electrodes, which plays a dominant role in charge transport.

2.3.2. Molecule-electrode coupling. In single-molecule devices, the molecule–electrode coupling has a significant effect on charge transport. The smaller the difference between the frontier molecular orbital and the  $E_{\rm F}$  of electrodes is, the stronger the electronic coupling and the higher the charge transport efficiency will be. The coupling strength is described by two parameters: the coupling parameter ( $\Gamma$ ) and the addition energy ( $U_{\rm add}$ ).  $\Gamma$  means the broadening of the energy level in the molecules, which depends on the intramolecular coupling parameter and the bond strength

between the molecule and the electrodes. The intramolecular coupling parameter refers to the coupling strength between the central part and anchor groups at the ends of the molecule.  $U_{\rm add}$  means the energy difference between the energy required to take one electron from the HOMO and the energy obtained by adding one electron to the LUMO [96] (figures 5(a) and (b)).  $U_{add}$  can be measured as the difference between the ionization potential and the electron affinity in solution by electrochemistry or in the gas phase. The ionization potential and the electron affinity refer to the difference in total energy between the neutral molecule (with N electrons) and the cation (N - 1) and anion (N + 1), respectively [97]. Based on the relative relationship of  $\Gamma$  and  $U_{add}$ , the coupling strength between molecule and electrode can be classified into three types: strong coupling ( $\Gamma \gg U_{add}$ ), weak coupling  $(\Gamma \ll U_{add})$ , and intermediate coupling. For the strong coupling, the number of extra electrons on the molecule is not well defined, and a discrete set of the energy levels of the molecule will be significantly expanded to a width  $\Gamma$ . In this case, an obvious overlap of electronic states and the partial CT between molecule and electrodes can be observed. When the broadening is large enough, the properties of the original molecular orbital are essentially lost, along with the lost intrinsic function of the molecule. For the weak coupling, the energy levels of the molecule are relatively narrow. The charge carriers can interact strongly with molecules, and the mechanism of charge transport is incoherent transport, also known as hopping. In the strong coupling limit, the charge carriers interact weakly with the molecules, and the transport mechanism is coherent tunneling.

2.3.3. Charge transport mechanisms. To fully explain the charge transport mechanisms of single-molecule devices, some theories have been developed. Generally speaking, coherent tunneling can be described by Landauer theory, while incoherent transport can be described by Marcus theory. Considering that the net current flow occurs only between the energy levels of  $\mu_L$  and  $\mu_R$ , the tunneling current depends on the transmission probability *T* of a charge carrier and can be expressed in a form of the Landauer formula as follows:

$$I = \frac{2e}{h} \int T(E)[f_{\rm L}(E) - f_{\rm R}(E)] dE$$
$$f_{\beta} = \frac{1}{1 + \exp\left[\frac{E - \mu_{\beta}}{k_{\rm B}T}\right]} \left(\beta = {\rm L, R}\right),$$

where is the Fermi distribution function for the left ( $\beta = L$ ) and right ( $\beta = R$ ) electrodes with an electrochemical potential  $\mu_{\beta}$ ;  $T(E) = \frac{\Gamma_L \Gamma_R}{[E-E_0]^2 + [\Gamma_L - \Gamma_R]^2}$  is the transmission function when a single spin-degenerated molecular orbital with an energy  $E_0$ is regarded as the channel for charge transport. Since the thermal broadening of the  $E_F$  of electrodes has a small temperature dependence, charge transport in the coherent tunneling regime is almost independent on temperature. In the coherent tunneling regime, the conductance can be simply described by  $G = G_0 e^{-\beta L}$ , where  $\beta$  represents the decay coefficient,  $G_0$  is related to the contact resistance and L represents the molecular length. The coherent and incoherent transports are believed to depend significantly on the coupling strength between molecule and electrodes, which is related to the molecular length. As the molecular length increases, the charge transport mechanism gradually changes from coherent tunneling to incoherent hopping transport. In the strong coupling regime between molecule and electrode, the electrons interact weakly with the molecule and the coherent transport is dominated. Specifically, coherent tunneling indicates that electrons go from the source to the drain electrode through a one-step process without stopping in the molecule, while in the weak coupling regime between molecule and electrodes, the electrons interact strongly with the molecule and the incoherent transport is dominated. In the incoherent transport, the electron transports in a two-step process through the molecule, in which the electron first hops from the source electrode to the molecule, and then hops from the molecule to the drain electrode over the activation barrier  $(E_A)$ . If a charge resides on the molecule, it will prevent further CT to the molecule due to Coulomb interactions. Then, Coulomb blockade can be observed in the hopping regime. In the incoherent transport regime, the conductance obeys an Arrhenius relation according to Marcus theory,  $G \propto \exp(\frac{-E_A}{k_B T})$  [98]. Therefore, incoherent transport depends on temperature but is almost independent on molecular length. Therefore, coherent tunneling and incoherent transport can be distinguished by temperature dependence.

2.3.4. Length-dependent charge transport. As mentioned above, the molecular length is an important factor for charge transport in single-molecule devices and has been extensively investigated. A smaller  $\beta$  indicates that the conductance is less dependent on the length of the molecule. Generally, coherent resonant tunneling presents an extremely weak length dependence; and the coherent off-resonant tunneling is the dominant mechanism of charge transport in small molecules, especially with lengths of 1-3 nm, which decays exponentially with the change of molecular length. While incoherent transport dominates in large molecules with a weak dependence on molecular length. Therefore, as the molecular length increases in the off-resonant regime, the charge transport could change from coherent tunneling to incoherent hopping transport, which has been directly verified by a series of experimental results. For instance, the conductance of oligophenyleneimine (OPI) with length from 1.5 to 7.3 nm, correspondingly the number of repeat units from 1 to 10, presents an obvious transition near  $\sim$ 4 nm at length. Specifically, when the molecular length is less than 4 nm, charge transport is dominated by coherent tunneling. The decay coefficient  $\beta$  is about 3 nm<sup>-1</sup>, which is within the range of  $\beta$  values of typical conjugated molecules. Accordingly, the conductance of OPI-4 is independent on temperature at 246-333 K in this case. When the length is greater than 4 nm, the  $\beta$  is extremely reduced to ~0.9 nm<sup>-1</sup>. The activation energies extracted from the relationship of resistance versus molecular length are the same at 0.28 eV for both OPI-6 and OPI-10 (figure 6(a)). These characteristics indicate



Figure 5. Principles of charge transport in single-molecule devices. Reproduced from [96], with permission from Springer Nature.

that incoherent transport is dominant in the longer molecules [99]. Similar results are observed in oligo-DNA with different molecular lengths (figure 6(b)) [100, 101].

In addition, incoherent transport is a thermally activated process, and charge transport is temperature-dependent. Specifically, the higher the temperature is, the higher the charge transport efficiency in this regime will be. In some cases, incoherent transport at a higher temperature of a longer molecule will yield a higher conductance than that yielded by coherent tunneling of a shorter molecule. For a series of conjugated molecules from 3.1 to 9.4 nm, length-dependent and temperature-independent conductance is observed at a shorter length, while a contrary result is observed at the longer length. This indicates that the charge transport mechanism changes from coherent tunneling to incoherent hopping transport with increasing the molecular length. Meanwhile, the conductance at 50 °C for a 7.3 nm length molecule is higher than that for a 5.2 nm length molecule at 25-50 °C (figure 6(c)) [98].

It is worth noting that effective charge transport for long molecules in the resonant regime is coherent tunneling, in which the conductance is almost independent on the molecular length. In this case, the conductance is considered to depend only on the contact resistance. For instance, the conductance of polyporphyrin measured by STM-BJ under high bias voltages is almost independent on length (attenuation  $< 0.001 \text{ Å}^{-1}$ ) at a long range (>6 nm), and is accompanied by a high conductance of 20 nS. The first-principles calculations can further demonstrate that the conductance is coherent resonant transport through the delocalized LUMO (figure 6(d)) [102]. In addition to the transfer between coherent and incoherent at a different length, as the length of the Au-C bonded alkane molecule increases, the charge transport mechanism changes from resonant to off-resonant [54]. Furthermore, at low biases, the conductance of diketopyrrolopyrrole oligomers (n = 1-4) decays exponentially, indicating that charge transport follows the coherent off-resonant tunneling. Under high bias voltages, a similar higher conductance is presented for all four oligomers, which indicates that charge transport follows coherent resonant tunneling [103].

#### 3. Single-molecule charge effects

The charge effect is a very important scientific phenomenon, which is of great significance for realizing the functions of optoelectronics devices. Single-molecule charge effects are an effective perspective and means to understand charge effects. In addition, single-molecule charge effects have guided significance for various applications, such as the realization of single-molecule functions. In this chapter, the typical singlemolecule charge effects are analyzed from the aspects of the single-molecule structure, charge source, electron hopping transport mechanism, image-charge effect, Coulomb blockade effect and the specific applications of 'charge effects' in singlemolecule devices. The principles are described and summarized, which has a certain guiding significance for the design of single-molecule devices in the future.

#### 3.1. Single organic electroactive molecules

Single-molecule charge effects are often based on organic electroactive molecular materials. These can be divided into two species in general: one can undergo the redox process with different valence states while the structure remains unchanged; the other will manifest different chemical structures when the redox occurs.

3.1.1. Redox-active molecules with different valences. Due to the specific intrinsic characteristics, the valence state of some redox-active molecules will change while their structures remain unchanged during the redox process. These molecules can be roughly divided into two categories according to the types of redox centers. The examples mentioned in this section are shown in figure 7. One has a metal ion center, while the other has no metal ion center. The following is the case for molecules without a metal ion center. As a redox molecular center, viologen undergoes redox reactions by gaining or losing electrons. In the traditional case, when the electrochemical potential is regulated, the viologen center carries out a reversible electrochemical redox reaction. In this process, two N atoms gain or lose an electron, respectively, thus the viologen center transforms between three reduction-oxidation states: V,  $V^+$  and  $V^{2+}$ . In addition, to



**Figure 6.** Length-dependent charge transport in single molecules. (a) Semilog plot of resistance versus molecular length of OPI. Inset: a linear plot of *R* versus *L*. From [99]. Reprinted with permission from AAAS. (b) Seebeck coefficients of DNA with different molecular lengths and sequences. Reproduced from [100]. CC BY 4.0. (c) Measured conductance as a function of the wire length at T = 25, 40 and 50 °C. Reprinted with permission from [98]. Copyright (2010) American Chemical Society. (d) Differential conductance of the bp-ppo and the Fe-bp-ppo molecules plotted against tip retraction height. Reprinted with permission from [102]. Copyright (2016) American Chemical Society.

use these redox-active centers as a molecular functional center in single-molecule devices needs further external modification, such as forming structures like a classic symmetrical molecular line with mercaptans at either end of the viologen center, or asymmetric 1-(4-aminophenyl)-1'-methyl-4,4'bipyridinium bis-hexafluorophosphate [104, 105], etc. Similarly, conjugated oligophenylene imine (OPI) and perylene tetracarboxylic bisimides (PBI) are also revealed to be capable of gaining or losing electrons at the N center to form free radical ions [99, 106, 107]. In the PBI system, when the oxidation reaction occurred, the odd electrons would be delocalized in the whole system, translating into PBI<sup>•+</sup>. In addition, the bisthienylbenzene containing S atom has similar properties [108]. As is known, S has two lone pairs of electrons, one pair of which will conjugate with the double bond in the ring to a delocalized  $\pi$  bond, which makes it prone to losing electrons in oxidation.

The other case of redox-active molecules is with a metal ion as the redox center. Metallocene complexes is a kind of redox systems. The general formula of the cyclopentadiene organometallic complex is  $(C_5H_5)_2M$ , where M can be a metal ligand such as Fe, Co and Ru, and the most stable one is ferrocene (Fc), which is the first sandwich complex discovered. Taking Fc as an example, it has the satisfactory thermal stability, chemical stability and low HOMO, similar to aromatic compounds. In the electrochemical environment, Fe contributes or accepts electrons through changing the valence state, resulting in the widespread application as a single-molecule redox-active center. Based on this, various single molecules regarding Fc as the core group have been designed, including structures using Fc as a center,



Figure 7. The chemical structures of redox molecules discussed in this section. *R* represents tert-butyl-phenoxy, pyrrolidinyl, chlorine, and thiobutyl moieties, and *M* represents Fe, Co, Ru, Al, Ni, Zn and Cu.

end groups, and even multiple Fc units connected in series [14, 17, 109–112]. Moreover, porphyrin complexes with metal ions exhibit unique photoelectric properties and satisfactory thermal stability as another kind of classical redox systems. The planar macrocyclic structure of porphyrin molecules makes it easy to chemically modify and form stable metal complexes with a diverse variety of metal ions (such as Fe, Co and Al) [113], M represents the metal ion center. When the electron passes, the M in the center will gain/lose electrons and change the valence state without structural changes of porphyrin. Similar to porphyrin, phthalocyanine is an 18electron macroconjugate compound composed of four isoindole units. Co, Ni, Zn, Cu, Fe and other metal ions chelate with phthalocyanine through two covalent bonds and two coordination bonds in the cavity to form a highly stable metal phthalocyanine. However, the two complexes mentioned above have the problem of low solubility in the aqueous solution. By adding certain substituents and placing intrinsic metal ions nearer to the center of a large ring, not only the solubility can be promoted, but also the complexes of new properties such as spatial effect can be ensured. Mononuclear compounds  $(MeCOSC_6H_4-C\equiv C-)_2M(P \cap P)_2$  (M = Fe, Mo, and Ru,  $P \cap P = 1,2$ -bis(diphenylphosphino)ethane, designed with metal ions as the center possess similar effects [18]. The metal

center is placed in the transport path to regulate the singlemolecule conductivity. For example, the electron transport by an incoherent hopping mechanism due to the weak coupling between the local redox-active orbital and the electrode caused by the unique spin-polarized ground state of the Mo center. In addition, fullerenes and endohedral metallofullerenes can undergo redox reactions, and valence changes are also expected to occur when used in single-molecule devices [114, 115].

3.1.2. Molecules with redox-induced structure changes. Unlike single molecule mentioned in the previous section, some redox-active molecules gain or lose electrons along with the formation and breaking of chemical bonds, leading to the variation of the chemical structure (figure 8). In general, tetrathiafulvalene (TTF) can undergo reversible redox reaction [116]. The transition of TTF from the neutral state to the oxidized state is accompanied by the increase of the aromatization energy, which partly explains why TTF is a good electron donor [117]. In detail, neutral TTF loses two electrons in two steps, and the C=C in the middle of TTF will break during this process. Different from TTF, the anthraquinone (AQ) group has the property of conjugated unsaturated ketone. In an acidic liquid, two electrons are easily reduced to AQ<sup>2-</sup>, and the CH<sub>2</sub>=O bond is destroyed in this process. Then, H<sup>+</sup> in the solution is combined with  $AQ^{2-}$  to form hydroanthraquinone (H<sub>2</sub>AQ), where H<sup>+</sup> plays a stabilizing role. From the above reaction principle, it can be found that the pH of the solution has a certain effect on the potential of the redox reaction. It is noted that the AQ-based norbornylogous bridge tetrathiol-5AQ5 molecular chain with cross-conjugated AQ as the molecular center has low conductance due to the destructive quantum interference (QI) between different conductance channels. When the redox reaction occurs, AQ is transformed into linear conjugated H<sub>2</sub>AQ and the destructive QI effect will disappear, resulting in conductance increase [118]. Tetracyanoquinodimethane unit has an anthracene skeleton similar to AQ [119]. In contrast to AQ, two  $CH_2 = C(CN)_2$  replace two  $CH_2 = O$ , but their properties are similar. In addition, naphthalenediimide (NDI) is composed of naphthalene in the center and diimine units suspended on both sides [120]. Diimine is vulnerable to getting electrons, so NDI molecules can be converted from neutral NDI (NDI-N) to NDI radical anion (NDI-R), then converted into a dianion NDI (NDI-D). And NDI-D further forms hydroxyl groups with hydrogen ions in the solution. Because the redox states of NDI are all stable and the conductance difference between NDI-R and NDI-N is more than one order of magnitude, this provides an ideal molecular system to construct functional single-molecule devices. Dimerization is the polymerization of two identical molecules A into one molecule A<sub>2</sub> (dimer). Monomers such as viologen, TTF and oligothiophene (OLT) can form conjugated radical cations through oxidation reactions, and two identical conjugated cations can further form a stable dimer by the inherent multicenter covalent  $\pi - \pi$  bonding [121].

For example, the methylviologen (MV) unit switches between three redox states through electrochemical oxidationreduction reactions [13]. Dimerization occurs when the molecule center is in the state of  $MV^{\bullet+}$  radical, which is accompanied by the migration of counterions and the approaching between adjacent molecules. It should be noted that dimerization can occur between different types of units, even within the same molecule. Analogical design ideas can also be extended to other dimerization, multimerization and supramolecular formation.

#### 3.2. Charge state control in single-molecule devices

Based on redox-active molecules, the charge state in the single-molecule optoelectronic device can be controlled by external fields. These are two charging modes in single-molecule optoelectronic devices: charge trap and redox regulated by a gate. In addition, the mechanisms involved in the charge state control process are specifically introduced in this chapter.

3.2.1. Charging modes of single-molecule devices. The charge state control mechanism of single-molecule devices includes a charge trap in the two-terminal device and redox regulated by a gate in the three-terminal device. The charge trap of the two-terminal device refers to the charges traveling from the source electrode to the drain electrode, leading to the change of the molecular charge state. In detail, the charges

enter the connected molecule from one electrode first under the action of the potential difference and are captured or released by the redox center of the molecule, thereby causing a redox reaction (figure 9(a)). In addition, for some single-molecule devices without redox reactions, when electrons pass through the molecule, charges only stay on the molecule for a short time. Usually, a two-terminal single-molecule device refers to a single redox molecule connected to electrodes forming an electrode-molecule-electrode junction. The charge trap occurs on the molecule driven by the bias voltage in such a single-molecule device. At the same time, the conductance of the molecule changes because the redox of the molecule is caused by a charge trap on the molecule. For example, the conductance of molecules in different redox states in a singlemolecule device using viologen as the redox center can be measured by the STM-BJ technology (figure 9(b)) [122]. The conductance changes as molecules gain or lose electrons from the electrodes through redox processes.

Apart from the charge trapping in a two-terminal device, a gate electrode can be added so that the electrostatic potential of the molecular bridge can be independently controlled by a third non-contact electrode, leading to the occurrence of redox reactions. The change of gate voltage can regulate the gate electric field and make the single molecule undergo a redox reaction. The typical gate electrode is divided into solid gate electrodes and liquid gate electrodes. The composition of a solid single-molecule electronic device generally includes a gate electrode, a solid dielectric layer and a single-molecule junction. Special attention should be paid to the fact that to apply the gate electric field effectively to molecules, the gate electrode needs to be as close as possible to the molecules and accompanied with a sufficiently thin dielectric layer (figure 9(c)). Since the operation is carried out at the molecular scale, the process requirements are extremely high. There are two typical methods. One is to use the nano-lithography technology to manufacture solid-state three-terminal devices, in which the gate electrode is as close to the molecule as possible and the vacuum acts as a dielectric layer in this case. However, the placement precision of the gate nanoelectrode is uncontrollable, which affects the repeatability of single-molecule devices. The electrostatic coupling parameter  $\xi$  is used to describe the coupling strength between the applied gate voltage and the molecular frontier orbital, such as HOMO or LUMO. The larger the value of  $\xi$  is, the higher the electrostatic coupling strength between the gate electrode and the molecular frontier orbital will be. In addition,  $\xi = 1$  represents a complete electrostatic coupling. At this time, when the gate electrode voltage varies by 1 V, the molecular orbital energy changes by 1 eV. A large number of experiments have proved that the  $\xi$  of solid-state three-terminal devices is insufficient and has poor repeatability, so it is difficult to prepare single-molecule devices with superior gating performance. Another method is to use an ultra-thin high ksolid dielectric layer. In this way, on the one hand, the gate and the single molecule can be separated. On the other hand, it has a high dielectric coefficient, which ensures the effective regulation of the redox state of the single molecule. In specific,



Figure 8. The redox-active molecules with structural changes discussed in this section.  $X^-$  represents counter ions.

the single-molecule device consists of conductive gate electrodes [123], a high-k solid dielectric layer (such as aluminum oxide) and a source/molecule/drain junction, also known as the back-gate device. In addition, the electrode material of the single-molecule device can be metal or carbon material, such as graphene. The transport characteristics of electrons show different effects according to the coupling strength of the single molecule with the electrode. Theoretically, the back gate can achieve high efficiency during the weak interfacial coupling. However, it is difficult to make the dielectric layer ultrathin at the molecular level and reduce current leakage, so the device design needs to be further improved.

Corresponding to the solid gate, in a liquid gate device, the gate electric field is applied to the single-molecule junction by using an ionic electric double-layer. The liquid gate can be divided into a three-electrodes system and a four-electrodes system according to whether the reference electrode is added or not. In a single-molecule device with a liquid gate structure, the applied gate voltage will form an electric double layer near the gate. Since the ionic double layer is ultra-thin, a large gate electric field can be applied to the single molecule, and the single-molecule energy level can be effectively regulated. In order to precisely control the energy level position, the reference electrode and counter electrode are introduced to form an electrochemical gate according to the setting of the electrochemical experiment [124]. In specific, a single-molecule device with an electrochemical gate consists of two working electrodes (source-molecule-drain), a reference electrode and a counter electrode (figure 9(d)). The molecular energy levels of a single-molecule device can be shifted by means of controlling the electrochemical potential. In addition, the ionic liquid gate platform has strong repeatability under appropriate electrolyte concentration conditions. The electrochemical gating can establish a functional relationship between the electrical characteristics and the redox state of the single molecule, which provides an important platform to study the electrochemical characteristics of single molecules. For example,

6-[1'-(6-mercapto-hexyl)-[4,4']bipyridinium]-hexane-1-thiol iodide (6V6) has been proved that the conductance of the molecule increases with the increase of the negative overpotential of the electrode, following the *s*-shape function (figure 9(e)). Due to the electrochemical gating, the conductance at the negative potential plateau is 6 times the conductance value at the positive potential plateau. This is because when the potential in an aqueous electrolyte solution changes from positive to negative, V<sup>2+</sup> is easily reduced to V<sup>+</sup>, resulting in an increase in molecular conductance [124].

3.2.2. Mechanisms during charge state control. The CT mechanism of molecules is tightly related to the properties of molecules themselves and the coupling strength ( $\Gamma$ ) between the molecule and electrodes. There are two situations in this process. One is that the charge states of the molecule does not change during the CT process. In the other case, the charge states of the molecule change with redox reactions. Specifically, when the coupling strength between the molecule and electrodes is strong, the electrons will pass through the molecule in one-step tunneling, and the redox reaction is difficult to occur in this case. When the coupling strength between the molecule and electrodes is weak, the electron transports from one electrode to the molecule after a short delay, then from the molecule to another electrode, this process is called two-step hopping (figure 10(a)). During this period, the electron will have a strong interaction with the single molecule, leading to a redox reaction. In specific, the single molecule gains or loses electrons, but the final molecular charge state does not change. The above mechanism can be revealed by the change of molecular conductance. For example, viologenbased molecular wires in the ionic liquid electrolyte and aqueous electrolyte systems both reflect a peak value in line with the electron hopping transport mechanism. The bell curve of conductance and potential reflects the relaxation process of electrons on molecules, which is confirmed by the hopping



**Figure 9.** The single-molecule devices. (a) Schematic diagram of single-molecule junctions, where the red spheres represent the redox units and the gray spheres represent the molecular backbone. Reproduced with permission from [125]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC 4.0. (b) Schematic diagram of a typical two-terminal device. Reprinted with permission from [122]. Copyright (2003) American Chemical Society. (c) Schematic diagram of solid single-molecule electronic devices. Reproduced from [123], with permission from Springer Nature. (d) Schematic diagram of a single-molecule device with an electrochemical gate. (e) Relationship between single-molecule conductance and electrochemical overpotential of the viologen molecular bridge (6v6). (d) and (e) Reprinted with permission from [124]. Copyright (2016) American Chemical Society.

model proposed by Kuznetsov and Ulstrup (figure 10(b)). The conductance increases suddenly near the redox potential, indicating that the redox reaction affects the molecular conductance to a great extent [105]. As for the redox process of molecules, Marcus theory can explain the charge state changes of single molecules well. It is generally used to explain the transfer process of electrons between an electron donor and an electron acceptor. It can be observed that an energy barrier

needs to be crossed during the oxidation of M to form  $M^+$ in the typical Marcus parabolas (figure 10(c)) [125]. In other words, the process from M to  $M^+$  needs to pass through the crossover point of two parabolas, and the energy required from the equilibrium point of M to the crossover point is the energy barrier of the reaction. Under the assumption that the relevant atoms do not change during electron transfer, the crossover point represents that the nuclear coordinates of M and  $M^+$ 



**Figure 10.** The mechanisms during the charge state control. (a) Schematic diagram of a two-step hopping process. Reproduced from [125]. CC BY 4.0. (b) Single-molecule conductance and potential data in ionic liquid (top) electrolyte and aqueous (bottom). Reprinted with permission from [105]. Copyright (2015) American Chemical Society. (c) Schematic diagram of typical Marcus parabolas. Reproduced from [125]. CC BY 4.0. (d) Arrhenius plots of OPI 4, 6 and 10. From [99]. Reprinted with permission from AAAS.

molecules are the same. Only when the electron energy of M and M<sup>+</sup> is the same, the electron transfer process will occur. The  $\Delta G_0$  in figure 10(c) represents the Gibbs free energy change of the reaction, and the  $\lambda$  represents recombination energy, making the molecule change from the reduced state to the oxidized state in a single-molecule device. Under the Marcus theory system, the electron transfer rate  $k_{\text{ET}}$  can be expressed by the following formula:

$$egin{aligned} k_{\mathrm{ET}} &= \left(rac{2\pi}{\hbar}
ight) \left|H_{\mathrm{MM}+}
ight|^2 (4\pi\lambda k_{\mathrm{B}}T)^{-rac{1}{2}} \ & imes \exp\left[-rac{(\Delta G_0+\lambda)^2}{4\lambda k_{\mathrm{B}}T}
ight], \end{aligned}$$

where  $H_{\rm MM^+}$  represents the electronic coupling strength between M and M<sup>+</sup>,  $\hbar$  represents the reduced Planck constant,  $k_{\rm B}$  represents Boltzmann's constant and *T* represents temperature. Therefore, when M and M<sup>+</sup> molecules are determined,  $k_{\rm ET}$  can be regarded as a temperature-dependent function, which corresponds to the thermally activated redox reaction involved in incoherent transport. For example, OPI wires with different lengths (named as OPI-n, n represents the molecular length) show different CT mechanisms [99]. When the molecular length exceeds 4 nm, the conduction mechanism changes from tunneling to hopping. Both OPI-10 and OPI-6 show an obvious correlation with temperature, which means thermally activated transport. Therefore, the temperature dependence of conductance is often used to judge whether the CT mechanism is a hopping mode (figure 10(d)).

# 3.3. Charge effects and applications of single-molecule devices

Through the control of charge states, specific charge effects, including image-charge effect and Coulomb blockade effect, can be realized in single-molecule optoelectronic devices. At the mean time, charge effects can bring many applications in single-molecule optoelectronic devices, such as charge induced rectification effect, electrochemical reactions and electron catalysis.



**Figure 11.** Image-charge effect in single-molecule devices. (a) Image-charge effect physics module for a point charge. (b) Image-charge effect for a single-molecule device. (a) and (b) Reproduced from [127], with permission from Springer Nature. (c) An image-charge model geometry with the image plane outside the first atomic layer. (d) A shift of occupied and unoccupied molecular orbital levels with a distance to the metal. The effects contained in  $\Delta$  shift all levels in the same direction, while image-charge effects are responsible for occupied and unoccupied levels moving closer to the Fermi energy of the metal (gap renormalization).  $\Phi_m$  represents the metal work function,  $\Delta$  the interfacial dipole,  $V_{\infty}$  the potential at infinity,  $V_S$  the potential at the surface and  $\varepsilon_F$  the Fermi energy.  $\varepsilon_{occ}$ ,  $\varepsilon_{unocc}$  and  $\varepsilon'_{occ}$ ,  $\varepsilon'_{unocc}$  are now the occupied and unoccupied levels of the molecule in the gas phase and at the interface, respectively. (c) and (d) Reproduced from [130], with permission from Springer Nature.

3.3.1 Image-charge effect. Image-charge effect is a general existing phenomenon, which is of great significance in the fields of interface physics and organic electronics. When a point charge or a polarized molecule is near a conductive plate, the electric field generated by the image charge can affect this system, leading to further charge redistribution on the surface. Specifically, when a point charge is set at a distance from the metal surface, the polarized electron cloud of surface charges can be induced. In other words, the metal surface is just like a mirror, and the external charge seems to generate an opposite charge at the position of the mirror image (figure 11(a)). Therefore, the electrostatic field of the system

can be described as the electrostatic field formed by the real charge plus its mirror image. In addition, due to the attraction of positive and negative charges, the energy of the system is reduced [126].

This image-charge effect can also be used to help understand some phenomena in single-molecule devices. For a typical molecular junction, the electrons can pass from one electrode to the other through the molecular orbital closest to the Fermi energy ( $E_F$ ) level of electrodes under a certain bias. In this system, the molecule is approximately neutral before the electron passes. When the electron passes, the neutral molecule is charged, which can be regarded as a point charge.



**Figure 12.** Coulomb blockade effect in single-molecule devices. (a) The Coulomb blockade regime. An energy gap forms between the chemical potential *E* of the *N*th and the (N + 1)th electrons. (b) A schematic diagram of Coulomb blockade oscillations  $(I_d - V_g$  characteristics) when  $V_{sd}$  is low. The number of electrons in the dot increases by 1 whenever  $V_g$  comes at the valley of the oscillation. (c) A schematic view of Coulomb blockade diagram (contour plot of  $I_d$  as a function of  $V_g$  and  $V_{ds}$ ). The dark gray regions denote the Coulomb blockade region where  $I_d$  is suppressed and the light gray regions are the single-electron tunneling regions where  $I_d$  flows. (a)–(c) Reproduced with permission from [133]. (c) Elsevier. CC BY-NC 4.0.

Regarding the metal electrode as a metal plate, an induced point charge near the metal plane will appear, thus forming the image charge effect (figure 11(b)). Like the stabilization in the physical model, the molecular junction is energetically stabilized, showing a unique renormalization of orbital energy levels. Therefore, both HOMO and LUMO will move toward to the  $E_{\rm F}$  of electrodes, leading to a smaller gap between HOMO and LUMO [5, 127–129].

Furthermore, through the regulation of molecular electronic states, the image-charge effect can be adjusted in single-molecule devices as well (figure 11(c)) [130]. For example, the electrode spacing can significantly affect this effect, which manifests that the effect gradually increases as the spacing decreases. Specifically, MCBJ can realize the ingenious adjustment of electrode spacing. This is because the architecture possesses a flexible substrate, which can be bent to adjust the gap of partially suspended electrodes with picometer precision. In a single porphyrin molecular junction formed by MCBJ, due to the position of the occupied and unoccupied molecular energy levels is varied at different electrode spacing, charge transport of the molecule is different, which reflects the influence of the image-charge effect (figure 11(d)).

In addition to experimental evidence, theoretical simulation also constantly improves this theory, providing theoretical support for the image-charge effect. In the beginning, theoretical studies of metal-molecule interfaces are basically based on density functional theory (DFT). To take account of dynamic effects, corrected DFT including dynamical polarization for describing image-charge effect like GW calculation is developed [131]. To be applied in larger systems, the corrected DFT based on the charge distribution of the molecule in different charge states is used to calculate the image charge effect [132].

According to the basic principles, the image-charge effect may bring about dipoles that facilitate fluorescence resonance energy transfer. However, if this phenomenon is applied to nanophotonic devices, one key issue needs to be paid attention to: the generated image dipole will cause nonradiative energy transfer near metal surfaces and quench the excited state properties of nano-optoelectronics.

3.3.2. Coulomb blockade effect. Coulomb blockade refers to that the Coulomb interactions on the isolated islands are strong enough to prevent electrons from entering or leaving the island, and it usually exists in quantum dots or single-molecule systems. If the island is small, the energy gap between the last electron (N) and the first empty electron (N + 1), which corresponds to the HOMO–LUMO gap of the molecule, is larger than the thermal energy  $k_{\rm B}T$  in the system, where  $k_{\rm B}$  is Boltzmann's constant and T is the temperature. Therefore, the energy for electrons to pass over the gap is not enough, resulting in the Coulomb blockade (figure 12(a)) [133].

There are two typical conductive states in a Coulomb island module. When the conductive energy levels are out of the bias window, which means that there are not any conductive states between source and drain potentials, the electron tunneling is forbidden. When the conductive energy levels are between source and drain, single electrons can tunnel from source to drain through the Coulomb island one by one, which is the so-called single electron tunneling. The relative position of conductive state and bias window can be adjusted by the bias voltage ( $V_{ds}$ ) or the gate voltage ( $V_g$ ) to achieve or destroy the Coulomb blockade.

By regulating the gate voltage, the condition of single electron tunneling and Coulomb blockade are alternately satisfied. As different energy levels will be used as the tunneling path, the drain current ( $I_d$ ) oscillates (figure 12(b)). Furthermore, the size of the conductive window can be controlled by the bias voltage. The larger the window is, the easier it is for the conductive energy level to be placed between the windows. Coulomb blockade diagram can be used to understand the Coulomb blockade effect better, which is the contour plot of  $I_d$  against  $V_g$  and  $V_{ds}$ . Each Coulomb blockade region possesses an integer number of electrons in the island. The light-gray diamonds existing between the two adjacent Coulomb blockade



**Figure 13.** Schematic diagram of single-molecule rectification devices. (a)  $M-S(CH_2)_{11}S-BTTF$ . Reprinted with permission from [137]. Copyright (2020) American Chemical Society. (b)  $HSC_{15}Fc-C \equiv C-Fc$ . Reproduced from [14], with permission from Springer Nature. (c)  $S(CH_2)_{11}CO_2H$ . Reproduced with permission from [138]. (c) American Chemical Society. CC BY-NC 4.0. (d)  $S(CH_2)_{11}MV^{2+}X^{-}_2$ . Reproduced from [13], with permission from Springer Nature. (e)  $FcC_6S$ . Reproduced with permission from [139]. (c) Elsevier. CC BY-NC 4.0. (f) TDO4. Reproduced from [74], with permission from Springer Nature.

regions are called single electron tunneling regions, where single electron tunneling is allowed and current flows from source to drain (figure 12(c)) [133].

For a single-molecule system, the molecule can be considered as small perfect quantum dots, where the tunneling paths correspond to the MO. Here, the electronic coupling strength between molecules and electrodes is the crucial factor to realize Coulomb effect. As defined in section 2.3.2, in the weak coupling regime, the Coulomb blockade effect will occur; but in the strong coupling regime, the Coulomb blockade breaks down, which manifests that the electrons effectively move from the source to the drain without stopping on the molecules. If the coupling is intermediate, the edges of the Coulomb diamonds become slightly blurred, and new transport channels will appear according to Kondo resonance at the co-tunneling regime [6, 96].

In single-molecule devices, both the adjustment of the electrodes and the bridge molecules can adjust the electron transport mode, so as to realize the control of the Coulomb blockade. For the electrode, the adjustment of the bias voltage [96] and the gate voltage [134] can change the coupling strength. Molecular design is also an effective way. Adjusting the connection properties of the molecule and the electrode [96], changing the length of the molecule, inserting non-conjugated groups [135] and adjusting the size of the conjugated region of the molecule are all effective ways to regulate the coupling strength between electrodes and molecules, leading to the control of Coulomb blockade [136].

3.3.3. Charge induced rectification effect. The rectification effect refers to different currents caused by the bias voltage with different directions in an electronic device. Rectification ratio (R) is used to evaluate the rectification effect, and its definition formula is as follows:

$$R = |\frac{J_{\rm f}}{J_{\rm r}}|,$$

where  $J_{\rm f}$  represents the current at a forward bias and  $J_{\rm r}$  represents the current at a reverse bias. Most single-molecule rectifiers realize the rectification effect caused by the molecular structure asymmetry, but this section only deals with the rectification effect caused by the charge effect.

In the traditional case, the asymmetry of the molecule itself and the asymmetry at the molecule–electrode interface can realize the rectification in a controllable direction. Asymmetric molecules with an alkyl chain and terminal group (figure 13(a)) are often used to prepare single-molecule rectifiers [137]. In addition, Coulomb interaction at the molecule–electrode interface can also affect rectification effects. Specifically, when the single molecules possess charge at the end, a rectifier with a high rectification ratio can be realized due to the different characteristics of Coulomb interaction between terminal group and electrode under positive and negative bias voltages. A typical example is a molecule consisting of a longer alkyl chain and Fc terminal group (figure 13(b)), the two Fc units are separated by an alkyne group [14]. When the electrode above Fc is negatively charged, it will attract the positive charge Fc through an electrostatic force, leading to a conductance increase in this bias direction. Otherwise, Coulomb repulsion causes only a small part of molecules in the selfassembled monolayer (SAM) participating in conduction, and the conductance decreases. It is worth noting that SAM can be viewed as a collection of parallel transport of single-molecule devices. The rectifier ratio of the molecular diode made by this principle can be up to  $\sim 6.3 \times 10^5$ . Furthermore, the rectification ratio of single-molecule devices can be adjusted by controlling the terminal groups with charge, such as the protonation of terminal groups. The protonation process can control the molecular charge state, and then change the Coulomb interaction between the molecular terminal group and the electrode to achieve a rectification effect. As shown in figure 13(c), the carboxyl group at the end of the  $S(CH_2)_{11}CO_2H$  molecule leads to a negative charge at the end of the molecule after protonation, so it produces opposite Coulomb interaction with electrodes of different polarity, thereby increasing the rectification effect [138]. In addition, the change of the charge state of a molecular terminal group can also be realized by molecular redox reactions caused by the charge trap. For example, the reduction reaction occurs under the action of the charge trap of the viologen group. Specifically, the change of the molecular charge state leads to the dimerization of adjacent viologen, which also leads to the directional migration of counter ions in the SAM, affecting the space charge distribution in molecular junctions in turn. Therefore, under positive bias voltages, the electrostatic repulsion between the positive charge of the molecule and the top electrode is large, resulting in low conductance. While under negative bias, the positively charged molecule is close to the top electrode, leading to high conductance. Furthermore, the electric field and ion migration driven effects enable the molecular devices to be preprogrammed in a single-molecule layer to achieve diode and memory functions (figure 13(d)) [13]. Furthermore, the regulation of the charged terminal redox state can be realized through a specially designed device with a vertical graphene/SAM/Au structure [139], in which the redox regulation of molecules can be realized through the top single-layer graphene electrode (figure 13(e)). The principle of rectification is due to the charged terminal groups, as they can electrostatically interact with the electrode. Since single-layer graphene can only allow electrons to pass through, the molecules can lose electrons for oxidization, while the anion outside graphene cannot pass through the graphene layer. Therefore, when the Fc group on the inner side of graphene is in the positively charged state, it will electrostatically repel the positively charged graphene electrode, increasing the spacing between them, thus resulting in the decrease of conductance. In addition to the above rectification initiated by the Coulomb interaction between molecules with a charged terminal group of the asymmetric molecule and the electrode, the uneven charge distribution of the electrode will also lead to rectification. For example, a single molecule with a symmetrical structure is fixed between the asymmetric top and bottom electrodes (figure 13(f)) [74]. In an ionic solution environment, the asymmetric electrode structure forms different ionic double-layer under positive and negative biases,



**Figure 14.** The experiments of electrochemical reactions. (a) Schematic diagram of the electrochemically gated MCBJ technique. Reproduced from [26], with permission from Springer Nature. (b) Schematic diagram of an energy barrier model. Reproduced with permission from [140]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC 4.0. (c) Cyclic voltammogram (left) of PTCDI and the conductance varying with the gate voltage (right) of single PTCDI. Reproduced with permission from [142]. (c) National Academy of Sciences. (d) Schematic diagram of the two-step adiabatic KU model. Reproduced with permission from [140]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC 4.0. (e) Schematic diagram of single molecule conductance-potential data. Reprinted with permission from [105]. Copyright (2015) American Chemical Society. (f) Structural transformation and cyclic voltammogram of AQ/H<sub>2</sub>AQ. Reproduced with permission from [118]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC 4.0.

so the energy level structure at the molecule–electrode interface is different under different bias voltages, resulting in different conductance. And the rectification ratio of this singlemolecule device can exceed 200 at a low bias voltage. This attractive and simple method of creating an asymmetric electrostatic environment in a liquid provides a new idea for the preparation of high-efficiency rectifiers.

3.3.4. Electrochemical reactions. Single-molecule devices are considered as a significant platform to study electrochemical reactions at the single-molecule level. Typical single-molecule devices used for investigating electrochemical reactions were described in detail in the section 3.2.1. The single-molecule devices can reveal the process and mechanisms of electrochemical reactions by monitoring the conductance change of single molecules during the reaction. Specifically, the relative position of the MO with the Fermi level of the electrodes can be regulated by the gate field. Since the thickness of the ionic double-layer formed during gating matches the molecular size, a strong gating electric field could be generated, which allows the redox-active molecules to undergo a reversible redox reaction thus affects the CT. Therefore, the electrochemical reaction can be detected by the

conductivity change of single-molecule devices. In addition, single-molecule research can uncover the hidden information in traditional ensemble experiments and explore the mechanism of molecular electrochemical reactions in-depth. And the mechanisms can further provide solutions to key issues in electrochemical research.

To study electrochemical reactions, such single-molecule devices often work in an electrolyte solution. By applying gate field to the molecule, the MO can be regulated. Thus, by monitoring the change of molecular conductance under different gate voltages, the mechanism of electrochemical reaction can be revealed to a certain extent. As shown in figure 14(a), a molecular junction is established with MCBJ, and bipotentiostat is used to provide independent voltages between source and drain, gate, and reference electrode, respectively [26]. The independent gate voltage will produce an electric double layer at the interface, and then produce a strong gate electric field. The gate electric field changes the molecular conductance by adjusting the relative position between molecular orbital energy levels and the Fermi energy level of electrodes. The above specific mechanism can be simply represented by a model (figure 14(b)) [140]. Here, it is described that the Fermi energy level of the electrode is located between the molecular LUMO and HOMO orbitals. The energy difference between the Fermi energy level of the electrode and the molecular LUMO/HOMO orbitals determines the electron tunneling barrier. The electric field generated by the gate voltage can regulate the position of the molecular energy level, so the energy difference and the potential barrier can be regulated. When the Fermi energy level of the electrode matches the HOMO or LUMO of the molecule, there is no energy difference between the electrode and the molecular orbital, so the molecule can gain or lose electrons to make the redox reaction occur in this case. After the redox reaction occurs, the structure and position of the molecular orbital will change, leading to a different potential barrier and conductance. For example, the conductance of perylene tetracarboxylic diimide (PTCDI) varies with the gate voltage in a typical three-terminal single-molecule device. It reaches the highest value near -0.65 V, which is close to the reduction potential (-0.55 V) of the molecule in the ensemble system. Moreover, it is found that the molecular conductivity has no obvious relationship with the gate voltage after replacing the molecule with different non-redox molecules, which further proves that the above phenomenon is related to the molecular redox reactions induced by the gate electric field [141].

Based on the study of single-molecule electrochemical redox reactions used in single-molecule devices, different mechanisms of controlling the conductance change of single redox-active molecules are summarized. The CT process is dependent on the molecular states at the single-molecule level, thus the conductance of the single-molecule oxidation state and reduction state is rather different. Therefore, conductance can be used to reflect the redox state of the molecule. When the coupling between the molecule and electrode is strong, the fluctuation of the single molecule between the oxidation state and the reduction state follows the first-order reaction kinetics, and its rate constant is related to the potential and can be expressed by Butler-Volmer formula. Although the single experiment of a single molecule has great randomness, the correlation between average conductivity and potential of single molecules conforms to the Nernst equation through a large number of measurements, and the average conductance (G) is as follows:

$$\langle G \rangle = G_{\text{red}} + \frac{1}{1 + \exp\left[\frac{e}{k_{\text{B}}T}(E - E_0)\right](G_{\text{ox}} - G_{\text{red}})}$$

where  $G_{ox}$  and  $G_{red}$  represent the molecular conductance of oxidized and reduced states, respectively. *e* is the electron charge,  $k_B$  is the Boltzmann constant, *T* is the temperature, *E* is the electrode potential and  $E_0$  is the equilibrium potential. When the single molecule and temperature remain unchanged, the dependence between average conductance and potential present sigmoidal, which is consistent with the correlation between current and potential in the ensemble system (figure 14(c)) [142]. The results not only help to understand the process of electrochemistry reactions occurring in single molecules, but also reveal the relationship between the single molecule and the corresponding ensemble system. Moreover, when the coupling strength between the molecule and the electrode is weak, the molecular orbital of the central redox molecule matches the Fermi level of the electrode through the environment and internal fluctuations, which makes the electrons hop from one electrode to the molecule following Franck-Condon type transition. After that, the molecule is reorganized under the adiabatic limit due to the environment and the internal relaxation. Finally, electrons hop from the redox center to another electrode (figure 14(d)) [140]. The change of conductance with potential presents a bell shape in this case, and the maximum conductance of molecules is close to the redox equilibrium potential. Since the probability of oxidation reaction of molecules is the largest, electrons are most prone to two-step hopping at this voltage (figure 14(e)) [105]. In addition, some single-molecule electrochemical reactions are accompanied by changes in molecular structure, which may lead to new quantum phenomena and then affect the molecular conductance. In an anthraquinone/hydroquinone (AQ/H<sub>2</sub>AQ) single-molecule system controlled by means of electrochemical gating, AQ/H<sub>2</sub>AQ have the structural transformation from cross conjugation to linear conjugation (figure 14(f)), resulting in the disappearance of destructive QI effect and a significant increase in molecular conductance [118].

3.3.5. Electron catalysis. The charge effect mentioned above can effectively affect the conductivity characteristics of single-molecule devices, but the specific role of charge in molecular redox reactions has not been involved, the theory of electron catalysis has filled the gap in this aspect. Electron catalysis is a branch of redox catalysis. In the early days, redox catalysis is called electron transfer catalysis, electron-induced catalysis, etc. Redox catalysis is divided into hole catalysis and electron catalysis. Hole catalysis refers to a reaction in which electrons are removed and then replaced, while electron catalysis means that electrons participate in chemical reactions but ultimately do not remain in the reaction system. In other words, an electron can be regarded as a catalyst.

Electron catalysis reactions can be divided into multiple steps, because the oxidation-state level of reaction intermediates is lower than that of the substrates and products, indicating that electrons are temporarily added and then removed in this process instead of being generated or destroyed. The process of electron removal/addition is called electron transfer [143-147]. The specific process of electron catalysis is shown in figure 15(a). The electrons are first transferred from a molecule with reductive activity to a radical anion intermediate  $(S^{\bullet-})$ . Then, they are transformed into a radical anion product  $(P^{\bullet-})$  through one or more reactions from  $S^{\bullet-}$ . Finally, the electrons are released and transferred back to the starting material, which means that one catalytic cycle is finished and the next one is about to start. It is obvious that the electrons in the whole catalytic process do not have a separate free state and are always transferred between different radical ion intermediates. In this process, the suitable donor with the electrons at the beginning is thought to be the initiator (pre-catalyst), which provides the actual catalyst-the electrons [145].



**Figure 15.** Electron catalysis. (a) Schematic diagram of an electron-catalyzed reaction. (b) The classical (left) and new (right) mechanistic picture of  $S_{RN}1$  reactions. (a) and (b) Reproduced from [145], with permission from Springer Nature. (c) Electron-catalyzed reaction cycle (DPA<sup>2+</sup>/DPE<sup>2+</sup>) in solution. (d) The electron-catalyzed dehydrogenation of cyclophanes. (c) and (d) Reprinted with permission from [148]. Copyright (2021) American Chemical Society.

Electron catalysis is ubiquitous in radical cascade reactions. Take single-molecule radical substitution reactions (S<sub>RN</sub>1-type chemistry) reaction as an example, as shown in figure 15(b). On the left side is the generally accepted mechanism of S<sub>RN</sub>1 catalytic reaction process. The electrons are transferred from the appropriate electron source to the electrophile (here is halide R-X) to form anion radical  $(R-X)^{\bullet-}$ . In the next step,  $(R-X)^{\bullet-}$  is cleaved to produce radical R<sup>•</sup> and halide X<sup>-</sup>. The radical R<sup>•</sup> is converted to the radical anion (R-Nu)<sup>•-</sup> under nucleophile attack. Finally, R-Nu coupling product forms after electron transfer. It is worth noting that electron transfer occurs at the beginning and end of the reaction, which proves that the electrons have participated in the reaction process without combining with the product, demonstrating that electrons are the catalysts here. Although both figures 15(a)and (b) describe the mechanism of electrons being catalysts, it is not intuitive enough. Figure 15(c) shows a simple formal mechanism of electron catalysis, where the electron itself is involved in the reaction process as a separate subject. If the electrons can return to the cycle after the reaction, the electron catalysis occurs. Such formal mechanism is helpful to understand free radical reactions such as transition metal-free Heck reactions, trifluoromethylarene synthesis by base-promoted homolytic aromatic substitution and crossdehydrogenative coupling reactions, and can better explain the reaction processes.

Single-molecule devices provide a useful platform to investigate electron catalysis reactions at the single-molecule level. The use of a single-molecule electrical platform to study the electron catalysis processes is of great significance for understanding the electron transfer process. For example, a converting process from non-conjugated 1,2-di(4-pyridinium)ethane  $(DPA^{2+})$  molecule to conjugated 1,2-di(4-pyridinium)ethene (DPE<sup>2+</sup>) molecule can occur under the catalysis of an electron (figure 15(c)). Through single-molecule electrical testing (detection of redox potential and conductance) and DFT theoretical calculation (calculate the interaction between electron and electric field in a dehydrogenation reaction), the mechanism of the electron catalyzed dehydrogenation reaction can be determined. Firstly, electrons combine with DPA<sup>2+</sup> to form DPA\*\* diradical. DPA\*\* dehydrogenates to produce DPE\*\* diradicals under the effect of a local electric field, and then DPE\*\* forms positive ions with different valence states through the process of losing electrons, in which  $DPE^{2+}$  is generated near the electrode. DPA<sup>2+</sup> has a similar electrical conductivity to DPE<sup>2+</sup>. Moreover, the aforementioned electron catalysis reaction still occurs in another double-channel asymmetric cyclophanes system (figure 15(d)), demonstrating the universality of electron catalysis [148]. It is a novel and promising research direction to explore the electron catalysis process by using a single-molecule device, which provides a reliable research platform for exploring the catalysis reactions of electron participation at the single-molecule level.

#### 4. Single-molecule spin effects

In single-molecule devices, spin effects including Kondo effect, Zeeman effect and spin coupling effect of single molecules, have attracted more and more attention due to their vital scientific values and wide range of applications. In general, this kind of molecular spintronics is usually based on single organic molecules, such as single-molecule magnets (SMMs), spin crossover (SCO) complexes, single organic radicals and chiral molecules with spin selectivity. These molecules always possess at least two states and can transform between these states under a certain external excitation. Thus, they can be well manipulated and applied to optoelectronic devices, including photoinduced switches and spin qubits. Here, the molecular basis for single-molecule spintronics and the spin effects are first introduced. After that, the manipulation of spin effects in single-molecule optoelectronic devices is discussed.

#### 4.1. Molecular basis for single-molecule spintronics

With the development of molecular spintronics, different kinds of molecules with spin effects are emerging. In this section, we will introduce four widely studied and promising kinds of single molecules: SMMs, SCO complexes, single organic radicals and chiral molecules. These single molecules are all based on spins, but they all have their own unique properties and can be applied in different fields.

4.1.1. Single-molecule magnets. SMMs are single molecules which can maintain the magnetic dipole moment for a period of time even after the removal of an external magnetic field, when the temperature is lower than the blocking temperature  $(T_{\rm B})$ . The blocking temperature is the point at which one can observe the magnetic hysteresis. Traditionally, magnets consist of magnetic domains and domain walls. Extra energy is required to break those domain walls to change the magnetization. Therefore, when the field is removed, hysteresis occurs due to the existence of domain walls. However, since each domain of SMMs only has one molecule, no domain walls exist. For instance, the energy potential of typical SMMs has two levels, +S and -S, without the interference of an external magnetic field. When there is an external magnetic field and the spin direction of one energy level state is antiparallel to the external magnetic field, the energy of this state will decrease, forming a potential barrier. After the removal of the external field, spins in that state need an extra energy to return to the initial level. If the temperature is low enough (below  $T_{\rm B}$ ), spins will not have enough energy to overcome the potential barrier, and then hysteresis will occur in SMMs. The spin-reversal barrier  $(U_{\rm eff})$  affects the magnetic properties of SMMs [149]. Here,  $U_{\rm eff} = |D| \cdot S^2$ , where S represents the intrinsic spin ground state and D represents the anisotropy of magnetization. So, both S and D will affect the magnetic properties of SMMs.

SMMs exhibit both classical and quantum mechanical properties, which provides the fundamental basis for various applications. They can perform hysteresis similar to traditional magnets and are expected to be used for information storage. Meanwhile, they exhibit quantum coherence, promising for quantum computing. Quantum tunneling is another prominent quantum effect that SMMs display. Quantum tunneling occurs as a result of the resonance of two energy levels  $(\pm S)$ , leading to the magnetization reversal [19].

In general, SMMs possess a similar structure where a shell of organic ligands surrounds the inner metallic core, and those ligands can also act as a bridge between the molecule and the electrode in single-molecule devices [19]. Those shells and cores can be specially tailored without changing the basic structure to regulate the performance. The reason for designing this core–shell structure is that the coordination spheres of central metals need to be filled to avoid the radiationless deactivation process [150]. Ligands can isolate the molecule to avoid the bulk magnetic behavior. In addition, SMMs also possess some similar properties. Most of SMMs are monodisperse and often crystallize with high quality. They all exhibit a large spin ground state and distinct anisotropy of magnetization.

To exhibit SMMs behaviors, there are several requirements [151]. The molecule should possess a non-zero spin ground state to reduce the antiferromagnetic interaction. This interaction is undesirable because it may cause the canceling of spins. So far, three kinds of SMMs have been found, 3d metal complexes, 4f metal complexes and 3d-4f metal complexes. It is hard for pure 3d metal complexes to realize the blocking of magnetization due to their small anisotropy of magnetization. Lanthanide-based SMMs (Ln-SMMs) have strong spin-orbit coupling and large orbital angular momentum, which leads to a distinct magnetic anisotropy [152]. However, most Ln-SMMs will change the structure and magnetic properties when deposited on metallic substrates. Therefore, it is hard to build a device based on these molecules. Here, we introduce two kinds of Ln-SMMs that are chemically stable after the deposition,  $[Ln(Pc)_2]^-$  (Pc = phthalocyanine) and  $[Ln(Cl_2q)_4]^- \ (Cl_2q=5,7\mbox{-dichloro-8-hydroxyquinoline})$  with  $Ln^{3+} = Tb^{3+}$  or  $Dy^{3+}$  (figure 16(a)) [20]. The basic structure of  $[Ln(Pc)_2]^-$  is that the  $Ln^{3+}$  ion is sandwiched between two Pc rings. This lanthanide monometallic complex has attracted the attention due to the slow relaxation of magnetization at 1.7 K and its chemical robustness. For instance, for  $[Ln(Cl_2q)_4]^-$  deposited on a ferromagnetic substrate, an interface coupling between the substrate and the spins of the molecule appears at the interface, thereby preventing the reversal of magnetization. Therefore,  $[Ln(Cl_2q)_4]^-$  has the potential to construct devices.

For homonuclear Ln-SMMs, the f-f exchange coupling is complicated [150]. This exchange coupling may affect the SMMs behavior effectively. In terms of stability, different types of ligands, especially the bridging ligands, are of great importance. In a radical-bridged dinuclear



**Figure 16.** The molecular structures of SMMs. (a) The structure of  $[Ln(Cl_2q)_4]^-$  complex, where  $Cl_2q$  represents 5,7-dichloro-8-hydroxyquinoline and  $Ln^{3+}$  represents  $Tb^{3+}$  or  $Dy^{3+}$ . Reproduced from [20], with permission from Springer Nature. (b) The structure of  $[(Me_3Si)_2N]_2(THF)Dy\}_2(N_2)$  molecule, where Me represents methyl and THF represents tetrahydrofuran. Reproduced with permission from [149]. (c) Elsevier. CC BY-NC-SA 4.0. (c) The structure of  $Ln_3q_3$  molecule, where q represents 8-hydroxyquinoline and  $Ln^{3+}$  can be  $Tb^{3+}$ ,  $Dy^{3+}$  or  $Y^{3+}$ . Reproduced from [20], with permission from Springer Nature. (d) The structure of  $C_{29}H_{33}BrDyN_3O_{10}Zn$  molecule. Reproduced with permission from [149]. (c) Elsevier. CC BY-NC-SA 4.0. (e) The structure of  $[Co_2Ln(LH_3)_4](NO_3)_3$  molecule, where Ln can be Dy, Gd, Tb or Ho and LH<sub>4</sub> is 2-[2-hydroxy-3-(hydroxymethyl)-5-methylbenzylideneamino]2-methylpropane-1,3-diol. (f) The structure of  $Cu_3Tb(L)(NO_3)_2(MeOH)(H_2O)](NO_3)$ . (e) and (f) Reproduced with permission from [152]. (c) Elsevier. CC BY-NC-SA 4.0.

complex  $[(Me_3Si)_2N]_2(THF)Dy_2(N_2)$  (Me = methyl and THF = Tetrahydrofuran), each Dy ion is located in the center of a tetrahedral and one of the vertices is replaced by an  $N_2^{3-}$ ligand (figure 16(b)) [149]. The bridge  $N_2^{3-}$  strengthens the magnetic coupling and may have an impact on the magnetization relaxation barrier. The molecule can have a long relaxation time in a larger temperature range. In comparison with dinuclear complexes, polynuclear systems may be much more complicated due to the magnetic interactions between centers [150]. However, the ligands are still the most important part of the system. The above is the introduction of homonuclear systems with one or two Dy atoms, and the following will introduce multinuclear systems. For example, trinuclear complexes  $Ln_3q_3$  (q = 8-hydroxyquinoline) can host both paramagnetic metals  $(Tb^{3+} \text{ or } Dy^{3+})$  and diamagnetic metals  $(Y^{3+})$  (figure 16(c)) [20]. The Ln ion is located in the center of a distorted antiprismatic structure formed by ligands. Interestingly, a huge magnetoresistance (up to 15 nm molecular thickness) can be found in Tb<sub>3</sub>q<sub>3</sub>, Dy<sub>3</sub>q<sub>3</sub>, and Y<sub>3</sub>q<sub>3</sub> systems at

room temperature, indicating that it is the quinoline ligand state that governs the spin transport properties, not the magnetic moment of the metal ion. Furthermore, tetranuclear complexes are affected by the ligands as well. When the bridging ligands are OMe<sup>-</sup> and OH<sup>-</sup>,  $[Dy_4(bpt)_4(NO_3)_4(OMe)_2(OH)_2]\cdot 3MeOH$  with bpt = 3,5-bis(pyridin-2-yl)-1,2,4-trizole, the structure of Dy<sub>4</sub> core is a butterfly [150]. When the bridging ligands are OH<sup>-</sup>,  $[Dy_4(bpt)_4(NO_3)_6(EtOH)_2(OH)_2]\cdot 3MeOH$ , the core structure is a zigzag. The zigzag one shows a unique double relaxation process with energy barriers of  $\sim 3.596$  meV and  $\sim 3.844$  meV, while the butterfly one displays a single process.

In addition, since the spins have the probability to overcome the relaxation energy barrier, quantum tunneling in pure Ln-SMMs may cause a decrease in remnant magnetization [152]. This property is not obvious in 3d-4f heterometallic complexes. There is a moderate magnetic exchange between 3d and 4f centers, which may increase the reversal energy



**Figure 17.** The molecular structures of SCO complexes in different states. (a) The SCO phenomenon. Reproduced with permission from [155]. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC-ND 4.0. (b) The transition of a photoswitchable complex (Fe<sup>III</sup> tetraphenylporphyrin perchlorate) with different lights. Reproduced from [156]. CC BY 4.0. (c) The transition of a [Fe(bpy)<sub>3</sub>]<sup>2+</sup> complex from the LS state to the HS state. Reproduced from [157]. CC BY 4.0. (d) The LS state and HS state of a {[Fe<sup>III</sup>(Tp<sup>\*</sup>)(CN)<sub>3</sub>]  ${}_{2}$ Fe<sup>II</sup>(bpmh)}·2H<sub>2</sub>O complex, where Tp<sup>\*</sup> represents hydrotris(3,5-dimethylpyrazolyl) borate and bpmh represents N,N'-bis-pyridin-4-ylmethylene hydrazine. Reproduced from [158], with permission from Springer Nature. (e) The LS state and HS state of [Fe<sup>III</sup>(M<sup>e</sup>bik)<sub>2</sub> (NCS)<sub>2</sub>] molecules, where <sup>Me</sup>bik represents bis(1-methylimidazol-2-yl)ketone). Reproduced from [160]. CC BY 4.0. (f) The structures of [Fe<sup>III</sup><sub>4</sub>(L)<sub>4</sub>](BF<sub>4</sub>)<sub>4</sub>·2CH<sub>3</sub>CN and [Fe<sup>III</sup><sub>2</sub>Fe<sup>II</sup><sub>2</sub>(L)<sub>4</sub>](BF<sub>4</sub>)<sub>6</sub>·6CH<sub>3</sub>NO<sub>2</sub>·(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O·4H<sub>2</sub>O molecules, where L is 2-phenyl-4,5-bis {6-(3,5-dimethyl-1H-pyrazol-1-yl)pyrid-2-yl}-1H-imidazole. Reproduced from [162], with permission from Springer Nature.

barrier and reduce the quantum tunneling. Meanwhile, they have similar properties to pure 4f metal complexes, such as large magnetic anisotropies. For instance, the barrier of ZnDy SMMs is extremely high because of the large axial coordination (figure 16(d)) [149, 151]. The axial coordination environment may lead to a large ligand field splitting between two lowest levels called Stark sublevels. In this structure, the coordination of three oxygen atoms at axial positions that hold negative charges leads to an axially enforced ligand field. The Dy metal ion is in this ligand field. The structure of trinuclear complex  $[Co_2Ln(LH_3)_4](NO_3)_3$  is shown in figure 16(e), where Ln = Dy, Gd, Tb, Ho and LH<sub>4</sub> = 2-[2-hydroxy-3-(hydroxymethyl)-5-methylbenzylideneamino] 2-methylpropane-1,3-diol. The basic structure of this complex is linear, and the central Ln metal ion is in a square-antiprismatic geometry formed by eight oxygen atoms [152]. Studies have shown that only when Ln = Dy, the complex exhibits slow relaxation and behaves as an SMM. This may be due to the extended twodimensional network of hydrogen bonds leading to quantum tunneling and accelerating quantum tunneling relaxation. Tetranuclear SMMs have attracted attention as they have many different shapes and the reasons for some unique magnetic properties are still unknown. In propeller-shaped  $Cu_3Tb(L)(NO_3)_2(MeOH)(H_2O)](NO_3)$  (figure 16(f)) [152], the ligand L is obtained from the reaction of the dialdehyde 1,4-diformyl-2,3-dihydroxybenzene and 1,3-diaminopropane. The ligands form caves for metal ions, which improves the control of the nuclearity and structure. The molecule exhibits slow magnetization relaxation with  $U_{\rm eff} = \sim 19.5$  K. However, when Tb is replaced by Dy, the system does not exhibit the SMM behavior. The possible reason is that the symmetry of the ligand field is lower. In addition to the planar structure for M<sub>3</sub>Ln, the tetrahedral topology is usually for M<sub>2</sub>Ln<sub>2</sub>.  $[M_2Dy_2(OH)_2(L)_2(OAc)_5(EtOH)(H_2O)_x](ClO_4)$  (M = Ni, x = 1.5; M = Zn, x = 1) is a typical molecule, where all metal ions are in the vertices of a cube and form a tetrahedron to improve the symmetry [152]. Here, the ligand originates from the reaction between o-vanillin and 2-hydrazinopyridine. Only when M = Zn, the molecule will behave as an SMM. Because there may be an increasing transverse anisotropy strengthening quantum tunnelling of magnetization in the Ni<sub>3</sub>Dy system.

4.1.2. Spin crossover complexes. SCO complexes can switch between the high spin (HS) state and the low spin (LS) state [153, 154]. This change of spin states in SCO complexes often exists in transition metals with  $d^4$  to  $d^7$  electrons distributing the five d orbitals, such as Cr, Mn, Fe and Co, based on the ligand field theory [155]. In specific, the ligands can form a field around the center metal ions. When the ligands are approaching the center ions, the electronic clouds of some dorbitals meet with the ligand field, producing a large repulsive force. Thus, the energy of these orbitals increases and the five d orbitals will be split into two high energy orbitals and three low energy orbitals. Since each electron has a spin, the number of unpaired electrons determines whether the HS state or the LS state is displayed. According to the Pauli exclusion principle, the electron often singly occupies the lowest energy state. When an extra electron is added, it can couple with the previous electron in the lower energy state or occupy one of the higher energy states. When the electron is transferred from the lower energy state to the higher energy state, a certain energy is required during the process, which is called the splitting energy. This splitting energy can be affected by the ligand field. Specifically, the splitting energy increases as the field strength of the ligand increases. When the electron couples with the other electron in the lower energy state, the required energy is called the paring energy. If the ligand has the weak field strength and the splitting energy is lower than the paring energy, the electrons tend to separate rather than pair and individually occupy the orbitals (figure 17(a)) [155]. Therefore, the number of unpaired electrons becomes larger, forming a HS state. If the ligand possesses a strong field strength and the splitting energy is higher, the electrons will tend to couple with other electrons, which forms a LS state. When the splitting energy affected by the field strength of the ligand is comparable to the paring energy, the spin state can be switched, and SCO occurs. Furthermore, SCO complexes can be regulated by external perturbations, such as light and temperature [154]. A typical example is Fe<sup>III</sup> tetraphenylporphyrin perchlorate (FeTPPClO<sub>4</sub>) complex (figure 17(b)) [156]. Due to the transition between *trans* (LS state, S = 1/2) and *cis* (HS state, S = 5/2) configuration, the complex exhibits the SCO effect. The ligand has a nitrogen-nitrogen double bond, thus the 3,5-di-tert-butylaniline (t-Bu) part and the photodissociable ligand part may be in the same side or the opposite sides of the double bond, forming a transition between cis ligand and trans ligand. Specifically, the trans ligand configuration will transform to the cis ligand under 365 nm irradiation. While under the 435 nm light irradiation, it will return to the trans ligand form. However, due to the steric hindrance between the porphyrin and the t-Bu groups, the cis ligand form is hard to bind with the metal-porphyrin. Both of the two groups in the ligand occupy large spaces. If they are in the same side of the double bond, they will compete with each other for enough space. However, the space is not enough for two groups and they have to be close to form a stable ligand. In this situation, the t-Bu group is also close to the metal-porphyrin, producing a steric repulsion. Therefore, the binding possibility is low, leaving some unpaired electrons to form an HS state. Apart from this process for SCO, light-induced excited spin-state trapping (LIESST) is another common process, involving several excited spin states, which can induce SCO.  $[Fe(bpy)_3]^{2+}$  is an example of mononuclear SCO complexes, in which the SCO can be induced via LIESST (figure 17(c)) [157]. Here, 'bpy' represents 2,2'-bipyridine. After the irradiation, the complex is changed from the LS state ( $S = 0, t_{2g}^{6} e_{g}^{0} L^{0}$ ) to the HS state (S = 2,  $t_{2g}^4 e_g^2 L^0$ ). Notably, a metal-toligand charge transfer (MLCT) state  $(t_{2g}^{5}e_{g}^{0}L^{1})$  forms in the whole transform process due to the photoexcitation, where the light excites an electron to the highest energy level. However, the MLCT state only exists for  $\sim 120$  fs and the electron in the highest energy level will move to the  $e_{q}$ level to stabilize the system. Furthermore, the SCO of other single-chain magnets with more than one nuclear can also be induced by LIESST. An example of SCO single-chain magnets is  ${[Fe^{III}(Tp^*)(CN)_3]_2 Fe^{II}(bpmh)} \cdot 2H_2O$  complex  $(Tp^* = hydrotris(3,5-dimethylpyrazolyl)$  borate, bpmh = N,N'-bis-pyridin-4-ylmethylene hydrazine) (figure 17(d)) [158]. Though there are three metal ions in the system, only the middle Fe<sup>II</sup> ion can affect the electronic configuration. The LIESST is observed under 473 nm and 532 nm light irradiation, indicating that the effect is excited by the light. During the LIESST process, the molecule is changed from the LS  $(t_{2g}{}^6e_g{}^0)$  state to the HS  $(t_{2g}{}^4e_g{}^2)$  state.

In addition, the SCO effect of molecules can also be manipulated by the temperature. Generally, the LS state is stable at lower temperatures, while the HS state prefers higher temperatures. Because the entropy of the HS state increases more than that of the LS state as the temperature increases, which provides more electronic and vibrational contributions. The SCO temperature ( $T_{1/2}$ ) where the two spin states have the



**Figure 18.** The structures of single organic radicals. (a) The structure of a 1,2,4-benzotriazin-4-yl radical. Reprinted with permission from [164]. Copyright (2019) American Chemical Society. (b) The structure of a polychlorotriphenylmethyl (PTM) radical. Reprinted with permission from [165]. Copyright (2015) American Chemical Society. (c) The structure of another PTM radical. Reproduced from [166]. CC BY 4.0. (d) The structure of a *tert*-butyl nitroxide radical. Reproduced from [167]. CC BY 3.0. (e) The structure of a {4-[{[2,5-bis(4-sulfanylphenyl[eth-1-yn-2-yl])phenyl]carbonyl}(methyl)amino]-2,2,6,6-tetramethylpiperidin-1-yl}oxidanyl radical. Reproduced from [168]. CC BY 4.0. (f) The structure of a zinc methyl phenalenyl (ZMP) radical. Reproduced from [169], with permission from Springer Nature. (g) The structure of a 2,4,6-hexakis-(pentachlorophenyl)mesitylene radical. Reproduced with permission from [171]. (c) American Chemical Society. CC BY-NC 4.0. (h) The structure of a supramolecule with two cyclobis(paraquat-p-phenylene) molecules. From [172]. Reprinted with permission from AAAS.

same populations can be used to show the SCO effect [159]. In other words, at this temperature, the difference between the two enthalpies of the states ( $\Delta H$ ) is equal to the difference between the two entropy parts of the states ( $T\Delta S$ ). Typical examples are two Fe-based SCO complexes, a four-coordinated Fe<sup>II</sup> complex with formazanate ligands [159] and [Fe<sup>II</sup>(<sup>Me</sup>bik)<sub>2</sub>(NCS)<sub>2</sub>] (<sup>Me</sup>bik = bis(1-methylimidazol-2-yl)ketone) (figure 17(e)) [160]. As the temperature increases, both of them exhibit a transition process from the LS state to the HS state, but the mechanisms are different. The SCO temperatures  $T_{1/2}$  are 300–368 K and 260 K, respectively. Since the ligand exhibits  $\pi$ -acceptor properties and stable *d* orbitals even with high temperatures, the first complex is extremely stable in the LS state. As for the second complex, higher temperatures lead to a geometry distortion of the complex,

that is, the lengths of the Fe–N (<sup>Me</sup>bik) bond and Fe–NCS bond are elongated and the N–Fe–N angles are changed. Furthermore, a temperature-dependent change between the LS state and the HS state of a square planar nickel(II) porphyrin derivative, 5,15-bis(4-(methylthio)phenyl)-10,20-bis(2,3,4,5,6-pentafluorophenyl)-Ni(II) porphyrin, has been found [161]. The manipulation is governed by the complexation and decomplexation processes of the molecule.

Additionally, grid-like complexes can also exhibit the SCO phenomenon. Since they have multinuclear, they have multiple spin states. Here are two typical examples:  $[Fe^{II}_4(L)_4](BF_4)_4 \cdot 2CH_3CN$  ( $[Fe^{II}_4]$ ) complex and  $[Fe^{III}_2Fe^{II}_2(L)_4](BF_4)_6 \cdot 6CH_3NO_2 \cdot (C_2H_5)_2O \cdot 4H_2O$ ( $[Fe^{III}_2Fe^{II}_2]$ ) complex (figure 17(f)) [162]. Here, the ligand L is 2-phenyl-4,5-bis{6-(3,5-dimethyl-1H-pyrazol-1-yl)pyrid2-yl}-1H-imidazole. The two complexes exhibit the transition process via different external perturbations. One is temperature and the other is light. In specific, [Fe<sup>II</sup><sub>4</sub>] can change from [(HS-Fe<sup>II</sup>)<sub>4</sub>] at room temperature to an intermediate state with an average formula [(HS-Fe<sup>II</sup>)<sub>3</sub>(LS-Fe<sup>II</sup>)], and finally to [(HS-Fe<sup>II</sup>)<sub>2</sub>(LS-Fe<sup>II</sup>)<sub>2</sub>] at 100 K. [Fe<sup>III</sup><sub>2</sub>Fe<sup>II</sup><sub>2</sub>] with four LS states is changed to [(LS-Fe<sup>III</sup>)<sub>2</sub>(LS-Fe<sup>II</sup>)(HS-Fe<sup>II</sup>)] under the irradiation of 532 nm light and further changed to  $[(LS-Fe^{III})(HS-Fe^{III})(LS-Fe^{II})(HS-Fe^{II})]$  under the irradiation of 808 nm light. In addition, some other SCO complexes can be controlled by at least two perturbations. For example, in  $[FeL_3](ClO_4)_2$  (L = N-4-methoxyphenyl-(1H-imidazol-2-yl)-methanimine) SCO complex [163], the transition between the HS state and the LS state can be thermally driven with  $T_{1/2} = 158$  K. Meanwhile, the HS state can return back to the LS state at 10 K under the irradiation of 647 nm light.

4.1.3. Single organic radicals. Organic radicals which possess characteristics of spins are promising for future devices. Radicals are neutral molecules with at least one unpaired electron in the ground state. The spin of the unpaired electron is a basic property like other physical quantities such as the mass and charge. It describes the inherent characteristics of microscopic particles and the phenomenon of intrinsic motion caused by intrinsic angular momentum. Therefore, the unpaired electron is responsible for the intrinsic magnetic moment. Organic radicals hold some unique magnetic properties, including paramagnetic, antiferromagnetic and ferromagnetic. Specifically, since the spin of the electron can generate a magnetic field, the molecule becomes paramagnetic when there is an unpaired electron; when the number of unpaired electrons is more than one and the unpaired electrons are parallel, the molecule exhibits paramagnetic as well; while if they couple with each other, the situation is different. Under the suppose that two molecular parts A and B are adjacent and both have an unpaired electron, due to the influence of spin polarization, each part may have a positive or negative spin. Moreover, the spins of the two molecular parts have an overlapping area. If the overlapping area of two adjacent molecular parts has the same sign, the molecule will exhibit antiferromagnetic, while it will exhibit ferromagnetic if the signs are opposite.

However, organic radicals are usually unstable. For instance, 1,2,4-benzotriazin-4-yl radicals (Blatter radicals) are a typical class of radicals (figure 18(a)) [164]. The reason why Blatter radicals are unstable is that the oxidization of the unpaired electron results in the delocalized lone electrons. In specific, the unpaired electron is not localized in the nitrogen atom and can be transferred from the molecule to the metal substrate quickly when connected to a substrate, so the unpaired electron, a singly occupied molecular orbital (SOMO) forms which is slightly higher than the Fermi level of Au substrates. Small changes in the environment will cause a change in the alignment of the MO. So, the molecule is very sensitive to the environment. Even with the same substrate, different environment leads to different behaviors of the radical. Review

Thus, the stability of radicals is of great importance, which will affect the practical application. In general, Kondo resonance can confirm the existence of radicals. This is due to that Kondo resonance originates from the interaction between the spin electron on the molecule and electrons in the electrode, thereby affecting the conductance. In this system, the interaction between the unpaired electron of the molecule and the electron in the electrode causes Kondo resonance. While the spin often arises from the unpaired electron. Therefore, if Kondo resonance can be detected for a long time, the radical is stable.

As is said above, organic radicals always have unpaired electrons. Some are intrinsically formed and stable, while others are formed from redox reactions. Those intrinsically formed radical systems are usually stable because the electrons are stably trapped in the newly generated spin orbitals in this case. PTM radicals are a typical example of stable single organic radicals with an intrinsic unpaired electron (figure 18(b)) [165]. Unlike the unpaired electron in the Blatter radical, it is on the trivalent carbon atom and is blocked by three adjacent rings in the PTM radical. Therefore, the rings shield and protect the electron from chemical reactions. This molecule exhibits paramagnetic properties due to the spin of the unpaired electron. Furthermore, the magnetic moment is extremely stable owing to the stable radical even after some mechanical or electrostatic changes near the interface between electrodes and the molecule. Since the electron has two spin directions (spin up and spin down), there are two spin channels in the molecule, which can be represented as  $\alpha$  and  $\beta$ . The HOMO and the LUMO are related to both  $\alpha$ channel and  $\beta$ -channel, whereas the SOMO only exists in  $\alpha$ channel. For a common spin-unpolarized channel, electrons travel through HOMO. Here, an additional spin-flipping channel in this molecule appears, which is SOMO. Both SOMO and the accompanying  $\beta$ -LUMO are spin-polarized. So, HOMO is responsible for spin-independent conductance, while SOMO is related to spin-dependent conductance, such as Kondo phenomenon. Due to the protection of adjacent rings, the localization of SOMO leads to stable Kondo resonance, which proves the stability of free radicals from another perspective. Moreover, when a PTM radical is bonded to the Au electrode with one end, the influence of the chain length on the conductance can be directly observed (figure 18(c)) [166]. In specific, PTM radicals possess a SOMO with an  $\alpha$ -spin electron and a singly unoccupied molecular orbital (SUMO). The molecular energy of the SOMO-SUMO gap of the open-shell form (i.e., PTM radicals) is much smaller than that of the HOMO-LUMO gap of the closed-shell form (i.e., non-radical PTM molecules). Therefore, the energy-level alignment is changed, leading to a change in the tunneling barrier height. In parallel, the charge transport mechanism of this system is tunneling because the tunneling decay rate increases as the length of the chain increases. Thus, the change of the tunneling barrier height will affect the charge transport. Apart from the PTM molecule, 2,2'-bipyridine with a tert-butyl nitroxide (BPyNO) radical is another stable system, prepared via detaching the hydrogen atom from the oxygen atom of a BPyNO molecule (figure 18(d)) [167]. The radical is stable because of the confinement of the aromatic ring in the BPy molecule. During the detachment, the HOMO of the BPyNO molecule split into an  $\alpha$ -SOMO and a  $\beta$ -SUMO. Two new transport resonances are observed between HOMO and LUMO due to the majority ( $\alpha$ -SOMO) and minority ( $\beta$ -SUMO) spin orbitals. Since the majority spin orbital creates a new resonance, the conductivity is much higher than that of pure BPy molecules.

Besides SOMO, there are mechanisms related to single organic radicals. For example, in {4-[{[2,5-bis(4sulfanylphenyl[eth-1-yn-2-yl])phenyl]carbonyl}(methyl) amino]-2,2,6,6-tetramethylpiperidin-1-yl}oxidanyl (TEMPO-OPE) single-molecule junctions fabricated by MCBJ (figure 18(e)) [168], a large positive magnetoresistance can be obtained. Specifically, OPE is the backbone while the unpaired electron is in TEMPO. Since the conjugation of the OPE  $\pi$ -orbital and the unpaired electron orbital is so small that it can be ignored, the unpaired electron can be isolated from the main chain and is chemically stable. In most cases, the magnetoresistance is negative due to the spin-flip scattering reduction. However, in this case, it may be the reduction of the coupling strength between the electrode and the current-carrying molecular orbital that leads to a huge positive magnetoresistance.

In addition, radicals obtained from redox reactions are promising as well. They are stable and can change the state by chemical reactions. Therefore, the magnetic moment of the molecule can be changed independently and can be used as an information source. Surface hybridization is also an important mechanism, in which the charge is transferred between the molecule and the electrode, causing the redox reaction and forming a radical. For instance, in a ZMP (figure 18(f)) system [169], the interfacial spin transfer is caused by the hybridization of the ZMP *p*-orbital and the *d*-orbital of the Co surface changes the neutral molecule into a radical. In addition to reversible redox, redox controlled by oxidizing reagents can also generate radicals, such as a phenothiazine (PTZ) radical (figure 18(h)) [170]. It is formed through an oxidation reaction via adding acid oxidants trifluoroacetic acid (TFA) into a mixed tetrahydrofuran/1,3,5-trimethylbenzene (THF/TMB) solution in the ambient air. Since the HOMO-LUMO gap decreases when the radical forms, the tunneling barrier is lowered, which may increase the conductance.

Different from the single radical systems, the organic diradical systems often display spin coupling between two radicals and exhibit ferromagnetic or antiferromagnetic properties as previously described. One of the typical organic diradical systems is a neutral system with two radicals, 2,4,6-hexakis-(pentachlorophenyl)mesitylene (figure 18(g)) [171]. The two radicals with two unpaired electrons form a two-spin magnetic system. Adding a third electron to the system via changing the gate voltage could change the redox state of the molecule and form a new spin system with antiferromagnetically coupled spins. The third electron couples with the original two radical spins instead of occupying the half-filled orbital, changing the singlet magnetic state to a doublet magnetic state. The two new couplings are not the same, indicating

that the third electron is close to one of the previous radicals. In addition, supramolecules can also be used for single organic radicals. They often have more than one stable radical and more than two stable states, and can change directly between multiple stable states. Therefore, they have great potential for memory devices. Two bisbromomethyl(bispbenzylbipyridinium) dication molecules react with two 4,4'bipyridine (BIPY) molecules to form a supramolecule with two cyclobis(paraquat-p-phenylene) (CBPQT) molecules as shown in (figure 18(i)) [172]. The radicals are chemically stable, mainly because the BIPY units are tightly stacked, which can confine the unpaired electron. The stacking is enhanced by forming bonds between two electron-deficient CBPQT rings. Through electron paramagnetic resonance spectroscopy, the supramolecules with more than one radical  $(HC^{4(\bullet+)}/HC^{2\bullet6+})$ are diamagnetic, while the supramolecules with one radical  $(HC^{\bullet,7+})$  are paramagnetic. Furthermore, the two states, diamagnetic and paramagnetic, can change between each other by applying different voltages.

These radical molecular systems provide a basis for the study of spins. They possess some general characteristics. For example, they have unique magnetic properties due to the magnetic moment of the unpaired electron or the coupling between two magnetic spins. Meanwhile, quantum effects can be found in these systems owing to the unpaired electron, such as Kondo effects. In addition, diradical systems are different from single-radical systems, they have special intramolecular magnetic interactions which can be applied in the quantum SWAP gate. In a word, organic radicals are competitive in molecular spintronic devices, such as memory devices and quantum computing devices as qubits.

4.1.4. Chiral molecules for spin selectivity. Chiral molecules possess the chirality-induced spin selectivity (CISS) effect, in which the electron transmission probability of chiral molecules depends on the spin of electrons. Specifically, most electrons have two spin states, spin up and spin down. When these electrons move through chiral molecules (left-handed or right-handed), their spin orientation will be parallel or antiparallel to their velocity. Thus, only when the spin orientation matches the molecular chirality, the electrons can travel through the molecule (figure 19(a)). Furthermore, chiral molecules with this effect will push forward the development of organic spintronics and other applications. For instance, devices based on chiral molecules can generate polarized electrons without necessarily containing a magnet and can realize some functions, such as memory or spin injection by changing the chirality of the molecules. However, the basic principle of chiral molecules with CISS effect is still unclear [173, 174]. So far, the two most discussed principles can explain the coupling between chiral molecules and electron spins. One is through spin-orbit coupling and the other is through the formation of induced magnetic flux. In the former principle, the direct spin-orbit coupling on the chiral molecule is not strong enough to cause CISS. Therefore, some scientists predict that by combining the strong spin-orbit coupling in the substrate with the selective orbital angular momentum exerted by chiral molecules, a strong spin polarization can be obtained. In the



**Figure 19.** CISS effect and the molecular structures of chiral molecules for spin selectivity. (a) Schematic representation of the CISS effect. (b) Schematic representation of the individual memory units based on an  $\alpha$ -helix L-polyalanine molecule. Reproduced from [177]. CC BY 4.0. (c) Schematic representation of the monolayer of dsDNA acting as a spin filter. From [175]. Reprinted with permission from AAAS. (d) The different structures of OCA molecules and the transition between them. Reproduced from [178]. CC BY 4.0.

latter case, when a current flows through the chiral molecule, the magnetic field induced by a current flow is coupled with the intrinsic magnetic moment of the electron.

There are many kinds of chiral molecules that exhibit CISS effect. Two typical examples are deoxyribonucleic acid (DNA) and other organic small molecules. These two molecules are usually used in the study of CISS effect. The doublestranded DNA (dsDNA) is a chiral molecule because of its primary and secondary structure. A DNA molecule often consists of deoxyriboses, bases and phosphates. Bases (including purines and pyrimidines) are flat molecules without chirality, while deoxyriboses are D-configuration (opposite to Lconfiguration) and phosphates are chiral molecules. Therefore, some of the small molecules that make up DNAs are chiral molecules. For the secondary structure, two single-stranded DNAs coil antiparallel to form a double helix structure. The coil direction may be  $\alpha$ -helix or  $\beta$ -helix. Thus, dsDNAs are chiral molecules. It has been proved that chiral dsDNAs can exhibit the CISS effect. For example, a SAM of dsDNAs on Au substrates performs the CISS effect (figure 19(c)) [175]. When the light is incident perpendicular to the Au substrate, unpolarized electrons are emitted. However, only the electrons with antiparallel spin to their velocity will pass through dsDNA, and other electrons cannot pass through. Therefore, the current is polarized. In addition, the CISS effect of chiral dsDNAs has also been proved in another systems. Specifically, the electron through dsDNA is spin selective in the structure of Au nanoparticle-dsDNA-nickel substrates [176]. When a magnetic field is applied to the device, the Ni substrate generates spins that are parallel or antiparallel to the direction of the current. Due to the CISS effect of DNA, the conduction electrons with a certain spin direction that match the chirality of DNA molecules can pass. If the spins generated by the magnetic field are downward, the conductance is enhanced, which means that a large number of conduction electrons pass through the chiral DNA molecule. However, in the other direction, the conductance is not greatly enhanced. Thus, the CISS effect of chiral DNA molecules can affect the conduction.

Furthermore, organic chiral molecules can be used to construct spintronic devices utilizing the CISS effect. Because of the chiral center in the molecules or the chirality of the molecules, they usually perform the CISS effect. A typical example is a device based on the amino acid molecule (figure 19(b)) [177]. An  $\alpha$ -helix L-polyalanine (AHPA-L) molecule can exhibit the CISS effect and is applied in a spin memory device. AHPA-L is a right-handed chiral molecule and can produce spin-polarized electrons in the device. When the electrons pass through the molecule, only those spins that match the chirality of the molecule can pass, that is, the electrons passing through the molecule are spin-polarized. As the number of spin-polarized electrons increases, the spin information can be passed onto the nickel layer. Thus, the nickel layer becomes magnetized, and the density of minority and majority spin states is split near the Fermi level, filling most of the majority spin states of the nickel layer. Therefore, the resistivity of the nickel layer increases, and the device exhibits memory characteristics. However, the devices based on the chiral molecules and nickel electrodes are unstable and need further study. Since the easy axis (the easiest direction to magnetize) of the nickel substrate is in-plane and the magnetization induced by spin-polarized electrons that are generated by the chiral molecule is perpendicular to the nickel surface, the spin will flip after removing the current, which affects the magnetization. Some systems can be controlled by external stimuli through the inversion of the configuration. For example, the overcrowded alkene (OCA) can change its chirality via irradiation and thermal treatment (figure 19(d)) [178]. The driving force of this chirality change is the *cis*trans isomerization of the carbon double bond. When a cis molecule is irradiated at 435 nm, the molecule becomes a trans configuration. When the trans molecule is heated and further irradiated, it will transform back into the cis configuration. Use 'M' and 'P' to represent up-spin and down-spin, respectively. 'M' stands for 'Minum' and 'P' stands for 'Plus', and they are expressions of chirality. Here, up-spin means that the spin angular momentum is parallel to the electron propagation, and down-spin means antiparallel. When the chirality of the molecule changes, the selected spin changes. By measuring the magnetoresistance of the M-trans device and the P-cis device, the two results obtained are exactly the opposite. This demonstrates that devices based on OCAs can exhibit the CISS effect. In addition to the applications in single-molecule optoelectronic devices like spin light-emitted diodes [179], there are many other applications of chiral molecules, such as enantiomeric separation [27], 3D displaying, tomography and bioencoding.

## 4.2. Spin effects and manipulation of single-molecule devices

Single molecules used in spintronics usually exhibit Kondo effect and Zeeman effect. Two adjacent spin centers usually have spin coupling. These spin effects have been investigated in single-molecule optoelectronic devices, especially the spin behavior. For example, the Kondo effect can be considered as an indicator of spin in single-molecule optoelectronic devices. Later in this section, some single-molecule spintronic devices and their operation by external stimuli including light irradiation are also described, such as single spin switching based on the SCO or quantum spin qubits, and the manipulation of single nuclear spin and single molecular spinterface.

4.2.1. Kondo effect and Zeeman effect. In most cases, the resistance of a metallic conductor will decrease as the temperature decreases. However, the resistance of some unique metals with magnetic impurities will increase as the temperature reduces, when T is lower than a certain temperature. This phenomenon refers to Kondo effect and the special temperature is called Kondo temperature  $(T_K)$  under which Kondo effect occurs. In addition to macroscopic systems, Kondo effect is also observed in the single-molecule devices with odd charge occupation, in other words, nonzero net spin. Because in these molecules, the spin electron on the molecule will have a strong spin coupling with the conduction electron. The movement of the conduction electrons is hindered and the conductance of the device decreases. In single-molecule systems, when the conduction electron stays on the lone electron with spin S = 1/2, the single-channel spin-1/2 Kondo effect often exists [6, 180, 181]. At low temperatures, the delocalized conduction electrons are polarized to be antiparallel to the spin of the lone electron. Thus, the conduction electrons form a screening cloud called 'Kondo screening cloud' (figure 20(a)). The cloud of electrons on the electrode shields the spin, thereby increasing the DOS in the electrodes. Because of this, a sharp zero-bias differential conductance dI/dV peak appears in the  $dI/dV - V - V_g$  gap with the width  $k_BT_K$ . Here, V is the bias voltage,  $V_g$  is the gate voltage and  $k_B$  is the Planck constant. Another explanation of this phenomenon is the Anderson single-level model [181]. In this model, a SOMO is formed with the unpaired electron below the Fermi level. The electron has the possibility to hop from the molecule to the electrode, and another conduction electron jumps from the electron sea into the left site of the molecule. The coherent superposition of tunneling events leads to the screening of the spin and produces the Kondo resonance. In naddition, Kondo effect has obvious temperature-dependent characteristics (figure 20(b) bottom). As the temperature increases, the Kondo peak is becoming lower. When the temperature is higher than  $T_{\rm K}$ , the Kondo peak disappears.

Kondo effect can be used as an indicator that the molecule has spins in single-molecule devices, such as stable free radicals due to the unpaired electron of radicals and unpaired


**Figure 20.** Kondo effect and Zeeman effect in single-molecule devices. (a) Schematic representation of the Kondo effect. Reproduced from [6], with permission from Springer Nature. (b) The structure of the device based on a single  $[(N,N',N''-trimethyl-1,4,7-triazacyclononane)_2V_2(CN)_4(C_4N_4)]$  molecule and a plot of conductance versus voltage at various temperatures, which is a typical example with Kondo effect. (c) A dI/dV plot as a function of *V* and *B* and a dI/dV plot as a function of *V* and  $V_g$  at T = 300 mK, which are typical examples with Zeeman effects. (b) and (c) Reproduced from [182], with permission from Springer Nature. (d) The structure of a device based on a  $[Co(tpy-SH)_2]^{2+}$  molecule. Reproduced from [183], with permission from Springer Nature. (e) The structure of a device based on  $Co(tpy'-SH)_2$ , where tpy'-SH is 4'-mercapto-2,2':6',2''-terpyridine. From [184]. Reprinted with permission from AAAS. (f) The structure of a device based on manganese phthalocyanine. Reproduced from [185]. CC BY 4.0. (g) The Kondo peaks in various magnetic fields. Reproduced from [182], with permission from AAAS. (i) The two-stage Kondo effect at various temperatures. Reproduced from [185]. CC BY 4.0.

electrons of metal complexes. For instance, a single divanadium molecule, [(N,N',N''-trimethyl-1,4,7-triazacyclononane)<sub>2</sub>V<sub>2</sub>(CN)<sub>4</sub>(C<sub>4</sub>N<sub>4</sub>)] (V<sub>2</sub>), is deposited onto the Au electrode (figure 20(b) top) [182]. In the plot of dI/dV as a function of bias voltage (V) and gate voltage (V<sub>g</sub>), a zero-bias peak appears in the left region while the peak vanishes in the right region (figure 20(c) bottom). The result is mainly due to the number of electrons in the molecule. The V<sub>2</sub> molecule (the right region) has an even number of electrons, indicating that the net spin of the molecule is zero. The total number of electrons in the  $V_2^+$  molecule (the left region) is odd, indicating that there are unpaired electrons, and the net spin is 1/2.

In addition, the Kondo effect can be finely regulated by Zeeman effect, which means when a magnetic field B is applied to the molecule, the energy levels of spin electrons split. In specific, it refers to the phenomenon that the two original degenerated spin orbitals (parallel or antiparallel to the magnetic field) are not degenerate in an external magnetic field, leading to a split of emitting spectral lines of atoms, manifesting the zero-bias dI/dV peak splitting. Generally, assume that a state has a spin S = 1/2. The state has two (2S + 1 = 2) levels. If no magnetic field exists, the two levels will be degenerate. If there is a magnetic field B, the two degenerated levels will split into two states (spin-up and spin-down). The energy of the spinup state decreases, while the energy of the spin-down state increases. The energy change is  $g\mu_e B$  (g: electron g-factor,  $\mu_e$ : Bohr magneton), which is called 'Zeeman energy'. For a free electron, the Zeeman energy is 115  $\mu$ eV per Tesla [180]. For example, in the transistor based on the single molecule  $[Co(tpy-SH)_2]^{2+}$  (figure 20(d)), where tpy-SH stands for 4'-(mercapto)-2,2':6',2"-terpyridinyl, Zeeman effect is observed [183].  $Co^{2+}$  ion is in the center of an octahedral formed by N atoms and has seven 3d electrons, meaning the total net spin is not zero. Therefore, the zero-bias dI/dV peak splits in the magnetic field (figure 20(g)). The splitting enhances with the increase of the magnetic field and is equal to  $2g\mu_e B$ , where g is about 2 in this example.

Kondo effect will change as the spin S of the molecule is changed. For instance, when the  $Co(tpy'-SH)_2$  molecule is stretched, two isotropic spins of the molecule become anisotropic. Thus, the spin of the molecule is S = 1 and the split of the peak is proved to be caused by S = 1 underscreened Kondo effect, instead of S = 1/2. Here, tpy'-SH is 4'-(mercapto)-2,2':6',2"-terpyridine (figure 20(e)) [184]. Specifically, as the stretch increases, the zero-bias conductance peak (Kondo peak) begins to split (figure 20(h)). This is mainly due to the high-spin S = 1 Kondo effect and the degeneracy of the triplet ground state. The triplet ground states ( $S_z = -1, 0$  and 1) are degenerate in the initial molecule. When the molecule is stretched (the *z*-axis), the  $S_z = 0$  state will move down, and  $S_z = -1$  and 1 states will lift. The breaking of the degeneracy makes the Kondo resonance diminish and forms two new peaks due to the inelastic tunneling.

Apart from the traditional Kondo effect, the two-stage Kondo effect occurs in some cases. The main difference is that it is a multi-level multi-channel Kondo effect [185]. In this effect, the spins couple with two independent channels of electrons, and the resonance peak shows a sharp drop at the center of the peak, which is different from the traditional Kondo peak. Only when the coupling between the two channels and the spin is equal, the state will be symmetric. Since each channel may screen the spins, the number of channels that screen the spin is vital. Assuming that the two channels have different parities, the symmetric combination leads to shielding the symmetric orbital, while the asymmetric combination leads to screening the asymmetric one. Each of the two situations has a Kondo temperature, and the Kondo temperature is different for the two situations in the asymmetric one. Therefore, the singlet forms in two situations, which is the origin of the 'two-stage Kondo effect'. For instance, a two-stage Kondo effect exists in the single manganese phthalocyanine (MnPc) transistor (figure 20(f)) [185]. The zero-bias conductance peak of the system shows a sharp dip and behaves as a split of the broad peak as a function of drain-source voltage  $(V_{sd})$  at low temperatures (figure 20(i)). The drop only exists when the temperature is between 0.3 K and 3 K. If the temperature is high than 3 K, the dip will disappear, which shows the first stage Review

of Kondo effect. As the temperature continuously increases, even the broad peak will disappear, which is the second stage. From another perspective, a zero-bias peak appears in region while a zero-bias split peak appears in region . The different results in two regions also demonstrate that there is a two-stage Kondo effect in this transistor. Another explanation of this phenomenon may be that at high temperatures, delocalized electrons screen one spin and cause a spin-1/2 Kondo effect peak. However, at low temperatures, the binding energy of the singlet may make a second spin destroy the Kondo screening cloud. Therefore, there is a sharp dip, and it looks like that an inverted spin-1/2 Kondo effect peak appears. However, it is not a simply inverted peak of the spin-1/2 Kondo effect and the detailed mechanism requires further research.

4.2.2. Spin coupling effect. Spin coupling effect usually occurs between two adjacent spin centers. It refers to the spin interaction between two spin centers (spin-up or spin-down). When there is no magnetic field, spin-up and spin-down are paired. While applying an external magnetic field, the spincoupling effect can be controlled by the magnetic field itself or gate voltage, resulting in energy level splitting and even spin flipping. In specific, if the spin center has a non-zero spin quantum number in an external magnetic field, it will generate a small magnetic field. The generated small magnetic field will have a superposition effect with the external magnetic field on the adjacent spin center, causing the interference and splitting of the resonance signal. When spin A is parallel to the external magnetic field, the magnetic field increases, thereby spin B is in a stronger field. When they are antiparallel, spin B is in a weaker magnetic field. This is the spin-spin coupling effect for short or exchange coupling in an external magnetic field. The coupling constant J reflects the strength of the mutual interference between spins, and its magnitude has nothing to do with the strength of the external magnetic field.

The ability to control the spin coupling via gate voltages provides the possibility to build a single-molecule quantum gate. For example, a diradical molecule with two spin centers can be reversibly transformed into a threespin system by manipulating the gate voltage (figure 21(a)), leading to the switching of the spin coupling [171]. Specifically, a 2,4,6-hexakis-(pentachlorophenyl)mesitylene diradical molecule has two unpaired electrons with an initial spin coupling constant  $J_{12}$  in a three-terminal device. After changing the gate voltage to 3 V, the spin of the system becomes 1/2, indicating that a third unpaired electron is added to the system. The added electron couples with the previous two electrons with spin coupling constants  $J_{13}$  and  $J_{23}$ . Therefore, when the added spin couplings exist, the switch is on, otherwise it is off. Additionally, the spin coupling constants  $J_{13}$  and  $J_{23}$  are 2 and 23 meV, respectively, indicating that the added electron is closer to one of the initial electrons. Furthermore, since the molecule is based on light elements, such as carbon, the spin-orbit coupling of the system is weak, indicating that the spin of the molecule is stable. Therefore, the molecule can be used to construct a spin device due to its good stability. Generally, spin-orbit coupling refers to the interaction between the spin motion of an electron and its orbital motion around the nucleus. According to Coulomb's law, the nucleus creates an electric field around the electron. The electron has a spin magnetic moment and moves around the nucleus. Therefore, the field interacts with the moving magnetic moment, leading to spin–orbit coupling. If there is no spin–orbit coupling, the energy of the electron is related to the orbital motion and spin, respectively, that is, the energy level corresponding to the quantum number of each orbital is degenerate. When the spin–orbit coupling exists, the energy level distribution is changed. Therefore, whether spin–orbit coupling is weak or not will affect the stability of the spin. The fact is that if the spin–orbit coupling is weak, the spin is stable.

Apart from molecules with at least two radicals, dimer complexes with two spin centers may also have a spin coupling effect. In such molecules, certain metal atoms possess the characteristics of spins and often become the spin centers, exhibiting the spin coupling effect. The spin coupling effect in a molecular dimer with equivalent molecules can be explained by a simple model (figure 21(b)) [186]. In this model, the MO involved in intermolecular tunneling are regarded as effective MO. The spin at the energy level  $\varepsilon_0$  of the left molecule interacts with the localized spin of the right molecule with the tunneling rate  $\tau_{\rm c}$ . Therefore, the effective MO are  $\varepsilon_0 \pm \tau_{\rm c}$  (the green lines). Furthermore, the spin also has an exchange interaction with the electrons in the left electrode with coupling  $\Gamma$ . This coupling will directly affect the effective magnetic interaction between the two spins in adjacent molecules. Because the effective magnetic interaction parameter J is proportional to  $-\Gamma$ . Therefore, if the coupling  $\Gamma$  increases, the intermolecular tunneling will decrease. Another model is based on the bias voltage. A typical example of dimers is a Co-dimer complex, which shows a coupled spin pair (figure 21(c)) [28]. Since a Co ion has a  $3d^7$  configuration with a spin S = 3/2, each  $Co^{2+}$  ion is a spin center. Since the ion pair is not aligned but orthogonal to the direction of the current, the applied voltage can change the spin coupling pathway. By detecting the coupled spin pair, the spin coupling of this system is found to be very weak and the spin coupling constant is only  $1-2 \text{ cm}^{-1}$ (0.248–0.372 meV). The reason for the weak spin coupling may be that two  $Co^{2+}$  ions are separated by more than three chemical bonds. The larger the number of separated chemical bonds, the smaller the coupling constant.

Furthermore, the molecular conductance can be controlled by spins, and the device using this principle is the spin valve. The molecule for a typical single-molecule spin valve has two magnetic centers between non-magnetic electrodes, or the molecule has one magnetic center between the electrodes, one or two of which are magnetic (figure 21(d)) [19]. For the spin valves with at least one magnetic electrode, the magnetic source electrode provides both spin-up and spin-down carriers. Assuming that the majority carriers are spin-up and are parallel with the molecular magnetization, the transport of spin-up carriers is not affected but the transport of minority carriers have antiparallel spins, they will be reflected and the minority carriers will be unaffected, causing a low conductance (figure 21(d) top). For non-magnetic electrodes, the molecule is usually a two-spin system and has a spin coupling effect (figure 21(d) bottom). Each spin center may have a conductance jump under certain conditions. Considering the conductance jump as a 'switch', the two spin centers interact to affect the final conductance together. When only one or none spin center switches on, the conductance of the device is not changed. Because there is still a molecule that only allows for the low conductance. If both two spin centers switch on, the conductance is largely enhanced. For instance, a supramolecular spin valve based on the SMM has non-magnetic electrodes with two  $TbPc_2$  (Pc = phthalocyanine) molecules on one SWCNT. These two TbPc<sub>2</sub> molecules become two spin centers [187]. For a TbPc2 molecule, Tb3+ ion has the intrinsic magnetic moment, and the two Pc rings have a delocalized spin S = 1/2. As an SMM, due to the quantum tunneling between the ground state and the spin states, the conductance of one TbPc<sub>2</sub> system can be switched by different magnetic fields. As the magnetic field increases, a conductance jump appears. When two molecules (A and B) are parallel on the SWCNT, the molecules will switch successively. When only molecule A switches, electrons can pass through molecule A but cannot pass through molecule B, which results in an antiparallel spin valve with low conductance. When molecule B switches under an efficient external field, the device becomes a parallel spin valve with high conductance.

4.2.3. Single spin switching with spin crossover. The device based on a single SCO molecule often refers to the switch between a LS state and a HS state of the molecule caused by external stimuli, such as electric field, light, temperature, coordination and so on [188]. Due to the d orbital splitting of the metal ion, the LS state and the HS state are formed, and the ligand field around the central metal ion usually affects the spin state. Therefore, controlling the ligand field is a common approach to control the switch in a SCO-based device. For example,  $[Fe^{II}(tpy)_2]$  (tpy: terpyridine) is a typical SCO complex in single-molecule junction (figure 22(a)) [189, 190]. When there are no external stimuli, the two ligands are perpendicular, and the molecule is in the LS state (S = 0). Since the ligands are dipole molecules, they will rotate for a certain angle under a bias voltage, changing the molecular structure. Therefore, the ligand field is distorted and decreased, forming a HS state. Thus, with appropriate bias voltage, the molecule will exhibit an HS state (S = 2) instead of an LS state, and the spin switching process based on SCO molecules takes place. The spin switch in this system is mainly due to the ligand distortion in an electric field, while other switches based on the bias voltage are related to additional excited states. One of the typical examples is a Fe(1,10-phenanthroline)<sub>2</sub>(NCS)<sub>2</sub> molecule deposited on the Cu(100) surface [188]. If the molecule is in the LS state, the transition to the HS state occurs directly when a -1.2 V voltage pulse is applied, because the initial electrons in the LS state have enough energy to tunnel through the gap between the HS state and the LS state. When a +1.5 V voltage pulse is applied, the electrons are excited from the HS state to the excited state of the ligand. Meanwhile, the central metal ion is not affected during this process. If the lifetime of the excited state is long enough, the excited state will have enough time to



**Figure 21.** Spin coupling effect in single-molecule devices. (a) The structures of the 2,4,6-hexakis-(pentachlorophenyl)mesitylene diradical molecule and reduced form of the diradical. Reproduced with permission from [171]. (c) American Chemical Society. CC BY-NC 4.0. (b) Schematic representation of the spin coupling effect in a molecular dimer. Reprinted with permission from [186]. Copyright (2016) American Chemical Society. (c) Schematic representation of the experiment that can detect the spin coupling pathway and the structure of a Co-dimer used in the experiment. Reproduced from [28], with permission from Springer Nature. (d) Schematic representation of a spin valve based on molecular magnets. Reproduced from [19], with permission from Springer Nature.

relax back to the ground state with low energy, that is, the LS state. However, the lifetime of the excited state in this system is only  $\sim$ 5 fs, resulting in a low probability to realize the transition from the HS state to the LS state. In addition, the switching probability may be enhanced by increasing the thickness of an insulating layer, which can increase the lifetime of the excited state. Therefore, a stable transition process from the HS state to the LS state can be obtained.

In addition to the bias voltage, the stretching force can also affect the ligand field, resulting in spin switching based on the SCO phenomenon. A typical example of a stretching-induced SCO-based device is a Fe<sup>II</sup> terpyridine complex between two gold electrodes (figure 22(b)) [189, 191]. Before being mechanically pulled, the molecule is in an LS state with S = 0. When the two electrodes are pulled away, the ligands are separated, leading to a reduction of the ligand field. When the distortion is large enough, the ligand field energy is smaller than the exchange energy between two electrons. Therefore, the molecule can be changed to the HS state.

In addition, temperature and light can also control the SCO phenomenon and realize spin-switching in SCO-based devices. The light-induced process often involves a MLCT state. After the optical excitation from the LS state to the MLCT state, the electrons relax to the HS state and are trapped due to the energy barrier. This is the LIESST effect [192, 193]. As for the temperature control, the system usually has a SCO temperature  $(T_{1/2})$ , which represents the temperature at which the LS state and the HS state are equally popularized. For instance, a typical single SCO moleculebased device consisted of a  $[Fe(bpz)_2phen]$  (bpz = dihydrobis(pyrazolyl)borate) molecule and an oriented pyrolytic graphite surface can be switched on (from the LS state to the HS state) under the irradiation at low temperatures and switched off (from the HS state to the LS state) at higher temperatures [192]. The relaxation of electrons from the MLCT state to the HS state instead of the LS state is mainly due to the slow relaxation to the LS state at low temperatures, which may be due to the distortion of the molecule interacting with the surface. Meanwhile, since the energy barrier for the transition of



**Figure 22.** Switching devices based on the SCO effect in single-molecule devices. (a) Schematic representation of a voltage-triggered SCO switch. Reproduced with permission from [190]. (c) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. CC BY-NC-ND 4.0. (b) Schematic representation of a two-terminal mechanically controlled SCO switch. Reprinted with permission from [191]. Copyright (2016) American Chemical Society. (c) Schematic representation of a SCO switch based on the coordination. Reproduced from [194], with permission from Springer Nature. (d) Schematic representation of a two-centered molecule that is involved in a SCO switch. Reproduced from [196], with permission from Springer Nature.

electrons is higher than the external thermal energy, the electrons are stable after the LIESST process. Furthermore, a quantum tunneling process occurs as the temperature increases, which is related to the thermally activated vibrational energy levels, leading to the change of the spin state.

Another switching mechanism in the SCO-based device is the coordination. Adding new ligands to the central metal ion can form new bonds and decrease the number of unpaired electrons. Therefore, the total spin is changed, and the spin state is different. Cobalt tetraphenylporphyrin (CoTPP) on Ni substrates is a system that exhibits SCO switching (figure 22(c)) [194]. In the initial state, the molecule with a spin S = 1/2 (HS state) is coupled to the substrate. When the NO molecule is added to the system, because the unpaired electron of the CoTPP molecule couples with the  $\pi$ -electron of NO molecule, the NO-CoTPP complex is chemically formed. In other words, the chemical reaction occurs due to the interaction between the singly occupied  $d_z^2$  MO of CoTPP and the  $\pi^*$  orbital of NO. Thus, the total spin of the system is zero, which is the LS state. Specifically, the NO molecule will detach from the NO-CoTPP molecule by heating, causing the system to return to the origin state. In addition, chemical switches can also exist in other molecules based on the formation of new bonds between ligands and the central atom. For instance, 5,15-(2'-(4"-(3",5"'-pyridinylen)-oxymethylphenyl)-phenyl)-10,20-bis-(2,3,4,5,6-pentafluorophenyl)-Ni porphyrin on the Ag(111) surface can be switched by optical excitation. However, the lifetime of the HS state is rather short, because the molecule in the HS state prefers a flat structure with low steric hindrance. Therefore, it requires another switching approach. Under normal circumstances, the central atom is not coordinated with any ligands and forms a LS state. After compressing the molecule, one of the rings is connected to the metal ion, forming a flatter structure. The ligand can provide  $\pi$ electrons and a weak ligand field, leading to a HS state [195]. If the system is stretched, the molecule will change back to the ruffled form, that is, a LS state. Therefore, by compressing and stretching, the SCO complex can be switched between the two states very well.

In addition, SCO complexes with at least two metal ions usually possess a different switching mechanism because the super-exchange interaction occurs between the two metal ions, which can be applied into devices. The two spin centers with S = 1/2, the bridge part of the molecule, can exchange the electrons through the doubly occupied singlet state. If the molecule is symmetric, only two excited states may form, that is singlet or triplet. If the molecule is asymmetric, the electron in the bridge may hop to one of the two sides, resulting in four excited states that are  $\uparrow\downarrow -\uparrow -\uparrow$ ,  $\uparrow\downarrow -\uparrow -\downarrow$ ,  $\uparrow -\uparrow -\uparrow\downarrow$  and  $\uparrow -\downarrow -\uparrow\downarrow$ ( $\uparrow$ : spin-up,  $\downarrow$ : spin-down). This singlet to triplet crossover is induced by the electric field, while the external stimuli can also be temperature or light. A typical example of a two-center SCO molecule is the MeO-CoCp2-Ac-CoCp2 (MeO-diCo) between two Au electrodes, where CoCp<sub>2</sub> is cobaltocene and Ac is acetylene (figure 22(d)) [196]. Since the molecule is asymmetric, the molecule has different electrical dipoles along the electric field direction, which comes from the polarization of two spin states. Thus, the electrical dipoles lead to an electrostatic SCO effect (ESCE), indicating that spin switching can be realized by creating different electric fields. If the electric field is higher than  $1.5 \text{ V} \text{ nm}^{-1}$ , the molecule becomes the triplet state (HS state) due to more unpaired electrons. When the electric field is lowered, it will change back to the singlet state (LS state). Thus, the switching of this system is based on the electric field.

4.2.4. Single nuclear spin manipulation. The nuclear spin is one of the most significant properties of nuclear. The nucleus is composed of protons and neutrons. Both protons and neutrons have spin angular momentums. They also have orbital motions in the nucleus, and correspondingly have orbital angular momentum. All these angular momentums combine to form the spin angular momentum of the nucleus. If the numbers of protons and neutrons are even, the net nuclear spin will be zero; if one of them is odd or both are odd, the net nuclear spin will not be zero. Specifically, the even mass number (odd + odd) indicates that the spin is an integer, which follows the Bose–Einstein distribution. An odd mass number (odd + even) means that the spin is a half integer, which follows the Fermi–Dirac distribution.

Whether the molecule has a nuclear spin will affect the magnetic properties of the system. For instance,  $[(^{163}Dy(tmhd)_3)_2(bpym)]$  (complex 1) and  $[(^{164}Dy(tmhd)_3)_2$ (bpym)] (complex 2) (tmhd = tris(tetramethylheptanedionato) and bpym = bipyrimidine) show the different relaxation time of magnetization related to the nuclear spin [197]. A Dy atom has 66 protons so that  $^{163}Dy$  atom has 97 neutrons and  $^{164}Dy$ has 98 neutrons. Both the numbers of protons and neutrons in  $^{164}Dy$  are even, indicating that  $^{164}Dy$  has no nuclear spin. Generally speaking, *I* is used to represent the spin quantum number of the nucleus. For complex 1, the distribution of valence electrons in Dy element is  $4f^{10}6s^2$ . Since the orbital angular momentum for *f* orbital is 3 and the spin angular momentum of an electron is 1/2, the spin quantum momentum of the nuclear is the sum or the difference of two angular momentums,  $3 \pm 1/2 = 5/2$  or 7/2. The molecule is in the ground state, so complex 1 has I = 5/2. For complex 2, the nuclear spin is zero, I = 0. So, only complex 1 has hyperfine split levels. The hyperfine interaction refers to the coupling between the nuclear magnetic moment and the electronic magnetic moment. For example, the electron may be spin-up or spin-down and the spin of the nuclear may be spin-up or spin-down as well in a hydrogen element [189]. Thus, there are four possible spin states. The energies of these four spin states are not completely same, leading to hyperfine splitting. Here, in complex 2, the nuclear spin is zero and the coupling does not exist. However, in complex 1, the nuclear spin I = 5/2. Therefore, the hyperfine split levels only exist in complex 1. If the total electron angular momentum quantum number is J, it can be coupled into the following states:  $F = I + J, I + J - 1, \dots, |I - J|$ , where F is the total angular momentum quantum number. Therefore, the total number of states in complex 1 is much larger than that in complex 2. With more states, it takes electrons more time to go back to the lowest energy state, leading to a slower relaxation of magnetization.

The nuclear spin states can be read out by a spin-dependent current that varies with different nuclear spins. The spin-flip is accompanied by a conductance jump at an 'anticrossing' between electronuclear spin levels [198]. It is noted that the anticrossings only exist in specific magnetic fields, which are determined by nuclear spins. Under the magnetic field, the crossing between two spin levels due to the state mixing is avoided, showing a sudden jump in the current [198]. Therefore, to read out the nuclear spin by a spin-dependence current, the anticrossings should appear. For instance, a theoretical study of a vanadium complex  $[V(\alpha-C_3S_5)_3]^{2-}$  demonstrates that the nuclear spin can be read out by a spindependent current [198]. As the nuclear spin polarization changes in an external magnetic field, the current behavior changes and shows a jump at the point when the spin flips. According to the calculation, the net spin is on the vanadium atom in this molecule, indicating that the current change is not directly related to the unpaired electron. Therefore, the nuclear spin can be read out by detecting the current change. Furthermore, a single nuclear spin transistor with a TbPc<sub>2</sub> (Pc = phthalocyanine) molecule is designed, and the nuclear spin can be read out and manipulated (figure 23(a)) [199]. Due to the coupling between the magnetic momentum of electrons in the f orbital and the magnetic momentum of the nuclear, Tb ion has a partially filled 4f orbital, which causes a hyperfine split. In addition, the f electrons will couple with the electrons that flow through the molecule. Thus, the nuclear spin can be read out by the current. Specifically, the nuclear spin of a Tb<sup>3+</sup> ion is 3/2, providing four different states (-3/2, -1/2, +1/2, +3/2). When a specific external magnetic field causes the resonance of energy levels of the electron-nuclear spin states, a quantum tunneling process occurs between these states and causes spin flip. Therefore, the nuclear spin can be manipulated.

However, since the required current to perform the quantum operation is large and the parasitic crosstalk between two



**Figure 23.** Manipulation of single-molecule devices based on the nuclear spin. (a) Schematic representation of a TbPc<sub>2</sub> spin transistor manipulated by electrons. Reproduced from [199], with permission from Springer Nature. (b) Schematic representation of a nuclear spin qubit transistor manipulated by an electric field pulse. From [200]. Reprinted with permission from AAAS. (c) Schematic representation of the electron transport process in the STM junction. Reproduced from [201]. CC BY 4.0.

neighboring spins exists, the integration of the single nuclear spin transistor read out in a specific magnetic field is limited. Using electric fields to manipulate the nuclear spin only requires small displacement currents. Therefore, this is better for integration. For instance, further research on the TbPc<sub>2</sub>based transistor demonstrates that the nuclear spin can be manipulated by an electric field pulse (figure 23(b)) [200]. Due to the hyperfine Stark effect, the electric field can be transformed into a magnetic field. Specifically, in an external electric field, the positive and negative charge centers of the atoms can be separated by an electric field, and the separated atoms will generate an induced dipole moment. The induced dipole moment interacts with the electric field, causing the atomic energy levels to split and move. This phenomenon is the Stark effect. Here, the hyperfine Stark effect refers to the change of the hyperfine coupling constant A in the Hamiltonian  $H_{\rm HF}$ , which describes the magnetic interaction between the spin dipole moment and the magnetic nuclear. The Hamiltonian is initially a function of the electric field. However, the expression of  $H_{\rm HF}$  can be transformed into  $H_{\rm HF} = g_{\rm N} \mu_{\rm N} I B_{\rm eff} (A,$ J), modifying the electric field into the magnetic field. Thus, due to the hyperfine Stark effect, the spin can couple with the electric field and realize the transformation. The manipulation is related not only to the nuclear spin and the electronic spin, but also to the readout quantum dot created by the Pc rings. The delocalized electron of the Pc ring tunnels and couples to source and drain electrodes, producing a quantum dot near the electronic spin. Due to the spin coupling interaction, the electronic spin affects the chemical potential of the readout quantum dot. Thus, the current change is related to the readout quantum dot, while the quantum dot is related to the nuclear spin, indicating that the nuclear spin is manipulated by the electric field.

Apart from the readout of the nuclear spin, the direction of the nuclear spin can also be manipulated by a magnetic field. Here, the direction is not just spin-up or spin-down, but also perpendicular or parallel to the molecular plane. For instance, the tip-FePc-Au substrate junction shows a reorientation of the Fe nuclear spin in the STM measurement (figure 23(c)) [201]. In this junction, the molecule is lying on the substrate. During the process of electron transport through the molecule, two MO  $(d_z^2 \text{ or } d_{xz}/d_{yz})$  may be the possible channels for tunneling electrons. In a weak magnetic field, the spin direction of the nuclear is in-plane, that is, the magnetic moment of the Fe nuclear is in the plane of the molecule. In this case, the current flows through  $d_{xz}$  or  $d_{yz}$  orbitals. In a strong magnetic field, the spin direction is out-of-plane, that is, the magnetic moment of the Fe nuclear is perpendicular to the plane of the molecule. The current flows through  $d_z^2$  orbital. This phenomenon may be due to the comparable energy of Zeeman energy generated by the external magnetic field and the in-plane magnetic anisotropy energy of the nuclear spin. Therefore, with a strong

magnetic field, the molecule may have enough Zeeman energy to overcome the magnetic anisotropy energy. As the magnetic field increases, it is possible to reorientate the magnetic moment of the Fe nuclear spin.

4.2.5. Quantum spin qubits. Quantum qubit is a system whose state is a quantum superposition state with two eigenstates,  $|0\rangle$  and  $|1\rangle$ , which is different from the states of classic bits, 0 and 1 [20, 202]. The states of qubits are expressed as  $|\Psi\rangle = \alpha |0\rangle + \beta |1\rangle$ . Different qubit systems have been studied, including photons, semiconductor quantum dots and atom or ion traps. In addition, effectively reading out and manipulating the quantum qubits are the key to practical applications. However, for photons, it is difficult to manipulate the quantum states with two or more photons; for semiconductor quantum dots, the actual scaling has not yet been demonstrated; for atom or ion traps, they are used for specific quantum simulators instead of general quantum computing. The electronic or nuclear spin state of a single molecule is another system. Due to the intrinsic quantum property of spins, the quantum spin qubits in a single molecule can be generated in an external magnetic field and manipulated by microwave pulses (figure 24(a)) [20]. Therefore, quantum spin qubits have the potential to be applied in quantum devices, such as quantum computers.

However, the development of quantum spin qubits has two main challenges, scalability and the maintenance of coherence [20, 203]. Scalability refers to the ability to increase the number of spin qubits without affecting the coherence, to read out and manipulate spin qubits. In addition, the quantum superposition in real devices is fragile, and it is easy to lose quantum information, leading to decoherence. In specific, at low temperatures, the decoherence mainly comes from the magnetic noise, which is related to the hyperfine interaction of electronic spin and nuclear spin [20, 203]. And the magnetic noise often leads to the spin information dispersion without control. At high temperatures, the decoherence is destroyed by the thermal vibrations or phonons of molecules. The thermal relaxation of the spin system may lead to the loss of spin information [20]. In general, the phase memory time  $T_2$  is used to quantify the coherence. Specifically, a longer  $T_2$  indicates that the coherence of the quantum spin qubit is better maintained. To reduce the magnetic noise, decreasing the interaction between molecules is a good approach. By magnetically isolating the molecule, the hyperfine interaction is alleviated. Three typical molecules  $[Cu(mnt)_2]^{2-}$ ,  $[V(C_8S_8)_3]^{2-}$  and [VO(Pc)] $(mnt^{2-} = maleonitriledithiolate, Pc = phthalocyanine)$  are designed as spin qubits (figure 24(c)) [203]. All the magnetic isolations of the three quantum spin qubits have robust coherence with  $T_2$  larger than 1  $\mu$ s under optimized conditions [20, 203]. The  $[V(C_8S_8)_3]^{2-}$  molecule can even maintain the coherence for milliseconds at low temperatures. Although the isolated quantum spin qubits exhibit good coherence, the position of the quantum spin qubit is random in the isolated sample. Therefore, it is difficult to manipulate them directly. Thus, a new method is required to improve anti-interference ability. One possible solution is to design a spin qubit insensitive to the magnetic noise, which needs to design the energy level. In an external magnetic field, the qubit states are mixed and can create a tunneling gap, protecting the quantum spin qubit from decoherence at the atomic clock transition point [20, 203]. Specifically, when two states with comparable energy interact with each other in an external magnetic field, the atomic clock transition will occur. If the energies of two states are close enough, a repulsion between energy levels will appear due to the quantum mechanical interaction of the two states. The repulsion avoids the cross of two levels, generating a tunneling gap. When this repulsion appears, the clock transition is the transition between the two states. Since this clock transition is used as the standard time for cesium atomic clocks, it is called atomic clock transition. In a normal transition with the Zeeman effect, the energy difference between quantum spin qubit states changes with the change of the external magnetic field. However, at the atomic clock transition point, the Zeeman effect is zero. This indicates that the spin qubit is insensitive to the magnetic field noise and has robust coherence. Thus, the phase memory time can be enhanced and the coherence can be maintained by setting the atomic clock transition point. An example of this kind of spin qubits is the complex  $[HoW_{10}O_{36}]^{9-}$  (figure 24(b)) [20]. The molecule has a four-fold rotational symmetry and the ground state  $m_J = \pm 4$ . Therefore, in this spin qubit, there are four atomic clock transitions. Even with external magnetic noise, the coherence at these points can be maintained for a long time  $(T_2 = 8.4 \ \mu s \text{ at } 5 \text{ K}).$ 

Furthermore, a large number of spin qubit-based devices have been designed. A typical example is a nuclear spin qubit transistor based on the single  $TbPc_2$  molecule [200]. The molecule has a nuclear spin with the spin quantum number I =3/2, which is the origin of the spin qubit. There are four qubit states,  $|-3/2\rangle$ ,  $|-1/2\rangle$ ,  $|1/2\rangle$ , and  $|3/2\rangle$ , produced by nuclear spin. To test the phase memory time, the initial state is set to be  $|3/2\rangle$ . Then, two microwave pulses with an interval  $\tau$  are added to induce an oscillating magnetic field and probe the final state,  $|1/2\rangle$ . By repeating this procedure, the phase memory time is obtained,  $T_2 = 64 \ \mu s$ . In this transistor, the decoherence comes from the magnetic noise, which is caused by the magnetic field fluctuation due to the hyperfine Stark effect. With more robust spin qubits, the increasing phase memory time is expected. However, the integration of single-molecule spin qubits is the ultimate goal and has not yet been explored. Therefore, there is still a long way to go before practical applications.

4.2.6. Single molecular spin interface. Spin interface, an interface between molecules and metals, possesses spin effect related to the interface, which is also called spinterface. It usually has spin-dependent interfacial states, which can control the spin of the conduction electron and even invert the spin polarization of the current through the spinterface [204]. Specifically, single molecular spin interfaces often refer to electrode–molecule interfaces. Therefore, in this system, at least one of the electrodes is metal. The molecule can be either magnetic or non-magnetic, and both of them can be spin-activated.



**Figure 24.** Quantum spin qubits. (a) Schematic representation of a quantum spin qubit. (b) Schematic representation of the atomic clock transition in a  $[HoW_{10}O_{36}]^{9-}$  complex. (a) and (b) Reproduced from [20], with permission from Springer Nature. (c) The development of molecular complexes in quantum spin qubits. Reproduced from [203], with permission from Springer Nature.

Based on the above, the excited electrons and holes are usually generated in the spintronic devices under external stimuli. In specific, when electrons or holes move to the interface between magnetic and non-magnetic materials, a spin-dependent current will form [205]. Since the electrons have two spin directions, spin up and spin down, the electrons are classified into majority electrons and minority electrons according to the numbers of electrons with different spins. The majority electrons often have a larger mean free path than the minority electrons, that is, the average distance an electron travels before the collision with other electrons. Therefore, it is more possible for the majority electrons to pass through the metal-molecule interface, resulting in a spin-dependent current. When the current propagates to the metal-molecule interface, which forms a single-molecule spinterface, the molecule is spin active and becomes a spin-filter, thereby enhancing or reducing the current. This is the spin filtering effect. The hallmarks of forming a spinterface and showing the spin filtering effect are the broadened DOS in the molecule and the shift of the energy level. Assuming that only the HOMO is sufficiently close to the Fermi level of the electrode, only HOMO contributes to the current (figure 25(a)) [206]. When the molecule and the electrode are separated, the total DOS is the superposition of the two individual DOS. When they are approaching and in contact with each other, the DOS of the molecule will broaden and the energy level will shift. In specific, the molecular orbital is stable in this case, leading to electron leakage in and out of the molecule. Thus, the DOS is broadened. In addition, as the direction of the electron spin in the electrode is different, the broadening of spin-up and spin-down energy levels is also different. If they are close, one of the energy levels will shift to the Fermi level. This shift is also spin-dependent and finally affects the spin polarization of the current, parallel or antiparallel to the polarization in the electrode (figure 25(a)).

Magnetoresistance effect, the resistance of the system changes as the external magnetic field changes, which usually appears when the system has a spin interface. For magnetic molecules, the presence or absence of the spin interface will affect the magnetoresistance. For example, based on the complex  $[M(tzpy)_2(NCSe)_2]$  (M = Co, Mn and Ni) (figure 25(b)) [207] placed between a gold surface and a Ni tip, forming a device, a spinterface can be formed between the Ni tip and the molecule. Although the  $Mn^{2+}$  complex has the largest spin S = 5/2, only the Co<sup>2+</sup> complex (S = 3/2) exhibits good magnetoresistance, which is related to the spin interface. Use  $e_g$  and  $t_{2g}$  to represent the *d* orbitals with relatively higher energy and lower energy, respectively (e: two-fold degenerate, t: three-fold degenerate). Use  $\alpha$  and  $\beta$  to represent spin-up and spin-down, respectively. The Mn<sup>2+</sup> complex has a  $t_{2g}^{3}e_{g}^{2}$  configuration. Both the occupied  $\alpha e_g$  orbitals and the unoccupied  $\beta t_{2g}$  orbitals are far away from the Fermi level. Therefore, it is hard to exhibit tunneling magnetoresistance at low voltages. However, the Co<sup>2+</sup> system has a  $t_{2g}^{5}e_{g}^{2}$  configuration. The two  $\beta t_{2g}$  orbitals are near the Fermi level and are broadened in the Co<sup>2+</sup> system. Thus, electron transport is in the  $\beta$ channel, which results in a  $\beta$ -spin filter. In addition, the asymmetric hybridization in the molecule/Au spinterface may cause large magnetoresistance.

Based on the two kinds of energy level splitting related to the spinterface, a single-molecule device is designed with a [Fe(tzpy)<sub>2</sub>(NCS)<sub>2</sub>] complex (figure 25(c)) [208]. The system exhibits a large magnetoresistance switch by applying different bias voltages. The change is mainly due to the change of Fe energy levels in the spinterface. For a diamagnetic complex, the spin *S* is zero and the configuration is  $t_{2g}{}^6e_g{}^0$ . In this case, all the orbitals are far from the Fermi level and the interface is not a spinterface, indicating a low magnetoresistance. The spin of the paramagnetic one is changed to S = 2, and its



**Figure 25.** Single molecular spin interfaces. (a) Schematic representation of the spin-filtering mechanism at an organic/inorganic interface. Reproduced from [206], with permission from Springer Nature. (b) Schematic representation of the single-molecule devices with different Ni tip magnetic polarizations. Reprinted with permission from [207]. Copyright (2017) American Chemical Society. (c) Schematic representation of the single molecule devices with different complexes. Reprinted with permission from [208]. Copyright (2016) American Chemical Society. (d) Schematic representation of a non-magnetic spinterface device. Reprinted with permission from [210]. Copyright (2015) American Chemical Society. (e) Schematic representation of the junction magnetization changes as changing the magnetic field. Reprinted with permission from [211]. Copyright (2016) American Chemical Society.

configuration is  $t_{2g}^4 e_g^2$ . Here, the spinterface exists and similar broadened  $\beta t_{2g}$  orbitals are observed, which are near the Fermi level, leading to a large magnetoresistance. Therefore, the non-magnetic complex can be activated by switching the bias voltage, and the magnetoresistance can be switched in the spinterface.

As for non-magnetic molecules between magnetic electrodes, they can also form a spinterface device. To activate the non-magnetic spinterface device, the non-magnetic molecules should obtain the spin polarization near the Fermi level of the electrode [204, 209]. For instance, a 4,4'-bipyridine (44BP) single-molecule junction between two Ni electrodes is a typical system (figure 25(d)) [210]. The control of this device is based on non-redox electrochemical gating. When the gate voltage increases, the Fermi level of the electrode is closer to the LUMO of the molecule, forming a spinterface in the system. The hybridization of d orbitals of the Ni electrode and the LUMO of the molecule increases, thus the conductance increases. By calculating the transmission of the junction, extra peaks appear close to the LUMO, which are mainly related to the hybridization. For the minority spin channel, the Fermi level is just on the peak, making the molecule spin active and leading to a higher conductance. For the majority spin channel, the extra peak is low, indicating that the transmission near the Fermi level is weak. Therefore, the final current is spindependent due to the formation of a spinterface. The nonmagnetic molecule between two magnetic electrodes cannot only be activated to form a spinterface device, but also exhibit anisotropic magnetoresistance at the spinterface. A singlemolecule junction based on a benzene molecule and two Ni electrodes is designed to study the anisotropy of magnetoresistance at the metal-molecule interface (figure 25(e)) [211]. The current through the junction also exhibits spin polarization and the non-magnetic molecule is activated, which has a similar reason with the previous system. For the spin-up channel, the hybridization of the Ni d orbitals and the molecular  $\pi$ -orbitals is weak; while for the spin-down channel, the hybridization is strong. Therefore, a spin-dependent current forms at the spinterface. As the applied magnetic field changes from -0.5 to 0.5 T, the direction of magnetoresistance changes from parallel to antiparallel to the current. Meanwhile, due to the formation of a spinterface, when the molecule is added to the junction, the magnetoresistance is enhanced. The anisotropy is mainly due to the anisotropic spin-orbit coupling and the HS polarization. The shift of the spin-polarized hybridization states to the Fermi level may result in the enhancement of the magnetoresistance as well.

## 5. Single-molecule exciton effects

Excitons, tightly bound electron-hole pairs via Coulomb force, can be formed in the molecule after inter-band excitation [212], such as the energy absorption from photon or plasmon. Recently, the development of various optoelectronic experimental technologies and the maturity of theoretical simulations have promoted a clear understanding of the processes of the formation, migration, transport and recombination of excitons at different stages. A comprehensive understanding of exciton effects at the single-molecule level will promote the construction of high-performance molecular optoelectronic devices, which is also the focus of this section.

## 5.1. Single-molecule exciton excitations

Generally speaking, there are two ways to stimulate exciton formation in a single molecule: photon excitation and indirect plasmon induction. In specific, the former corresponds to the situation where the exciton states are formed in the excited molecules under light irradiation of a specific wavelength. The latter, indirect plasma excitation refers to the formation of molecular excitons excited by the plasma generated by photon or electron injection. In comparison with light excitation, the plasmon has the advantage of realizing the utilization of nano-level photons by virtue of its strong local field enhancement effect and breakthrough of the diffraction limit. Herein, we analyze the formation of excitonbased on recent typical works.

5.1.1. Coupling between photons and molecules. Photoisomerization molecules are ideal model systems for studying various photoelectric or photochemical effects, such as conformational changes, photovoltaic and photo responses. In these molecular systems, the excitons can be directly formed by absorbing photon energy. Furthermore, these photoisomerization effects may affect the coupling between photons and molecules, resulting in the change of the characteristics of excitons formed after the photons are directly absorbed. Taking an azobenzene molecule [94] as an example, it can transform from planar trans configuration to curved cis configuration that possesses a larger HOMO-LUMO energy gap under UV light. The two isomers exhibit well-separated absorption bands because they correspond to different excitation transitions [213]. Another reflection of the coupling between photons and molecules is photoconductivity, that is, the adjustment of the electronic conductance under illumination. In specific, the exciton formation due to the light excitation could lead to photoconductivity, just as drawn in figure 26(a) [214]. When a single-molecule junction with a symmetric molecular moiety is excited by light whose frequency is in or close to resonance with the HOMO-LOMO gap of the molecule, due to the Coulomb interaction between electrons and holes, the HOMO energy is pushed to the Fermi level leading to an increase of conductivity.

The optical microcavity, a micron-level optical resonator with high quality factor, can promote the strong interaction between the photons and the molecules placed inside the cavity due to the strong local optical field. When the strength of molecule-cavity coupling induced excitation is higher than the respective decay rates and dephasing processes [215], the system will enter a 'strong coupling' state and coherently exchange energy occurs. Photon irradiation changes the physicochemical properties of the molecule, the coupling degree between molecule and cavity is changed accordingly, and finally the interaction between molecule and photon is tuned. An appropriate example is the photochemically induced spiropyran molecule to reversibly switch from a weak- to ultrastrong-coupling regime in the cavity (figure 26(b)) [216]. Under the irradiation of 334 nm UV light, spiropyran undergoes photoisomerization from the spiropyran structure to the merocyanine structure. As more and more spiropyran transform into the merocyanine conformation, the molecule-cavity system varies from weak coupling to strong coupling. In this process, the molecules interact with the cavity and exchange energy. The rapid energy exchange promotes the molecules to oscillate back and forth between the upper and lower energy levels. Once the final oscillation frequency resonates with the cavity frequency, a Rabi oscillation is formed. Specifically, Rabi oscillation is a kind of quantum transient coherence effect, corresponding to the resonant coupling between photons and molecules, which is manifested as the splitting of resonance peaks in the spectrum.

Since the molecular conformation change can influence the behavior of molecular excitons, the length or size of the molecule can be regulated to obtain different degrees of conjugation, affecting the delocalization of excitons indirectly. For example, the degree of exciton delocalization of the  $\pi$ conjugated ring system is significantly affected by the effect of conformational disorder. On one hand, the C = C stretching motion causes excitons to self-trap, which causes the excitons to be localized in a specific conjugate section. On the other hand, dynamic planarization leads to exciton delocalization because the dynamic planarization will reduce the torsion angle between rings and strengthen the *p*-orbital overlap between chromonic units, thereby affecting the size of the excitons (figure 26(c)). In the system composed of less than eight thiophene subunits, the complete exciton delocalization on the whole backbone can be obtained. For the systems with more than eight thiophene subunits, excitons cannot extend to the whole carbon skeleton [217]. The fundamental reason is that the degree of conformational disorder of cyclic OLT in the excited state increases with the extension of the system size (figure 26(d)) [218]. With the increase of the system size, the cyclic symmetry constraint is gradually lifted, and disordered structures such as torsion and bending between rings are introduced. All the above causes the lifting of paired degeneracy and the redistribution of oscillator strengths corresponding to different energy levels, which in turn affects the excitonic state. Indeed, the molecule C-6T with 6 subunits has no significant expansion in the size of excitons because of its low initial disorder and dynamic planarization helps to form an ideal planar cyclic geometry. On the contrary, the dynamic planarization in



**Figure 26.** Models and performance diagrams about the coupling of photons and molecules. (a) Illustration of a NH<sub>2</sub>-PTCDI-NH<sub>2</sub> molecule trapped in an STM break junctions and its conductance histograms. Reprinted with permission from [214]. Copyright (2018) American Chemical Society. (b) Numerical simulations for a spiropyran (left) and merocyanine (right). Reprinted with permission from [216]. Copyright (2011) American Chemical Society. (c) Schematic representation of dynamic planarization processes for cyclic oligothiophenes. [217] John Wiley & Sons. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Illustration of the change in excitonic states of C-10T and C-12T (left) and linear dichroism histograms of cyclic oligothiophenes (right). Reprinted with permission from [218]. Copyright (2016) American Chemical Society.

C-12T enlarges the size of excitons [219], although the severe torsion disorder of the carbon chain prevents excitons from delocalizing on the entire ring.

In addition to the factors of the molecular structure and morphology, adjusting the incident light intensity can affect the excited states of molecules accordingly. In specific, under high photon flux, multiple excitons may be excited in one excitation pulse. Here, the multiple excitons mean that the donors and acceptors in a macromolecule are excited at the same time and they both form an exciton state under light excitation. In another case, exciton blockade may occur. When one excited donor transfers its energy to the acceptor, as long as the acceptor is in an excited state, the energy transfer from other donors will be prohibited or blocked. Therefore, in principle, the donor can relax to the ground state through fluorescence. Exciton blockade hinders the effective energy transfer between the donor and the acceptor and plays an important role in the dual-color emission phenomenon of specific molecular systems, such as polyphenylene dendrimers [220].

In addition, when the incident photon has strong energy, resonant light excitation may also give birth to multiple excitonic states through down-conversion. This phenomenon is called multiple exciton generation (MEG) [221, 222]. The emergence of MEG puts forward strict requirements on the energy level structure of the molecule. For regular molecules such as zinc chlorine-type molecules [223], the transition energy  $E_1$  from the ground state to the first excited singlet state is smaller than the energy difference between the first excited state and the next excited state  $E_2$ . The concrete relationship is  $2E_1 < E_2$ , so a part of excitons can resist the competition of exciton-exciton annihilation, transfer its energy to nearby electrons through collision ionization, and finally generate two or more pairs of electron-hole. For a multimolecular system with excitation energy transfer, the amplitude of exciton coupling will decrease as the excitation density increases, resulting in a decrease in the width of the exciton band and an increase in the excitation for a fixed pulse duration.

5.1.2. Coupling between light excitation plasmons and molecules. In addition, the molecular exciton can also be

excited by the plasmon, which is a surface electromagnetic mode formed by the resonance of free electrons. In comparison with visible light with a wavelength of hundreds of nanometers propagating in free space, the plasmon of the same frequency can be localized to the sub-nanometer level. So, the localized plasmons can significantly enhance the incident light field, thereby effectively promoting the light excitation of molecules. At present, light excitation and high-energy electron injection are widely used to generate plasmon. On one hand, when the photon matches the wave vector of the plasmon, the plasmonic metal strongly interacts with incident light and localizes the energy of the captured photons in the context of resonance excitation. On the other hand, the plasmon can be excited with a space-constrained broadband electron beam or high-energy tunneling electrons in the nanocavity [224].

Due to the significant field enhancement capability of plasmons, the interaction between light and molecule is effectively promoted. When the frequency of the plasmon resonance is close to the frequency of the molecular inter-band excitation, the energy exchange between them occurs, leading to the formation of an exciton. Furthermore, plasmon excitation can resonant with a broad range of electronic transitions [225, 226]. For instance, in the 2,7-diaminofluorene singlemolecule junctions, due to the resonance between photon and plasmon of metal electrodes, a plasmon is generated in the junction gap, resulting in molecular excitation. Meanwhile, due to the coupling of Fermi energy and the region below the HOMO caused by molecular excitation, the enhancement of photoconductivity is realized [227].

Furthermore, if the coherent frequency is appropriate, the near-field coherent interaction between the discrete state of the inter-band excitations of molecules and the continuous state of the nanocavity plasmon can result in Fano resonance. The interference between those two modes forms an asymmetry line, and this feature helps to distinguish the formation of Fano resonance. For instance, adjusting the distance between the STM tip and the polycyclic aromatic hydrocarbon molecules for molecule excitation, the emission spectrum roughly matches the Fano profile (figure 27(a)) [228]. Here, the plasmon environment is defined as a continuous state, in which inelastic tunnel electrons and molecular excitons could be coupled to it with variable intensities, so the tunneling electrons are also coupled to the excitons. The molecule is excited through plasmon-mediated energy transfer from the injected electron, and the resonance of plasmon and molecular exciton leads to the emergence of the Fano spectrum. Similarly, with the help of coherent coupling between an electronically decoupled single zinc-phthalocyanine (ZnPc) molecule and a plasmonic nanocavity in close proximity [229], spatial control of single-molecule Fano resonance with atomic precision is achieved (figure 27(c)). The broadband nanocavity plasma is also regarded as a continuous state, acting as a coherent source for exciting and disturbing the transition of discrete molecules. Such coupling enables the QI between two paths of emission through either the molecular transition or the plasmon resonance, leading to the Fano line shape. It should be noted that the coherent interaction between the excited state of a ZnPc molecule and the cavity plasmon further affects the energy level of the molecule itself and adjusts the energy of the optical transition, triggering the photon Lamb shift. Therefore, Fano line shape and the photon Lamb shift demonstrate the sub-nanometer spatial control of the coherent coupling between molecular excitons and adjacent plasmon of nanocavity.

5.1.3. Coupling between electrical exciton and molecules. In addition to photon excitation and indirect plasmon induction, excitons can also be formed by electrically excited mechanism through charge injection [230]. For example, when a rod-like molecule is attached to two metallic single-walled carbon nanotube electrodes to form a rigid connection, it can be electrically excited to generate excitons through the injection of electrons and holes [40]. In addition, vertical molecular tunneling junctions with Au/carbon/SAM/carbon/Au structure were also designed to generate electroluminescence [231].

Similar to optical excitation, electrical excitation can also be achieved through indirect plasmons. Specifically, plasmons can be excited by spatially confined broadband electron beams or high-energy tunneling electrons in nanocavities [224]. Next, the molecular excitons are excited by the plasmons.

In specific, when the resonant plasmon is tightly confined in the nanocavity defined by the metal nano-tip and the substrate in the STM, strong plasmon-exciton coupling can be observed. In a sense, nanocavity plasmons can act as a near-field light source with the adjustable energy to excite the electron to jump between HOMO-LOMO energy levels. The localized plasmon resonance mode of the nanocavity is modified by the state of STM-tip to perform spectral tuning to match the specific excitation of the tetraphenyl porphyrin molecule [232]. The tunneling electrons provided by STM create a plasmon field, and then the plasmon excites porphyrin molecule through energy transfer to form an electronically excited state. Notably, this process realizes the up-conversion electroluminescence, where the emitted photon energy is higher than the excited energy via plasmonic pumping. This reveals that plasmons not only participate in the exciton excitation process, but also interfere with the radiation channel of the exciton.

In addition to tunneling current excitation for forming plasmons, the high spatial resolution advantage of STM allows us to visualize the spatial distribution of molecules, which offers the chance of understanding plasmon-molecule spatial interactions at the sub-molecular level. Taking the system with interstitial plasmon and free alkali phthalocyanine (H<sub>2</sub>Pc) molecules located in the STM tunneling junction as an example, the near-field interaction between molecular excitons and plasmons induced by the tunneling current of the STM would be fine-tuned via changing the lateral distance between the molecules and the localized plasmon [233]. This interaction allows the energy of the localized plasmon to be absorbed by the electronic transitions and achieves the first and second singlet excited state transitions of excitons, which gives birth to the luminescence with peaks at  $\sim 1.81$  eV and  $\sim$ 1.92 eV (figure 27(b)). The local plasmon in this process acts



**Figure 27.** The interaction between plasmons and molecules, and the corresponding spectra. (a) Spatially resolved fluorescence spectra of a single DBP molecule at the indicated positions in the STM image. Reprinted with permission from [228]. Copyright (2018) American Chemical Society. (b) The near-field interaction between a localized plasmon and phthalocyanine molecule and the emergence of 'dip' structures in scanning tunneling luminescence spectra. Reprinted figure with permission from [233], Copyright (2014) by the American Physical Society. (c) Three different junction structures (top) and corresponding STML spectra (bottom). Reproduced with permission from [229]. (c) Springer Nature. CC BY-NC 4.0.

as a point light source coupled with molecules to excite electrons to transit between HOMO–LOMO energy levels to form excitons.

It is worth mentioning that the high locality and subnanometer resolution of tunneling electron excitation are used to precisely control the enhancement characteristics of nanocavity plasmons, ensuring that only specific molecules below the tip will be excited and detected [234]. Here, the precisely controlled nanocavity in the STM provides clearly defined single molecule, and the plasmon enhancement ensures strong and stable single-molecule electroluminescence, helping to advance the understanding of singlephoton emission of single molecules.

### 5.2. Single-molecule exciton states

According to the different spin directions of the excited electron and the left unpaired electron, the excited states can be classified into singlet excited state and triplet excited state. Meanwhile, when the excited electrons are back to the ground state, fluorescence and phosphorescence are emitted, respectively. The transition of electrons between these two states can also occur at a certain condition. Besides, there is another kind of excitons: trions with an extra positive or negative charge, which are different from singlet and triplet excitons. Here, we will introduce these three kinds of exciton states, including their own properties and the transition between them.

5.2.1. Singlet state. When an electron is excited from HOMO to LUMO, a hole is left in the HOMO, forming an electron–hole pair. Due to the Coulomb force, the hole and the electron will have an interaction between each other, and this bound state is an exciton state. Usually, most molecules have an even number of electrons paired in the lowest energy level, which is the ground state. When the molecule in the ground state is excited by certain external energy, such as light, one of the electrons will be excited to an energy state with higher

energy to form an excited state after absorbing the energy [219], leading to an exciton. If the spin of this excited electron is not changed, the two spins of the excited electron and the left unpaired electron are in opposite directions and the total spin is zero S = -1/2 + 1/2 = 0, and this state is called a singlet excited state (S); while if the spin direction is changed to the opposite one, the state is a triplet excited state (T). The excited electron is not stable and tends to jump back to the ground state. Due to the vibration of molecules, such as the stretching and bending, a given energy state of a molecule often includes many fine vibrational states. For example, the first singlet excited state  $(S_1)$  has vibrational excited states (v > 0) and a zero-point vibrational state (v = 0). When the electron jumps from a vibrationally excited state to the v = 0 state, the transition process is called vibrational relaxation. Additionally, owing to the vibration, the singlet excited state with relatively higher energy at v = 0 may have the same energy as the singlet excited state with relatively lower energy at v > 0. Therefore, an internal conversion occurs, which involves the transition between vibronic states with the same energy, e.g., from the  $S_2$  (v = 0) state to the  $S_1$  (v = 5) state. When the electron relaxes to the singlet excited state with relatively lower energy through vibrational relaxation and internal conversion processes, usually to the  $S_1$  (v = 0) state, the electron may jump from the singlet excited state to the ground state. This transition is radiative and the emitted light is the fluorescence. Thus, detecting the fluorescence is a good way to determine the existence of singlet states. For instance, both anthracene and tetracene consisting of carbons have singlet states and are detected by fluorescence [219, 235]. Since carbons have six electrons, both of them have an even number of electrons and all electrons are in pairs. Thus, they can produce singlet excited states with certain external excitation. Another example of single molecules that can emit fluorescence is the ZnPc molecule under STM [236]. The single ZnPc molecule has an even number of electrons and the spins of electrons are paired. Thus, the molecule can have a singlet excited state after excitation. By applying a voltage of 2.5 V, the light emission spectrum of a single ZnPc molecule shows a peak at  $\sim$ 1.89 eV, which proves the existence of fluorescence. Therefore, the existence of the singlet excited state requires that the number of electrons in the molecule is even and the excited electron has a different spin direction with the left unpaired electron in the HOMO. During the transition of the excited electron from the singlet excited state to the singlet ground state, fluorescence is emitted.

5.2.2. Triplet state. If the spin of the excited electron is parallel with the spin of the left unpaired electron in the ground state, the excited state is called the triplet excited state (T). In this case, the two electrons have the same spin, resulting in a total spin S = 1/2 + 1/2 = 1. Therefore, the magnetic quantum number of this molecule is 2S + 1 = 3. In general, due to the spin direction change of the excited electron during the absorption process, two parallel spins are often formed. The change of the spin is usually difficult to realize, so the transition probability is rather small. Meanwhile, the energy of a triplet state is often smaller than that of a

singlet state in the same molecule [219]. Since the transition to the triplet state is hard to happen, only certain single-molecule systems possess triplet states. A typical system is asymmetrical soft organic molecules, which usually have two different donor-chromophores and a central chromophore as the acceptor. For instance, phenoxazine (donor-O) and phenothiazine (donor-S) are good donor-chromophores, diphenyl sulfone core (D) is a good central acceptor in DOS molecules [237]. Due to the interaction between the donors and the acceptor, an intermolecular CT state is formed. Thus, the intersystem crossing between the singlet excited state and the triplet excited state is enhanced [238]. In addition, the triplet excited state can also be formed via an electric excitation process. For example, when a bias voltage is applied to a single-molecule device, the injection of an electron to the excited state can be realized. Specifically, when the bias voltage is larger than 1.8 V, the electron of the phthalocyanine (H<sub>2</sub>Pc) molecule can be excited to the singlet excited state. However, if the bias voltage is between 1.2 V and 1.8 V, the excited electron can only reach the triplet excited state [239]. Besides, other single molecules can form triplet excitons with the assistance of a tip removal process. A typical molecule is 3,4,9,10-perylenetetracarboxylicdian hydride molecules [240]. The absolute value of the threshold voltages of this molecule is  $\sim 2.1$  V for phosphorescence emitted during the transition process of the electron in the triplet excited state to the ground state and  $\sim$ 3.3 V for fluorescence emitted during the transition process of the electron in the singlet excited state to the ground state, respectively. At 2.1 V, an electron of the molecule is excited to LUMO and one of the paired electrons in the HOMO is removed by the tip. At this voltage, the spin of the electron that is antiparallel to that of the electron in the LUMO is removed by the tip (figure 28(a)). Therefore, the left two electrons have the same spin direction, forming a triplet state. When the voltage increases to 3.3 V, the electron paralleled to the electron in the LUMO can be removed by the tip, forming a singlet state.

Same as in the singlet state, electrons in the triplet states can experience vibrational relaxation and internal conversion during the whole process of light-emitting. The main difference is that the transition between the first triplet excited state and the ground state involves the emission of phosphorescence instead of fluorescence. Therefore, the emitted phosphorescence can be used to detect the triplet state. In addition, due to intersystem crossing, the transition between the singlet state and the triplet state may take place. If there are two isoenergetic states with two different multiplicities, the excited electron may jump from the singlet state to the triplet state, such as from the  $S_1$  (v = 0) state to the  $T_1$  (v = 3) state. A H<sub>2</sub>Pc molecule is a typical molecule that can exhibit intersystem crossing under certain bias voltages (figure 28(b)). When the bias voltage is between 1.2 V and 1.8 V, one electron in the substrate will be transferred to the tip and provide some extra energy. Thus, one of the electrons in the HOMO can be injected into the LUMO and form a triplet excited state. After this process, there are two possible excitation channels. One is the other electron in the substrate transferred to the tip, and the other is based on the unstable triplet exciton. Therefore, when another electron





**Figure 28.** Formation of single-molecule exciton states. (a) Schematic representation of the exciton formation by a tip. Reproduced from [240], with permission from Springer Nature. (b) Schematic representation of the molecular excitation mechanism and the inelastic scattering process. Reprinted figure with permission from [239], Copyright (2019) by the American Physical Society. (c) Schematic representation of the transition between four states including an exciton state and a trion state. Reprinted with permission from [242]. Copyright (2021) American Chemical Society.

is transferred from the substrate to the tip, it can provide the energy for the electron in the triplet excited state. Then, the electron is transferred to a new molecular orbital with higher energy and forms a singlet excited state, realizing the intersystem crossing. This transition from a low energy state to a higher energy state is called up-conversion. When the electron in the triplet excited state jumps to the tip, the transition of the electron in the substrate to a new molecular orbital with higher energy can be promoted, thereby forming a singlet excited state. Furthermore, due to the instability of the excitons in the singlet excited state, the transition from the LUMO to the HOMO will happen with light-emitting.

In addition to the transition process between the singlet state and the triplet state, these two states can also be transformed into each other during the singlet fission (SF) and the triplet-triplet annihilation (TTA) process [235]. In the former process, the singlet excited state of a chromophore shares its energy with another chromophore. Both of the chromophores generate the triplet excited state. As for the TTA process, two triplet states of two chromophores quench, leading to one chromophore in the ground state and the other one in the singlet excited state. In terms of energy, to realize the SF process, the energy of the singlet state is higher than that of two triplet states  $(E(S) \ge 2E(T))$ ; while to realize the TTA process, the energy of two triplet states is higher than that of the singlet state  $(2E(T) \ge$ E(S)). For instance, the energy of a singlet state of 9,10bis(phenylethynyl)-anthracene (BPEA) is  $\sim$ 2.46 eV and the energy of two triplet states of BPEA is  $\sim$ 2.49 eV. Therefore, it satisfies the requirement of TTA. Therefore, the molecule can perform the TTA phenomenon with a certain resonant laser energy to ensure that the  $T_1$  population is sufficient [235].

5.2.3. Trion. Trions are the excitons with an extra positive charge or negative charge. They are usually formed by charge injection combined with the neutral excited state. Generally, a trion has three charges, the original negative charge of the electron, the hole of the exciton and an additional charge. Due to its small binding energy, the trion can be only observed at extremely low temperatures. If the trion is based on the charged sites fixed in a lattice, the trion will be immobile, such as the positive trion formed by the positively charged

particle; while if the trion is based on the electron in the conductance band or the hole in the valence band of a semiconductor, the trion will be mobile [241]. Similar to the excitons, trions also can produce photons during the transition to the ground state.

A typical example of trions is the single zinc phthalocyanine (ZnPc) molecule lying on the surface of NaCl/Ag(111) [240]. In this molecule, the neutral exciton can be converted to the trion through a charge trapping process. When a suitable bias voltage is applied, a considerable electric field can be formed to promote the charge injection process (figure 28(c)) [242]. Under the driving of the electric field, a hole has enough energy to pass through the barrier and be injected into the LUMO of the molecule, making the molecule in a charged state. Another possible explanation of the hole injection is that the certain bias voltage makes the SOMO of the molecule resonant with the Fermi level of the tip [236]. Therefore, the electron may tunnel from the molecule to the tip. In other words, the hole is injected into the molecule, generating a charge state. Then, an electron is captured by the LUMO of the molecule with the bias voltage reaching 1.9 V, resulting in a neutral exciton state. When the bias voltage increases to 2.6 V, the induced electric field is strong enough and another hole can be injected into the molecule. With further hole injection, the exciton becomes a positively charged exciton, that is a positive trion.

The properties of trions are rather different from the excitons [243]. Due to the extra charge of the trion, the repulsion between charges in the trions is larger than that of excitons. Therefore, the charges are delocalized in trions, changing the overlap of the charge densities of electrons and holes and increasing the overall effective Bohr radii [243]. Furthermore, the radiative probability is different because of the different oscillator strengths, which refers to the absorption and emission process. Usually, the absorption or emission of a molecule is expressed in terms of the equivalent number of harmonic oscillators within a defined spectral line. So, it directly affects the radiative probability. For an exciton, if the structure is a nanoplatelet, the radiative probability is linearly proportional to the area [243]. For a trion, as the area increases, the probability will reach saturation. Taking the negative trion as an example, the possible reason is that the extra electron initially



**Figure 29.** Exciton energy transfer process and molecular structure. (a) Schematic diagram of the energy transfer process of FRET and Dexter. Reproduced from [248] with permission from the Royal Society of Chemistry. (b) The energy transfer process and structure model of a PdPc–ZnPc–H<sub>2</sub>Pc trimer. Reproduced from [257], with permission from Springer Nature.

delocalizes over the nanoplatelet and is finally confined in the trion. The confinement may result in the decrease of the oscillator strength with a reduction factor 1/A, where 'A' represents the area of nanoplatelet. Therefore, the radiative probability of trions becomes saturated as the area increases.

## 5.3. Single-molecule exciton dynamics

After the formation of excitons by light irradiation, excitons will undergo dynamic processes such as energy transfer, CT or recombination. Understanding these dynamic processes is essential for the preparation of exciton-based molecular functional devices. Thanks to the application of ultrafast spectroscopy and other technologies, the microscopic dynamic processes of exciton energy transfer, CT and recombination have been fully explored up to now. Undoubtedly, the in-depth interpretation of exciton dynamics at the single-molecule level has laid a scientific foundation for the design and development of a new generation of functional molecular optoelectronic devices.

5.3.1. Exciton energy transfer. The excitons generated by light-excited molecules will migrate in space and undergo various energy transfer processes, which are critical to the performance of excitons. So far, a comprehensive understanding of the energy transfer mechanism of molecular excitons has been established.

The most widely studied mechanism is resonant energy transfer (RET), also known as Fo<sup>r</sup>rster resonant energy transfer (FRET). The energy transfer of singlet excitons is generally based on this mechanism. In specific, FRET originates from the resonance interaction of transition dipole moments of molecules. The term 'resonance' refers to the electronic excited states of donors and acceptors, which usually have a certain degree of matching energy levels [244]. The efficiency of FRET is proportional to the square of the electronic coupling, and its efficiency decreases as a description of  $R^{-6}$ , where R represents the distance of donor-acceptor [245]. When the distance between the donor and the acceptor molecule is relatively long, Fo"rster's 'hopping' energytransfer mechanism is believed to work. For molecular systems with more than one acceptor, the coupling of donors and acceptors mainly relies on Coulomb interaction, while the electron exchange is negligible and the point dipole approximation [246] can be applied to describe the energy transfer process. According to Fo"rster's 'hopping' energy-transfer model, energy transfer is carried out through point dipole interaction at this time, and the excited energy is gradually transferred between the donor and acceptor molecules step-by-step to realize exciton migration [247]. Thus, the FRET theory can also be used to explain the process of long-distance energy transfer. It should be noted that this mechanism is limited to a certain degree because the dipole–dipole approximation only works when the distance between the donor and the acceptor is larger than their own size.

Review

There are some well-recognized factors that affect the efficiency of FRET. One is the spectral overlap degree between the acceptor and donor molecules, since the electronic coupling is strongly affected by the degree of orbitals overlap between the acceptor and the donor. When the degree of orbital overlap is high, the energy transfer efficiency between the acceptor and the donor is generally higher. In other words, the small energy difference between donor and acceptor corresponds to the high energy transfer efficiency. Another factor is the spatial orientation of dipoles between the donor and acceptor. When the dipoles of donor and acceptor are arranged in a line, the efficiency is higher than arranged in parallel.

In addition to the FRET, Dexter energy transfer is another important nonradiative energy transfer mechanism. This spin conserved process relies on the interaction of electrons, showing the process of simultaneous intermolecular exchange of electrons in the ground state and excited state (figure 29(a)) [248]. It depends on the degree of orbital overlap between the donor and acceptor molecules as well. Both FRET and Dexter energy transfer follow the Fermi golden rule, and their energy transfer rates are all expressed as a function of spectral overlap. Unlike FRET, Dexter energy transfer is a short-range interaction that strongly depends on the electronic structures rather than the oscillator strengths of donor and acceptor [249]. Moreover, Dexter mechanism can be found in either singlet–singlet or triplet–triplet energy transfer process [250].

The molecular energy transfer relies on the molecular configuration and the external field environment [251]. Among them, the molecular structure is the most important factor



**Figure 30.** Energy level structure and CT process of molecules. (a) Energy diagram of  $\alpha$ -sexithiophene/C<sub>60</sub>. Reproduced with permission from [260]. (c) Institute of Pure and Applied Physics. (b) Diagram of models about exciton CT. Reprinted with permission from [263]. Copyright (2020) American Chemical Society. (c) Proposed mechanism of SF in crystalline pentacene. Reproduced from [269], with permission from Springer Nature.



**Figure 31.** Different forms of exciton recombination processes. (a) Graphical representation of the charge-exciton-photon three-states conversion processes in solid  $C_{60}$ . Reproduced with permission from [273]. (c) Springer Nature. CC BY-NC 4.0. (b) Model of exciton relaxation in the electroluminescence process. [276] John Wiley & Sons. (c) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) On the left refers to the potential energy surfaces of a tetraphenylethylene-based molecule in the ground state and excited state as a function of the (quasi) C = C bond twisting and phenyl torsion dihedral angles; on the right refers to the ultrafast processes responsible for the AIE effect in tetraphenylethylene derivatives. Reproduced from [277]. CC BY 3.0. (d) Exciton-charge annihilation via RET between an exciton and a charge. [285] John Wiley & Sons. (c) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

affecting the energy transfer process. Specifically, different main chain lengths, side chain positions, etc cannot only correspond to various molecular orbital levels, but also affect the delocalization and energy transfer of excitons. For example, long polymer molecular chains can be regarded as composed of many segments of uneven length. The influence of the conjugated polymer chain conformation in the polythiophene system on energy transfer has been investigated [252]. There are two conformations. The first is the molecule polythiophene without the side chains forming a collapsed globule-like conformation, thus resulting in a larger distribution of conjugated segment lengths with many shorter segments. The second is the polythiophene molecule with the polystyrene branches, where the polystyrene branches make the main chain to be effectively maintained in an extended coil-like structure. It is found that the distance between any two conjugated segments of the former is within the Fo<sup>°</sup>rster radius for efficient long-range dipole–dipole energy transfer. In contrast, energy can be only transferred between four adjacent segments for the latter. This means that further segments of the chain are not achievable for Förster energy transfer.

Besides molecular configuration, the influence of external field factors such as temperature and plasmon resonance on exciton energy transfer should not be ignored. One of the most obvious factors is temperature. For instance, intramolecular triplet energy transfer mechanism in polynuclear RuII-OsII complexes varies with adjusted temperatures [253]. Specifically, at extremely low temperatures in a glassy matrix, Forrster-type and Dexter-type mechanisms work together to achieve energy transfer. The rate limit of energy transfer mainly depends on the dipole-dipole interaction. At higher temperatures in the glass, Dexter-type electron exchange is gradually strengthened. From 77 K to the glass transition temperature, the super-exchange mechanism dominates. Under specific frequency, the strong coupling between the molecule and the plasmonic nanostructures will alter the ongoing dynamics process of the molecule. The interaction between plasmon and molecule not only affects the formation of exciton as mentioned above, but shows an important influence on energy transfer. For instance, through introducing plasmon, the effective dipole-dipole interaction in the molecule can be changed by the plasmonic response of the metallic contacts [254]. In the spin-free molecular wire model, for the molecules coupled with plasmon resonance in the gap between the two metal nanospheres, the efficiency of FRET can be enhanced. This may be due to dipole fluctuations in the donor molecule, which leads to dipole fluctuations in the electromagnetic environment [255]. Another argument tells that since FRET is an electron-electron interaction effect caused by a dipole electronic transition, plasmons can affect the Coulomb interaction, thereby altering the FRET efficiency [256].

Inserting auxiliary molecules between the acceptor and the donor to form a ternary system is also a feasible way to adjust the exciton energy transfer. After an auxiliary bridge is inserted between the donor and the acceptor molecule, the one-step energy transfer is replaced by a sequential energy transfer process (figure 29(b)) [257]. At this time, the position and energy gap of the auxiliary molecule need to be considered as well. For instance, a donor-ancillary-acceptor system has been constructed, where a large gap molecule PdPc is separated from a small gap molecule H<sub>2</sub>Pc by an intermediate gap molecule ZnPc. It is confirmed that successive energy transfer occurs between long-distance centers. In comparison with a single RET event with large energy gaps, the sequential RET with small energy steps may be more advantageous. In another configuration, H<sub>2</sub>Pc is placed in the middle as a trap to prevent the diffusion of an excitation. Although it captures most of the energy injected into the donor PdPc, it promotes the RET channel from PdPc to ZnPc to a certain extent.

Moreover, it needs to be emphasized that the direction of exciton energy is usually from molecules with high energy to molecules with low energy. The energy difference between the two is commonly dissipated in the form of heat. However, when donor and acceptor molecules with little difference in energy are very close in space, the possibility of reverse energy transfer cannot be ruled out [258]. For example, the tunneling current injected by the tip of the STM is applied to locally excite the molecular dimers containing MgPc and H<sub>2</sub>Pc molecules deposited on the ultra-thin NaCl (100) film [11]. In comparison with molecular MgPc with the  $S_1$  state at  $\sim$ 1.89 eV, the LOMO (HOMO) energy levels of molecular H<sub>2</sub>Pc with the  $S_1$  state at ~1.81 eV are slightly lower (higher). When the tunneling current locally excites the MgPc molecule, the luminescence of the adjacent H<sub>2</sub>Pc molecule can be observed at the same time. Meanwhile, based on the reverse relationship of the fluorescence intensity, it is presumed that RET occurs between the two molecules. Most notably, the occurrence of reverse energy transfer is observed. The avalanche resonance energy transfer model can be used to explain the energy transfer process from molecule H<sub>2</sub>Pc to MgPc. The hole injected into the HOMO of H<sub>2</sub>Pc and the electron transferred from the substrate to the LUMO or LUMO +1 of the  $H_2Pc$  can generate  $S_2$  state excitons, and its corresponding energy is  $\sim 1.92$  eV. It transfers energy to the  $S_1$  state of MgPc through RET, and then the energy of the  $S_1$  state of MgPc is reversely resonant transferred to the lower  $S_1$  state of  $H_2Pc$ . Since the energy transfer here shows weak sensitivity to tip position, the intermolecular dipole-dipole interaction dominates the energy transfer process, which is mainly determined by the relative configuration of the transition dipole moment between the donor and the acceptor.

5.3.2. Charge transfer of exciton. Electrons and holes are bounded by Coulomb force to form excitons. This bound state will be broken after being stimulated by external fields, such as an electric field. During the transition from bound excitons to free-moving carriers in organic photovoltaic devices, the Coulomb interaction between electrons and holes will lead to the formation of an electrostatic bound state, so-called CT state. In other words, the CT state is an intermediate state imprisoned by a high-energy trap [259]. The CT state consists of an electron on the LUMO of the acceptor and a hole on the HOMO of the donor (figure 30(a)) [260]. At this time, the wave functions of hole and electron are separated in space with relatively small orbital overlap [261]. The CT state can be regarded as a transition state, after which it either recombines to the initial ground state of the donor and acceptor, or further separates into free charges. In other words, the CT state mediates the conversion of excitons into charges. For example, the relationship of photogenerated charge carrier and CT state formation has been investigated [262]. Specifically, due to the CT state dissociation, the increase in charge photogeneration efficiency at low electric fields can be observed. Conversely, the photogenerated of fast charge carriers is more prominent under high electric fields.

The description of CT of exciton in molecular junctions often involves the coherent tunneling and the incoherent hopping processes, and the specific processes are presented in figure 30(b) [116, 263]. In addition, CT in molecular wires with a certain length is often realized through superexchange interaction. The coupling between bridging wire units and the coupling of terminal wire units to the electrodes promote the realization of super-exchange interaction. It should be noted that the superexchange assumes that the orbital states of molecular wires are not filled by transferred electrons/holes, so it participates in the generation of tunneling paths in a virtual way [264]. So far, there are massive related studies on the realization of charge tunneling via superexchange interaction. This model is extended to analyze long-distance donor-acceptor electron transport through molecular bridging structures [265]. In this mechanism, the molecule is viewed as a chain consisted of *n* local orbitals of the same unit at a distance of  $R_0$ , and the CT is promoted through the coupling between adjacent local energy states on the molecular skeleton [266]. If the exciton is excited, the singlet molecule undergoes a spin reverse process with changing from spin-antiparallel to spin-parallel, and it will be converted into an excited triplet molecule [267]. The energy of the triplet state is lower than the corresponding singlet state. Therefore, the ground state firstly transits to the singlet excited state after absorbing energy, and then transforms into the triplet state through the intersystem crossing. Furthermore, a unique phenomenon of the transition from one singlet exciton to two triplet excitons has been discovered. In specific, SF refers to the phenomenon of MEG in which organic semiconductor molecules are excited to generate singlet excitons and then undergo a spin-allowed splitting process to form two triplet excitons. This phenomenon has great application value in improving the conversion efficiency of solar cells.

If the energy of the singlet exciton is higher than twice the energy of the triplet, the SF will occur quickly, exceeding other decay channels [268]. Meanwhile, SF is said to proceed through a rapid transformation to a nearby dark state before splitting into triplet excitons (figure 30(c)) [269]. This dark state owns multiexciton characteristics and can be effectively dissociated into multiple electron-hole pairs. Subsequently, the dark state can be considered to correspond to a pair of spin-correlated triplet exciton (TT) states [270]. Numerous studies have pointed out that the interaction between TT state and singlet excitons may contain direct and CT-mediated indirect superexchange interactions [271]. It is found that after incorporating the CT state, a fraction of the singlet exciton group can temporarily occupy the CT state, and then quickly turn into the TT state. Therefore, the emergence of the triplet state is accelerated, showing exponential shapes. This is due to the influence of CT on the total population evolutions of TT state through an indirect superexchange interaction, which is a quantum tunneling mode of electrons from the donor to the acceptor [272].

5.3.3. Recombination of exciton. In addition to charge separation, the recombination of excitons makes them own a certain lifetime. The exciton recombination can be divided into three forms. The first way is radiative luminescence, that is, electron-hole pairs bounded by Coulomb interaction recombine and release photons. The second way is relaxation, which is due to lattice vibration or coupling with phonons. The third way is annihilation, a process that is caused by interaction between multiple excitons or between excitons and carriers.

In recent years, advances in fluorescence detection technologies have allowed the use of scanning near-field optical microscope to obtain sub-wavelength resolution addressing recombination, which makes it possible to detect single-photon emission caused by recombination of excitons. For example, due to the structural defects of single molecules in a C<sub>60</sub> film caused by excitation originated from charge injection of STM, a single electrically addressed single-photon emitter can be formed (figure 31(a)) [273]. According to the correlation between the increase of the applied current and the decrease of the fluorescence lifetime, the excitons are quenched by the next injected charge with a probability of 50%. This can prevent the formation of double excitons, thereby ensuring that only one pair of electron-hole recombine within a certain period to achieve single photon emission. There are many similar single-photon emission systems, which provide a good platform for exploring the dynamic process of recombination of the exciton.

In addition to single photon emission, the interaction between molecules can also cause luminescence, which is called aggregation-induced emission (AIE) [274]. Generally, for most  $\pi$ -conjugated molecules, due to the concentration quenching effect caused by strong intermolecular  $\pi$ - $\pi$  stacking interaction, once the number of molecules increases, the emission tends to weaken or disappear. On the contrary, for some systems like thiazole molecules [275], the interaction between multiple molecules increases the recombination path of an exciton, which enhances the luminescent intensity.

To explain this phenomenon, a generally accepted theory of restriction of intramolecular motion [276, 277] based on the molecular perspective is established (figures 31(a)-(c)). In specific, when the intramolecular interaction is weak, there is sufficient space for the relative movement of molecules, such as vibration and rotation. Therefore, through vibrational rotation, the excited molecules can convert light energy into heat for dissipation, reducing the fluorescence efficiency. When the interaction between adjacent molecules increases, the steric hindrance of molecules will increase. Specifically, the energy of the excited state  $(S_1)$  rises sharply after reaching the lowest point. Hence, the intramolecular motion is restricted by the high energy barrier. This reduces the energy dissipation caused by motion, and then indirectly increases the recombination ratio of excitons by light emission. In addition to considering the configuration and electronic properties of single molecules, analysis of different types of stacking modes should also be considered to gain insight into the mechanism of enhancement of fluorescence emission caused by molecular interactions [278].

The nature of the intermolecular interaction involved in AIE is closely related to phonon coupling. Thus, the potential field of the exciton can be regulated by exciton relaxation caused by external factors such as phonon. For example, the initial intramolecular exciton relaxation in P3HT is proved to be driven by strong selective exciton–phonon coupling to torsional motion [279]. The exciton relaxation usually results in its energy being captured at the local potential well. A typical case is the femtosecond excited perylene bisimide dimers formed through molecular interactions [280], and its excited state disappears rapidly within a few hundred femtoseconds.

Specifically, the system shows the transient CT characteristics to the lower energy Frenkel state on the sub-picosecond time scale after the femtosecond excitation of the higher energy Frenkel state. Subsequently, a relatively slow relaxation caused by a flat potential energy curve and a large moment of inertia corresponding to the rotation of two molecules appears. After this torsional movement reaches the lowest energy, an effective trap for the excitons can be formed. The characteristics of exciton trapping exhibit only small distortions and occur on the ultra-fast time scale. The exciton relaxation significantly changes the exciton decay kinetics, resulting in a narrowing energy band gap, thereby affecting the energy transfer efficiency and performance of the optoelectronic devices.

Furthermore, the interaction between excitons [281] or excitons and charges, that is, freely movable electron or hole states, can lead to the annihilation of singlet excitons [282]. The interaction between excitons provides the channel of exciton-exciton annihilation (EEA). In general, when multiple excitons are formed under high excitation density, one exciton relaxes to the ground state without radiation in the process of collision with another exciton. After nonradiative energy transfer, another adjacent exciton is pumped to the high-energy state and relaxes quickly to the lowest excited state. As a result, one exciton dissipates as heat, and only one exciton is left. EEA is the main loss mechanism under a high density of excitons [283]. For the high-density exciton group, even if the exciton lifetime is only 0.6 ns, the adjacent exciton interference is so strong that EEA becomes the main process of exciton loss [284]. Due to the decrease of the number of available excitons, this nonradiative process not only shortens the exciton lifetime, but reduces the luminescent efficiency.

The charge lifetime formed by singlet excitons in donor-acceptor blends usually ranges from femtosecond to tens of picoseconds, which is generally longer than the lifetime of exciton. When the excitation pulse width is shorter than the charge lifetime, excitons and charges with stable energies will overlap in time. In other words, the excitons exist on the time scale when adjacent charges are formed but not yet recombined, and the strong optical resonance between the excitons and the charges leads to annihilation [285] (figure 31(d)). Firstly, the exciton and the charge undergo RET, and the excitons return to the ground state, leaving behind the photoexcited charges. Subsequently, the photoexcited charges lose excess energy and rapidly relax to the ground state in a nonradiative manner. When the exciton holds a certain diffusion length and both excitons and charges possess sufficient density, exciton-charge annihilation is obvious.

# 5.4. Exciton effects and application of single-molecule devices

Single optoelectronic devices have provided a platform for investigating various interesting physical mechanisms at the single-molecule level. Among them, the exciton state possesses a profound impact on the optoelectronic properties of single-molecule devices. For instance, the research of the longlived charge separation state generated by photo-induced electron transfer under illumination can open up a new way for the preparation of single-molecule photovoltaic devices. Hence, the in-depth analysis of exciton effect lay a theoretical foundation for the structural design and performance optimization of single-molecule devices.

5.4.1. Photovoltaic effect. The electron-hole pairs generated by light excitation are separated to produce a charge separation state and form a potential difference. This phenomenon is called photovoltaic effect. In traditional, the photovoltaic effect can be used to convert solar energy into electric energy. Specifically, the photoactive materials will generate excitons under the radiation of light. Subsequently, the excitons diffuse and migrate to the interface of acceptor and donor interface before relaxing to the ground state, and then dissociate into free charges. Finally, the charges are transported to the electrode and collected to form a photocurrent through the electrode. In order to achieve high photoelectric conversion efficiency, the excitons are required to possess a long enough lifetime to achieve a certain diffusion length and effective photogenerated carrier separation. The charge separation process largely depends on the energy arrangement of the molecular frontier orbitals and the Fermi level of electrodes (figure 32(a)) [286]. Through the regulation of energy arrangement, the separation of electron-hole pairs can be driven, and the reverse recombination of electron-hole pairs can be prevented. Therefore, when constructing the molecular photovoltaic device, the energy arrangement between the molecules and the electrodes needs to be considered.

Studying the operation mechanism of the photovoltaic effect at the single-molecule level can provide the necessary theoretical guidance for the realization of the functional single-molecule devices. Recently, thanks to the progress of single-molecule construction technologies, the photovoltaic effect of molecular junction devices constructed by organic molecules sandwiched in specific electrodes has been explored [287]. For example, for ITO-gold junctions with molecules consisting of a porphyrin chromophore and a  $C_{60}$  electron acceptor under the 520 nm irradiation (figure 32(b)), the long-lived charge separation state can be formed and eventually migrate into the ITO conductive substrate [288]. A further study shows that photo-induced charge separation can also be detected by using spectroscopic imaging technique, where changes in photo-induced tunneling current are detected [289].

In the molecular junction, the built-in potential in the polar molecule promotes the directional transfer of excited electrons, which can be used to drive the separation of electron–hole pairs to trigger the photovoltaic effect. At the same time, the polar unit helps to reduce the quenching of the excited state caused by the reverse electron transfer from the metal to the photo-oxidized molecule. For instance, SAM with a hemicyanine molecule with strongly coupled of donor and acceptor units attached to the gold surface is constructed [290], where the acceptor moiety of the molecule is closer to the metal interface than the donor moiety (figure 32(c)). The optical excitation of hemicyanine manifests as the excitation of electrons from HOMO to LUMO. Specifically, the asymmetry in the electron transfer rate of LUMO and HOMO with the electrode leads to the formation of net photocurrent. In addition,



**Figure 32.** Photovoltaic effects of molecules with different energy level structures. (a) Schematic diagram of energy layout for charge transport of Au/OTP-Ru/Au molecular junctions. Reprinted with permission from [286]. Copyright (2014) American Chemical Society. (b) Porphyrin fullerene binary molecules forming charge separated states under irradiation. Reprinted with permission from [288]. Copyright (2011) American Chemical Society. (c) Metal organic monolayer interface and internal photocurrent generation mechanism. Reprinted with permission from [290]. Copyright (2013) American Chemical Society. (d) Band diagram for the reverse biased junction with nGaAs and simplified description of hemispherical space charge region under different bias values. Reproduced from [291]. CC BY 3.0. (e) SAM of nonadiyne on Si(111) electrodes (left) and the current–voltage characteristics of gold–nonadiyne–silicon junctions (right). Reproduced from [293]. CC BY 3.0.

the properties of the electrode have a great influence on the generation of photovoltaic effect, therefore the electrode materials should be carefully considered in the design of molecular junctions. Initially, noble metal materials are selected as electrode materials in most cases because of their simple ohmic resistance, excellent anti-oxidation capability, and easy formation of stable metal-molecular bonds. However, they are not conducive to the formation of the photovoltaic effect. Asymmetric junctions, where one electrode is a non-metal, have become a useful way to effectively realize the photovoltaic effect. One representative is the introduction of semiconductor electrodes to form the metal-molecule-semiconductor junction. In specific, the semiconductor electrode allows changing the doping type, such as N-type or P-type, to control the properties of the majority carrier. The different doping density can control the concentration of charge carriers and the thickness of the space charge layer (figure 32(d)) [291]. In addition, the electronic characteristics of the semiconductor electrode can impart the rectifying behavior. The rectification effect refers to the difference in the magnitude of the bias current in the forward and reverse directions under a fixed bias potential [10].

As mentioned above, the characteristics of electrode materials will affect the photovoltaic performance of single-molecule devices. Silicon is the typical semiconductor electrode material, and molecules are connected with Si electrodes by Si–C bonds to form Si electrode based devices [292]. For example, the attraction of symmetrical saturated alkyl chain molecules containing two terminal alkynyl groups on the Si(111)-H surface provides a verification platform for the construction of silicon–molecule–gold junction (figure 32(e)) [293]. In this structure, the silicon can be protected from oxidation and provide a distal alkyne unit with high affinity with the Au STM tip used as the top contact to construct the device. Under the depletion condition, a thick space charge region is formed on the surface of low *n*-doped silicon semiconductor, resulting in electron tunneling barriers. Due to the strong covalent Si–C bond formed in such a single-molecule junction, the average lifetime is about 30% longer than that of the same molecule connected to gold electrodes.

In addition to the introduction of asymmetric electrodes, the utilization of asymmetric molecular structures can also control the energy band arrangement of molecular junctions, thereby affecting their photovoltaic effect. A widely adopted measure is to change the molecular structure by adjusting the type of side groups to adjust the HOMO–LOMO energy level gap of the molecule, thereby regulating the internal charge separation. Moreover, the introduction of electron-donating or electron-absorbing groups can change the electron absorbing or donating ability as well [294], thereby improving the charge transport properties.

For instance, active materials with a D- $\pi$ -A (donor- $\pi$ bridge-acceptor) structure generally exhibit the good photovoltaic performance. Careful selection of various  $\pi$  bridges is an effective way to adjust molecular energy levels. A mature operation is to incorporate various electron-withdrawing units as auxiliary electron acceptors into the conjugate bridge to form the donor-acceptor  $\pi$  bridge-acceptor structure. It is expected that the additional electron acceptors of the molecules will promote charge separation and electron migration, and ultimately increase photovoltaic conversion efficiency [295]. For instance, CN units with strong electronwithdrawing properties will display electron trapped effect, and the use of some electron-rich rings acted as electron acceptors may help to weaken the electron capture effect of CN units, thereby optimizing the photovoltaic performance [296]. In further, when pyrrole as an auxiliary electron donor is introduced into the conjugate bridge and close to the acceptor side to replace the commonly used thiophene, the electrontrapped effect of CN group to prevent the electron injection can be effectively balanced. As a result, a three-fold increase in energy conversion efficiency is realized in this modified system.

5.4.2. Photoconductivity effect. In addition to the photovoltaic effect, another widely studied optoelectronic phenomenon is the photoconductivity effect. In the traditional case, it refers to the process in which photons absorb light energy to change the internal carrier concentration, which leads to a change in electrical conductivity. The increase of conductivity often means that the ability of materials to transfer current is enhanced. In single-molecule devices, photoconductivity effect has also been widely studied. Photon excitation can modify the electron transition mode of the HOMO-LUMO energy level in molecules, thereby affecting the excitation and transport paths of carriers. In specific, systems with different tunneling probabilities in dark and light states without any bond rearrangement or photoisomerization have been realized [297]. The specific structure is Au/SAM/Au tunnel junction, where SAM contains hemicyanine dyes that exhibit different conductivity under light and dark states. In detail, the electrode absorbs photons and transfers energy to the hemicyanine dyes in the SAM to form charge states. The excited SOMO of molecules under light resonates with the electrodes and the DOS of the frontal orbital delocalizes, which effectively reduces the width of the tunnelling barrier. Therefore, the possibility of molecular electron tunneling under light increases, ultimately leading to the increase in photoconductivity. One of the photoconductivity mechanisms in single-molecule device is exciton effect. In view of the photoconductivity changes of the asymmetric molecular junction with PTCDI attached to Au electrodes in the light and dark environments, an exciton binding mechanism is proposed [214]. The mechanism shows that in the dark, the conductivity relies on the energy difference between the molecular HOMO and the Fermi level of electrodes. When the photon energy is at or close to resonance with the HOMO-LUMO gap, electrons are excited from HOMO to LUMO, making LUMO partially filled. As exhibited in figure 33(a), the holes tunneling from the electrode to HOMO can feel the electrons in LUMO and are attracted by the electrons. The HOMO energy is pushed to the Fermi level, increasing the conductance. This hypothesis opens a new way for understanding the photoconductivity effect of molecular junctions.

In some single-molecule electronic devices, the excitons are excited at the interface of molecules and electrodes, which may also contribute to the total photocurrent of the molecular junctions. One way to describe this phenomenon is the internal photoemission (IPE). IPE refers to the process in which charge carriers are excited from one electrode to another electrode through a tunneling barrier, which is defined as the offset between the Fermi level of electrodes and the molecular orbital energies [298]. When the photon energy is lower than the work function of the electrode but high enough to inject carriers into or pass through the molecular energy level (figure 33(b)), the photogenerated carriers formed by the top electrode may pass through the middle molecular junction and enter the bottom electrode [299]. Thus, the photoconductivity is finally enhanced, and a measurable photocurrent is generated. When the energy gap between HOMO/LUMO of the molecule and the Fermi level of electrode is greater than kT, carriers cannot freely enter another electrode from one electrode via thermal excitation, thereby indirectly creating an electron/hole interface barrier. According to the IPE theory, the minimum photon energy required to generate a photocurrent is directly related to the interface energy barrier, which is essentially smaller than the HOMO-LUMO gap, depending on the involved molecules.

In large-area carbon/molecular layer/Cu tunnel junctions, IPE is also involved in inducing the photoconductivity effect [300]. When the low-energy photons incident on the top Cu electrode generate electron-hole pairs, the corresponding energy of the deepest hole at this moment is  $E_F - h\nu$ . If this energy exceeds the hole tunneling barrier, HOMO-mediated electrons will transport from the bottom carbon electrode to the Cu electrode with holes, thereby generating a photocurrent. It should be reminded that in this model, excitons are only produced in the Cu electrode, not in the carbon electrode or the molecular layer. During the IPE process, the electrode rather than molecules is responsible for absorbing photons, so the measured photocurrent will be different when irradiating the top or bottom electrode. This is a unique feature of IPE.

As a platform for molecular electronics research, largearea molecular junctions have gradually gained attention due to their advantages such as more suitable for large-scale production and well-integration with traditional electronic products. For the large-area molecular junctions, it is claimed that the strong coupling between the molecule and the electrode may induce hybridization, which creates orbitals that span the molecule and the electrode. Therefore, the gap of highest occupied system orbitals and lowest unoccupied system orbitals reflect the transport gap of the completed junction related to the determination of the tunneling barriers [301]. In other words, IPE contains the results of all the interactions between molecules and contacts. When the molecular layer



**Figure 33.** Photoconductivity process under different energy level structures. (a) Schematic diagram of exciton transmission in molecular junction. Reprinted with permission from [214]. Copyright (2018) American Chemical Society. (b) Energy level diagram of the nonresonant tunnel barrier for holes and electrons respectively. Reprinted with permission from [299]. Copyright (2015) American Chemical Society. (c) Schematic of the mechanism for photocurrent production in large area all-carbon molecular junctions. Reprinted with permission from [301]. Copyright (2018) American Chemical Society.

between conducting contacts of carbon-based molecular junctions reaches a certain thickness, the coupling between the subunits of molecule has a stronger effect on the CT forming photocurrent than the coupling between electrodes and molecules. On the contrary, the impact of charge injection barrier at the molecule/electrode interface can be neglected. Especially, when the thickness of the molecular layer is greater than the one-step direct tunneling distance, such as more than 5 nm, the carrier transport mode is more likely to adopt a multi-step tunneling mechanism. The multi-step tunneling model mainly relies on the barrier determined by the HOMO-LUMO gap inside the molecule, rather than the charge injection barrier at the molecule/electrode interface. In this case, the rate-limited step of photocurrent is CT in the molecular layer, and the transport mechanism depends on the characteristics of the molecular layer rather than the molecule/electrode interface [302], which is a feature significantly different from the IPE process.

The influence of the structure on photogenerated charge transport in molecular films with thickness >5 nm is subsequently investigated [301, 302], which provides guidance for the design of molecular electronic devices. For example, in a carbon-based large-area aromatic oligomers molecular structure with molecule layer thickness in the range of 5-12 nm, the photoconductivity is tightly determined by the

HOMO-LUMO energy gap [301]. The electrode with sufficient optical transparency is employed to allow light to pass through the entire molecular junction, such as graphene. If the energy of the incident photons is within the absorption band of the molecule, the photocurrent response is found to be completely different from these systems based on the IPE mechanism. On the one hand, the photocurrent appears to be electrode independent. On the other hand, the photocurrent density is not only wavelength dependent, but closely related to the UV-vis absorption spectrum of the molecular layer. Regarding the generation of photocurrent, it is believed that molecule layers absorb UV-vis photons, leading to the change in the HOMO-LUMO gap. Since the electronic interaction between molecular layer subunits is very weak, the molecular layer is regarded as a series of weakly interacting MO and the tunneling barrier is located between molecular subunits (figure 33(c)). In the case of weak intermolecular interactions, charge transport can proceed along with a series of localized HOMO or LUMO orbital molecules. In addition, the asymmetric electronic coupling between the bottom electrode and the top electrode with the molecule is considered to provide a driving force for the transport of photogenerated carriers.

In addition, carbon-based molecular junctions composed of aromatic oligomers also show that when the molecular length d > 5 nm, CT is controlled by the thickness of the molecular



**Figure 34.** The structures and energy level arrangement models of different electroluminescent molecules. (a) Overview of free Ir(ppy)<sub>3</sub> molecules and plasmon excitation between the Ag(111) substrate and an Ag-covered Au tip. Reprinted with permission from [303]. Copyright (2013) American Chemical Society. (b) Schematic diagram of normal luminescence and hot luminescence vibronic transitions. Reproduced from [232], with permission from Springer Nature. (c) Sketches of the diodelike emission mechanism (left) and of the energy transfer mechanism (right) about electroluminescence of phthalocyanine molecules deposited on NaCl/Ag(111). Reprinted figure with permission from [305], Copyright (2017) by the American Physical Society. (d) Model diagram of a self-decoupling porphyrin molecule on Au(111). Reprinted with permission from [307]. Copyright (2013) American Chemical Society. (e) The picosecond photon correlation spectroscopy combined with luminescence induced at the atomic scale with a STM. Reprinted with permission from [308]. Copyright (2020) American Chemical Society. (f) Schematic diagram of the luminescence mechanism of neutral and charged ZnPcs. From [236]. Reprinted with permission from AAAS. (g) View of fluorescent polythiophene connection. Reprinted figure with permission from [309], Copyright (2014) by the American Physical Society. (h) Energy transfer between molecules. Reprinted with permission from [11]. Copyright (2016) American Chemical Society.

layer rather than the offset between molecular orbital energies and the Fermi level of electrodes [302]. If the electronic coupling at the interface is stronger than the electronic coupling between the local states inside the molecular layer, the injection speed of the carrier at the interface is faster than the carrier shuttle speed in the molecular layer. The effect of the transport barrier due to the energy level difference at the electrode/molecular interface will be weakened. In such a device, the photocurrent is limited by the step through the oligomer subunits separated by a barrier determined by the HOMO–LUMO gap. Therefore, the properties of the molecular layer are also crucial factors affecting the photoconductivity effect. In general, both the IPE mechanism and the photocurrent induced by molecular absorption are powerful tools to explore the exciton effect of molecular junctions. In short, at the single-molecule level, both the photovoltaic effect and the photoconductivity effect can be used to enhance the photocurrent response. The photovoltaic effect mainly describes that photogenerated excitons overcome the Coulomb attraction and become separated electrons and holes under the induction of an external field. A relatively long separation lifetime is required to allow the electrons and holes to move in the opposite direction. Furthermore, the arrangement of the molecular frontier orbitals and the Fermi level of the electrode should be able to push the electrons and holes to move to the electrode. While the photoconductivity is a phenomenon in which photon irradiation increases the tunneling probability of charges, which causes the transformation of originally non-conductive electrons into movable conductive electrons and the increase of carrier concentration. In this process, molecules or electrodes can absorb photons to generate conductive carriers, and electron-hole pairs can move together without separating [214].

5.4.3. Single-molecule electroluminescence. In addition to photocurrent, the electron-hole can be injected into the HOMO-LUMO of the molecule by applying an external voltage. They will attract each other, causing the emission of photons, also known as electroluminescence. It is of great significance to realize single-molecule devices that can convert electrical energy into well-controlled optical signals [40]. In particular, a series of progresses have been made based on the highly localized tunneling current of the STM to excite single-molecule luminescence. By setting the metal STM tip close to the molecule, the local excitation of the plasma with atomic precision can be detected by a highly localized STM tunneling current. In further, the localized plasmons excited by the tunneling current can couple with molecules (figure 34(a)) to participate in the electroluminescence process [303].

STM tunneling electron-induced molecular luminescence shows the potential to detect the interdependence between the conformational structures, energy levels and optical properties of single molecules. In addition, the high spatial resolution of STM allows to obtain a real-space mapping of the fluorescence spectrum of a single molecule. Furthermore, the dynamic process involved in the light emission process can also be determined. Under specific mode, the energy of the tunneling electrons passing through the junction can be directly transferred to the molecular excitons. Alternatively, molecules resonate with plasmons, then energy transfer occurs between them to promote exciton excitation or emission [304], leading to the phenomenon of molecular luminescence. Therefore, the behavior of nanocavity plasma is somewhat similar to that of a strongly coherent light source with adjustable energy [232]. The radiation channel of excitons can be significantly controlled via strong resonance enhancement of excitation and emission by nanocavity plasmon. For example, the low-temperature electroluminescence of ZnPc molecules shows low-energy vibrational signals with sub-molecular resolution [305]. In specific, plasmons are believed to mediate the energy transfer between tunneling electrons and molecules (figure 34(c)). Due to the dipole symmetry of the entire ZnPc molecule, the local optical response is dependent on the relative orientation and phase of the transition dipole of the ZnPc molecule, hence the intensity of some peaks varies according to the location of the STM-tip [306]. The change of the plasmon field will affect the degree of molecular plasmon coupling, and then adjust the performance of molecular electroluminescence. This is because the plasmon mediates the energy transfer between tunneling electrons and molecules, and then the excited molecules relax to the ground state via releasing energy in the form of photons. Therefore, in comparison with photoluminescence, STM-induced molecular electroluminescence in the nanocavity exhibits many advantages, such as high local excitations, high spatial resolution and local plasmon excitation.

Nevertheless, the contact between the molecule and the metal substrate will result in the hybridization of the electronic state, resulting in the rapid transfer of charges to the substrate and quenching of molecular luminescence. In order to improve the electroluminescence efficiency of the excited molecule, in addition to the relative position of the STM-tip, the influence of the weak interaction between the molecule and the metal substrate must be emphasized. Therefore, efficient molecular electroluminescence usually requires a decoupling layer or a vacuum gap between the emitter and the metal. Up to now, a variety of strategies have been implemented to electronically decouple the adsorbed molecules from the metal surface. One way is to add an oxide or NaCl buffer layer between the molecule and the metal substrate. For example, an ultra-thin NaCl spacer layer can be used to suppress quenching to promote the electro-induced single photon emission of a single ZnPc molecule [234]. In addition, by using multiple monolayer molecular spacers, quenching of the substrate can be prevented. For instance, the multi-layer tetraphenylporphyrin molecules contact the metal substrate as a buffer layer (figure 34(d)), while the upper layer molecules realize electroluminescence [307].

A typical scenario of molecular electroluminescence is the single-photon source that is mentioned above. In fact, there are many studies on electrically driven moleculebased single-photon emitters. However, the low controllability of the molecular environment and background interference hinders the improvement of luminous efficiency. The subnanometer high-resolution and highly localized tunneling electrons in STM provide a solution for achieving high efficiency of single-photon electroluminescence (figure 34(e)) [308]. For example, the resonance-enhanced plasmons excited by STM tunneling electrons may help to obtain strong and stable electrically induced single-photon emission from a single ZnPc molecule [234]. As the distance between the metal tip and the molecule decreases, even less than 1 nm, the quantum efficiency of molecular fluorescence can be significantly improved.

Another ingenious path is to lift or suspend molecules. Taking polythiophene wires suspended between the metal substrate and the tip as an example (figure 34(g)) [309]. The two ends of the conjugate wire are directly connected to the electrode, while the long part of the polymer chain is suspended as the junction between the electrodes. Under a forward bias, the recombination of electrons injected at the LUMO and holes injected at the HOMO of the molecular wires occurs, leading to luminescence. Successive detachments of thiophene units from the surface lead to the conformational change of the wire, affecting the electron delocalization length and the emission wavelength. Because polythiophene wires adopt different structures, the slight shift of the fluorescence wavelength can be observed.

The realization of STM-induced single-molecule electroluminescence is usually related to the resonant coupling between the Fermi level of the STM-tip and the singly occupied orbital of molecules. Under a specific voltage, the injection of tunneling charges causes the relative position of the frontier orbit of the molecule and the Fermi level of the tip to change correspondingly. Therefore, the energy level arrangement of the system under consideration is altered, allowing the directional tunneling of electrons to realize molecular electroluminescence. The characteristics of the voltage field can not only determine the energy band arrangement of the studied system, but also further affect the electroluminescence of charged molecules. For charged molecules, different emission features can also be observed by adjusting the positive and negative voltages. Take a ZnPc radical cation adsorbed on a sodium chloride-covered gold(111) as an example here [236]. For high negative voltages, an electron is driven to tunnel from the ZnPc molecule to the STM-tip (figure 34(f)). The generated radical cation is stabilized at a negative voltage, leading to an emission line at 1.52 eV that cannot be observed at a positive voltage. Under certain circumstances, other electroluminescence mechanisms are also working. One case is hot electroluminescence [232, 272, 310]. Although Kasha's rule tells us that regardless of the wavelength of the excitation light, the fluorescence emitted by a molecule should be excited with a certain multiplicity from the lowest state. Specifically, when the molecule is excited to the highenergy state  $S_2$ , the molecule should relax to the vibrational energy level of S<sub>1</sub> before its radiation transitions to the ground state. Nevertheless, for some molecules with ultra-fast radiation transition rates or large energy difference between S<sub>2</sub> and S<sub>1</sub>, light emitted by direct relaxing from higher excited states to ground state often be observed [311]. This kind of the anti-Kasha behavior is so-called hot electroluminescence, which causes low-intensity vibration characteristics on the spectrum. This phenomenon has been successfully observed in some STM-induced molecular luminescence systems. For example, for polyatomic tetraphenylporphyrin molecules, due to their dense vibrational energy levels and close to metals, the rapid dynamic relaxation from highly excited states to the ground state radiation is equivalent to the competition of internal relaxation [232] (figure 34(b)). Furthermore, during hot electroluminescence, resonant plasmon can act as coherent excitation sources to enhance the probability of direct luminescence from highly excited states of such molecules [310, 312].

In addition to hot electroluminescence, up-conversion electroluminescence of molecules has also been realized. It refers to the phenomenon where the low-energy excited electrons transit to an excitation energy level higher than the initial excitation energy through a certain channel to achieve high-energy photon emission. Up-conversion luminescence can result in a blue shift of the luminescence peak, just like hot electroluminescence [313]. For instance, up conversion electroluminescence from 1.7 eV excitation to 1.81 eV emission is observed in monophthalocyanine molecules [239]. Initially, the electrons are excited to the spin-triplet state through the inelastic electron scattering mechanism. Subsequently, the tunneling electrons from the substrate to the tip can again excite the metastable electrons from the spin-triplet state to the higherenergy singlet excited state [240] by inelastic electron scattering. In parallel, the metastable electrons in a spin-triplet state can tunnel to the tip and directly inject the electrons into a singlet excited state. Finally, the spin-triplet-assisted luminescence is realized.

It is worth mentioning that when the donor and acceptor coexist in a system, molecular electroluminescence can include the phenomenon of energy transfer. The kinetic information of energy transfer in molecular electroluminescence can be obtained from the scanning tunneling luminescence spectrum. For the dimer containing MgPc and H<sub>2</sub>Pc molecules, the local excitation of MgPc with the STM tunneling current can produce a sharp luminescence peak at  $\sim$ 1.81 eV from the adjacent H<sub>2</sub>Pc molecules (figure 34(h)) [11]. The increase in fluorescence intensity of  $H_2Pc$  is accompanied by the decrease in MgPc fluorescence, which clearly shows that resonance energy transfer occurs between them, resulting in the transfer of excitation energy from the MgPc donor to the H<sub>2</sub>Pc acceptor. In addition, fluctuations in the efficiency of resonance energy transfer between MgPc donor and H<sub>2</sub>Pc acceptor lead to the formation of the blinking.

# 6. Single-molecule vibronic effects

The molecule–electrode coupling and electron–vibron coupling will induce the fluctuation of conductance. The study of vibronic effects is of great significance for revealing the comprehensive physical information of single molecules and realizing the functionalization of single-molecule optoelectronic devices. Here, we focus on the vibronic effects of single molecules, including single-molecule electron–vibron coupling, vibronic spectroscopy from single-molecule electroluminescence, thermal effects on vibration and single-molecule vibration dynamics.

#### 6.1. Single-molecule vibrations

The fluctuation of conductance is currently the major difficulty in realizing the functionalization of single-molecule optoelectronic devices. Previous investigations have indicated that the fluctuation may originate from the molecule-electrode coupling and electron-vibron coupling [314-319]. These different types of coupling can substantially modify charge transport within single-molecule junctions. The above-mentioned 'vibron' arises from the excited vibrational modes of the molecules. Each vibrational mode is equivalent to the 'elastic wave' with a certain frequency and a certain direction. Since the energy of the elastic wave is quantization, the vibron, also known as phonon, is defined as the quantum unit of the energy for vibrational modes. The vibron participates in various inelastic scattering processes, leading to significant changes in the transport properties [320]. The study of electron-vibron coupling (intriguing phenomena induced by molecular vibrations), vibrations excited with different approaches, as well as the detection and analysis of vibration characteristics, are of great significance for revealing and understanding the comprehensive physical information of single molecules.

In physics, the coupling refers to the interaction and mutual influence within multiple systems. Herein, the vibron can be coupled with various degrees of freedom in single-molecule junctions, so that the large changes in molecular properties, such as conductance and thermoelectric performance, subsequently appear. Since the coupling strength in the crystal



**Figure 35.** The single-molecule vibration effect in single-molecule junctions. (a) The Franck–Condon effect involving electronic transitions. Reproduced from [6], with permission from Springer Nature. (b) The gate-dependent current–voltage (I-V) curves obtained from a single-C<sub>60</sub> transistor. The lower inset is an illustration of the ideal C<sub>60</sub> transistor and measurement principle. Reproduced from [323], with permission from Springer Nature.

is much weaker than that in the single-molecule system, the investigation of vibron coupling in single-molecule junctions is more extensive in comparison with that in the bulk crystals. At the single-molecule scale, some effects and information, such as the vibrations of chemical bonds based on the inelastic electron tunneling spectroscopy (IETS) measurement, are related to the electron-vibron coupling to a certain extent [95, 321, 322]. In addition, molecules possess spin degrees of freedom. Since the vibron can be coupled with spin, the changes of magnetic moments and spin relaxation processes can be indirectly understood. In parallel, a promising way to measure and manipulate the magnetic quantum phase transition in single-molecule devices based on the spin-vibron coupling can be proposed.

In molecular tunneling junctions, the transport electrons will exchange energy with molecules through absorbing or releasing vibrons, and the energy levels of molecules will be described as a series of vibrational states. When the coupling strength between the molecule and the electrodes is different, the influence of electron-vibron coupling on the transport mechanism is very different [6]. Specifically, in the weak molecule-electrode coupling regimes, when the electron-vibron coupling strength is strong, the Coulomb blockade effect emerges in the tunneling process [323, 324]. This effect can be obviously manifested in the current-voltage (I-V) curves. The prominent characteristic is the exhibition of a suppression near-zero bias voltage, followed by the steplike features with the increase of bias voltages. The Coulomb blockade can be well understood through the Franck-Condon effect (figure 35(a)). Once a molecule is charged (or discharged), the equilibrium coordinates for the ground and excited states are significantly different. On the other hand, this denotes that the potentials along the vibration coordinates in the N and N + 1 charge states are different. The transition from the N to N + 1 states has a certain probability. Particularly within the low bias voltage, the transition between the vibrational ground levels in the N and N + 1 states will be suppressed. While the transition probability from the vibrational ground state of the N charge state to other high excited vibrational levels of the N + 1 charge state can be characterized by the Franck-Condon factor:

$$F_{n,0} = \frac{\lambda^{2n}}{nn!} e^{-\lambda^2},$$
(1)

where the parameters n and  $\lambda$  represent the vibrational quantum number and the electron-vibron coupling strength, respectively. At higher bias voltage, the vibrational quantum states with larger n are excited, and the transition probability increases. The bias-dependent transition generates the clear step-like features in the corresponding I-V curves (figure 35(b)).

For the strong molecule-electrode coupling, the interaction of electron and vibron will greatly change the conductance of the molecular junctions. In the tunneling regime, the excited vibrational mode leads to an increase in conductance, which can be detected using IETS measurements [325, 326]. In specific, when a bias voltage is applied to the molecular junctions, the IETS is based on the inelastic scattering mechanism that the transport electrons can lose energy to the vibrational mode, which is equivalent to add the additional inelastic transport channels for electrons. Consequently, the contribution from both elastic and inelastic channels significantly enhances the total conductance. The excited vibrational mode not only modifies the transport process of the single-molecule junctions, but also can be used for the detection and recognition of chemical bonds. Since various chemical bonds within the target molecules correspond to different vibrational modes, this indicates that the vibrational signals of the molecular junctions can be used as the 'fingerprint' for identifying molecules. Some optical methods such as Raman spectroscopy [327] and infrared spectroscopy [328] can also accurately obtain the vibrational modes, which are derived from the processes such as stretching and swinging of different chemical bonds. More information concerning the molecular vibrations for recognizing the chemical bonds will be illustrated in this section.

#### 6.2. Single-molecule electron-vibron coupling

The interaction of vibrations with electrons in single-molecule optoelectronic devices is one of the most significant mechanisms for electron transport through molecules in an



**Figure 36.** Electron–vibron coupling in molecular junctions. (a) The excitation of the vibrational mode with opening additional inelastic channels. Reproduced from [6], with permission from Springer Nature. (b) Current (*I*), differential conductance (dI/dV) and the derivative of differential conductance  $(d^2I/dV^2)$  change with the bias voltage. Reprinted from [330], Copyright (2008), with permission from Elsevier. (c) IETS measurement of the octane dithiol single-molecule junction. Reproduced from [95], with permission from Springer Nature. (d) Distribution of vibrational energy for  ${}^{13}C_6H_6$  and  ${}^{12}C_6H_6$  molecules. Reprinted figure with permission from [333], Copyright (2008) by the American Physical Society. (e) Periodic modulation of current for a pentacene molecule with different terahertz pump-probe time delays. Reproduced from [335], with permission from Springer Nature. (f) Physical mechanism of terahertz-induced vibron-assisted tunneling for a C<sub>60</sub> single-molecule transistor. (g) The dependence of the current intensity for a C<sub>60</sub> single-molecule transistor with different terahertz photon energies. (f) and (g) Reproduced from [336], with permission from Springer Nature. (h)–(k) Inelastic electron transport processes induced by the vibrations leads to the quenching of the QI effect. (l) The calculated *I–V* curves for the molecules with the destructive QI effect. (h)–(l) Reprinted figure with permission from [341], Copyright (2013) by the American Physical Society.

inelastic manner. Many systematical studies have been carried out from both theoretical and experimental approaches for vibrationally inelastic transport over the past few decades. Explaining the transport properties caused by the vibrational effects must consider the coupling of molecular energy levels and the vibrons. For strong electron–vibron interactions, the inelastic components are clearly shown in the measured conductance. In this section, we discuss the important potential of vibration-induced effects in revealing the physical information and intriguing phenomena.

6.2.1. Inelastic electron tunneling. Vibrational characteristics are of great importance to understand the internal structure of a molecule. It is vital to detect vibrations and understand the changes in the physical properties of single molecules resulting from the interaction of electrons with vibrons. Several factors, such as the molecule–electrode coupling strength, the thermal energy and the electron–vibron coupling strength, are revealed to change the electron–vibron effects in the

single-molecule junctions [320]. In the weak molecule-electrode coupling system, the transport electrons through the junction can excite the strong vibrational modes, and the conspicuous vibrational resonance features appear. If the vibrational mode has a certain frequency, several vibrons might be absorbed to give rise to a series of metastable states. The electrons can pass through the metastable states, causing these states to have a sufficiently long lifetime. Eventually, these states are thought to be the transport channels for the electrons through single-molecule junctions, and the transmission probability comes from the total channels. Consequently, the vibron-induced peaks in the enhanced transmission intuitively occur in the electronic device (figure 36(a)). IETS has been successfully used to detect the change in electron transport by the interaction of electron with vibron in different vibrational modes, resulting in the change of electrical properties. The current (I), differential conductance (dI/dV), and the derivative of differential conductance  $(d^2/dV^2)$  will change with the varies of bias voltages applied at the electrodes [329-331]. The change of these parameters is related to the excitation of the vibrational mode at a certain bias voltage. In detail, the vibrons originated from the vibrational mode give rise to the marked impact on electrons, then the transmission for the electrons will change, and subsequently, the varying signals are detected. Specifically, the I-V curves of the tunneling junctions will show obvious 'kinks', and the extra steps and peaks occur in the dI/dV and  $d^2/dV^2$  curves, respectively (figure 36(b)). The molecules usually consist of many chemical bonds, which means that the molecules have different excited vibrational modes. In addition, these modes exhibit different bias voltage dependencies. Based on this, the molecular properties, especially the recognition of chemical bonding can be investigated through the change of electron transport induced by the excited vibrons using IETS measurements.

As mentioned above, the peaks in the  $d^2/dV^2$  curves induced by the vibrons can be measured by the electrical spectrum. For example, in an octane dithiol single-molecule junction, the intensity of measured  $d^2/dV^2$  as a function of the bias voltage can be obtained (figure 36(c)) [95]. Several peaks clearly appear at different bias voltages, which correspond to the vibrational modes of the internal chemical bonds. The peaks are located at 694, 911, 1129, 1282, 1483 and 2879 cm<sup>-1</sup>, which are assigned to C-S stretching, C-H rocking, C-C stretching, C-H wagging, C-H scissoring and C-C stretching. In addition, a surprising discovery is one peak located at the low bias voltage, which corresponds to the vibrational mode of Au-S stretching. This indicates that the chemical bonding at the interface can be accurately determined, which also means that the investigation in the vibron-induced variations of transport based on IETS measurements is an otherwise way to check whether the molecules are well chemically connected to the electrodes. When a molecule is bridged to the electrodes, the IETS can also be used to check the stability of anchoring groups. For instance, a comparative study on the vibrational characteristics of the amine and thiol anchoring groups connected to Au leads shows that the energy of the  $\nu$ (Au–N) mode occurs in red shifts, while  $\nu$ (Au–S) mode does not [332]. Once the spacing between the electrodes increases, the energy of  $\nu$ (Au–S) mode remains unchanged. These phenomena directly prove that the Au-S bonding is significantly stronger than the Au–N bonding.

Since the energy corresponding to the vibron is related to the mass of an atom, the isotope effects of the atom in a molecule with the same conformation are detected. The vibrons induced in the isotopic molecules with different masses are coupled with the transport electrons, and the corresponding differences are reflected in the IETS. Theoretical analysis indicates that for a certain excited vibron, the relationship between the frequency  $\nu$  and the mass of a molecule *m* is expressed as:

$$\nu = \frac{k}{\sqrt{m}},\tag{2}$$

where k represents the spring constant of the molecule–electrode bonding. The calculated vibrational energy of molecules is consistent with the experimental

data. For instance, in  ${}^{13}C_6H_6$  and  ${}^{12}C_6H_6$  junctions with Pt electrodes, two energy peaks appear (figure 36(d)) [333]. These peaks are located at 40 meV and 42 meV, according to the harmonic oscillator model, which are assigned to the hindered-rotation mode, that is, a vibrational mode within the molecules. All these indicate that the inelastic electron tunneling with the interaction of electrons and vibrons plays an important role in identifying the components and structure of molecules, and has great potential in the detection of various properties.

6.2.2. Terahertz modulated vibron-assisted tunneling. The existence of vibrons in single-molecule junctions will affect the transmission characteristics, leading to a great modulation of the electrical properties of single-molecule devices. In the traditional case, the excitation of the vibron in the molecular junctions caused the inelastic process of the transport electrons. Terahertz radiation is an effective way to excite the vibrational modes, which is attributed to the consistent magnitude of terahertz frequency and the vibrational frequency of the molecules. Because the wavelength range of the terahertz electromagnetic waves is about 30-3000 microns, which is much larger than the size of molecules, the investigation on the interaction of terahertz pulses with molecules is usually carried out for the system with a large number of molecules [334]. However, it is of fundamental importance and practical value to develop the measurement approaches based on the terahertz technology at the single-molecule scale to reveal information such as electrical transport properties and ultrafast dynamics.

The pump-probe technique is considered to be able to accurately track the vibration process of single molecules. For instance, the fluctuation of current caused by the vibration of a pentacene molecule adsorbed on the substrate can be detected by STM with different THz pump-probe time delays (figure 36(e)) [335]. The two identical terahertz pulses, referring as pump and probe pulses, interact with the molecule, and the resonance of transport orbitals is possible to be excited by the pulses. The pump excites the transition of electrons from the transport orbitals of the molecule to the STM electrode, resulting in the variation of the charge states of the molecule. These changes cause changes in Coulomb force and van der Waals force, which causes instantaneous disturbance to the molecule. For example, the neutral molecule will produce vertical vibration at its equilibrium position. This type of vibration will lead to different barriers. The probe pulse can induce the pentacene molecule to generate a changing current. When the delay times between the pump and probe pulses are changed, it clearly shows that there is a significant periodic modulation of the recording current. This clearly indicates that the molecular vibrations can be reflected in the modulated current, and the oscillatory period of the molecule can be recognized from the pump-probe delay times.

In order to further reveal the novel physical phenomena arising from the terahertz-induced vibrations of single molecules, it is necessary to conduct a systematic study of introducing terahertz waves into single-molecule devices. This technology will not only reveal the mechanism of light-matter interactions, but also provide a promising approach to modulate the function of single-molecule devices [336]. A representative process is the vibron-assisted tunneling induced by the terahertz pulses. For example, in a C<sub>60</sub> single-molecule transistor (figure 36(f)), the physical mechanism of terahertz-induced vibron-assisted tunneling can be intuitively depicted. Initially, the electrons could not access the LUMO without the terahertz radiation. Once the terahertz pulses are introduced, the vibrons are possible to be excited in the single-molecule transistor. Thus, the electrons can absorb the vibrons to hop onto the LUMO of the molecule from one electrode. This process is defined as 'tunneling in', which drives the molecule in the charge states. In addition, a similar process occurs defined as 'tunneling out', in which the electrons absorb the vibrons to hop onto another electrode from the HOMO. Eventually, the transport of electrons gives rise to a visible increase in current. Furthermore, the dependence of current intensity with different terahertz photon energy in a C<sub>60</sub> single-molecule transistor can also be obtained (figure 36(g)). Several splitting peaks appear in the energy near 2 meV and 4 meV, indicating that the photons with the corresponding energies can effectively excite the vibrational modes as well as the vibrons with certain energies in the C<sub>60</sub> molecule. The energy of the vibron matches the energy difference of the Fermi level of the electrode and the transmission orbitals, forming the transition mechanism of the vibron-assisted tunneling [336].

The terahertz-induced vibrational modes affect the transport process of electrons and change the electrical properties in the single-molecule junction. Considering the strong modulation of the tunneling process by the photon-excited vibrons, the introduction of terahertz waves is expected to manipulate the charge transport dynamic behavior of single-molecule devices in real time.

6.2.3. Vibration-induced quantum decoherence. Vibron is a quantum unit of the vibrational mode. The vibron-induced changes in the transmission characteristics follow the quantum model rather than the classical approximation. In the meantime, exploring the quantum effects in the single-molecule functional devices is valuable [337–339]. Among them, the quenching of the destructive QI, one of the important quantum effects, from the strong electron and vibron coupling is a key issue [340].

The QI effect in the single-molecule junctions generally involves the participation of at least two MO. It is assumed that the orbitals contributing to charge transport are quasidegenerated. The difference in spatial symmetry of the orbitals will cause the phase difference of the electronic wave function. Once the outgoing electronic wave packets encounter and the phase difference of the two wave functions is odd times of  $\pi$ , destructive QI effect occurs, resulting in the small amplitudes of the coherent tunneling [338, 341]. In contrast, since there is only one orbital corresponding to one outgoing wave function, the tunneling amplitudes of the electron emitted from a single orbital are greater than that of the coherent sum of the two orbitals.

However, the QI effect in different electronic states is strongly correlated to the dynamic process of transport electrons. The external excitations may regulate the dynamic process, thus changing the QI effect. Specifically, the excited vibrons can easily couple strongly with the electrons. For molecules with QI effects, the vibron coupling in the transmission process is expected to be a feasible way to change this effect. For example, the electron-vibron coupling significantly quenches the destructive QI effect, thereby enhancing the original strongly-suppressed tunneling current of single molecules [341]. This process is named vibration-induced quantum decoherence. The QI and vibration-induced decoherence effects can be interpreted with the help of quantum calculation methods [342, 343]. In this sense, the issue of electron transport should focus on the energy of the overall molecular system, which includes the energy of electronic states  $H_{el}$  located at the molecular bridge and the energy induced by the vibrations  $H_{\rm vib}$ . Consequently, considering the energy for Hamiltonian systems of each part separately, the qualitative even quantitative analysis about the vibration-induced changing in quantum effects can be obtained.

Furthermore, the quenching of the QI effect needs to be discussed in the fundamental electron transport mechanism. In principle, one case of the transport process is that the electrons can excite the vibrational modes and lose energy, then traverse through the other low energy states of the molecules (figures 36(h) and (i)). Another case is that the electrons absorb the vibrons, and traverse through the high energy states (figures 36(j) and (k)), which is called an inelastic deexcitation process. Additionally, with the help of electron-vibration coupling, electrons can transfer from the electrode to the electronic states of the molecule (figures 36(h)-(j)), as well as the reverse process (figures 36(i)-(k)). All these indicate that electron transport can be changed by various vibrational properties. In specific, the involvement of vibrations changes the electronic states of electron transport and strongly destroys the electronic wave packets. Eventually, the transmission probability increases, which can be reflected through the electrical measurement. Theoretically, the calculated I-V curves can intuitively show the destructive QI and its quenching effects. For instance, the nonequilibrium Green's function approach is an effective way to deal with the above-mentioned effects. In this approach, it is assumed that the energy of two transmission states of the molecules is close to the Fermi level of the electrode. If the destructive QI effect is not considered, the current intensity results from the incoherent sum of the respective currents flowing through the two electronic states in the molecular junctions. In particular, the current of the incoherent sum will rise significantly with the increase of bias voltage (the dashed purple line in figure 36(1)) [341]. Assuming the destructive QI effect occurs, the current amplitude is at least one order of magnitude weaker than the former case (the solid purple line in figure 36(1)).

When the vibrons coupled with the transport electrons, the corresponding destructive QI is strongly quenched. Comparing the current intensity with or without the involvement of the vibrational coupling, the current in the vibration-induced decoherence case is dozens of times higher than the case involving the destructive QI effect, which is almost the same as the sum of the currents from the two transport states (the solid black line in figure 36(1)). Consequently, the modulation of the vibration-induced decoherence can effectively regulate the transport states of the single-molecule junctions, providing an effective way to construct a switch.

# 6.3. Single-molecule photon-vibron coupling

The study of single-molecule photon–vibron coupling is of great significance for decoding the fine energy level structure inside the molecule. In this section, we discuss the single-molecule photon–vibron coupling from two directions: vibronic spectroscopy from single-molecule electroluminescence and vibration detection by plasmon-enhanced Raman scattering.

6.3.1. Vibronic spectroscopy from single-molecule electroluminescence. The vibrations create a large number of vibrons, so the energy level within the molecules is no longer regarded as a single-level state. Specifically, after the electrons couple with different number of vibrons, a series of hyperfine vibrational energy level structures related to the vibrons appear near the main energy level of the molecules. Once the electronic transition takes place between the vibrational levels, a lot of phenomena appear, which can decode some important information inside the molecules. For example, Raman and infrared spectroscopies based on the electronic transition between the vibronic levels have been widely used to distinguish the chemical bonds of the molecules [328, 344-346].

Electroluminescence is a phenomenon that electrons transition or recombine with the holes between different energy levels, thereby generating photons. When the current or an external electric field is applied to the molecules, there are two typical electroluminescence mechanisms, injection electroluminescence and intrinsic electroluminescence in the electroluminescence process of molecules. The injection electroluminescence is caused by injecting electrons and holes into the molecule through the electrodes. When the electrons and holes recombine inside the molecule, the energy of the system will be released in the form of photons. While the intrinsic electroluminescence means that the electrons accelerate under the external electric field, excite the electroluminescent central ions by collision and subsequently emit photons through radiation transition.

The electroluminescence of the single molecules is generally based on the intrinsic luminescence mechanism. For example, the STM can be used to directly or indirectly drive electrons to enter the high vibronic excited levels of the molecule by applying a bias voltage between the tip and the substrate [305, 347, 348]. Then the electrons will relax to the ground or to an excited vibronic level of the electronic ground state by emitting a photon. Due to the large energy difference between the various vibrational levels, many photons with different energy are emitted during the radiation process. It is of great value for analyzing the distribution of vibronic energy levels from the electroluminescent emission spectrum to identify the chemical bonds.

Since different MO have different structures, the spatial distribution of photons generated by the electronic transition



**Figure 37.** Vibronic spectroscopy for single molecules. (a) Morphology of a single MgP molecule with electroluminescence. (b) Transition mechanism of vibronic levels with electrons injection into the LUMO. (a) and (b) Reprinted figure with permission from [348], Copyright (2010) by the American Physical Society. (c) TERS spectra of single H<sub>2</sub>TBPP molecule with different molecular alignments. Reproduced from [352], with

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between the vibrational energy levels can reflect the information of the spatial distribution of MO. Furthermore, the study of photon imaging of the electroluminescence mechanism can help understand the hyperfine spatial structure of the orbitals. For instance, through the photon image of a single magnesium porphine (MgP) molecule (figure 37(a)) [348], the degenerate energy levels can be identified. An obvious 'ring' structure appears in the image, which is attributed to the photon distribution radiated from two different orbitals with different spatial distributions. For MgP molecules, LUMO is double degenerate. The electrons in each vibronic energy state in the two degenerate orbitals have a certain probability of transition to the vibronic states of HOMO with radiating photons (figure 37(b)). Since the spatial configurations of the two degenerate levels of LUMO are orthogonal to each other, the spatial structure of photon imaging is consistent with the orbital configurations.

Furthermore, the diversity of molecular space structures and the sensitivity of structures to various environments make it important to study the transition spectra of the molecules with different configurations and to decode a lot of physical information [348]. For example, it is important to understand the symmetry of the vibrational modes through the transition spectra of electroluminescence. It should be emphasized that single-molecule electroluminescence uses electrons rather than photons to excite the transition of electrons between different vibronic levels and obtain photon signals. Analyzing the photon signals and their corresponding spectra, the sub-molecule scale spatial structure and energy levels can be identified. In a word, the investigation on the singlemolecule electroluminescence has become the dominant way for vibrational information recognition of the single fluorescent molecules. The vibronic spectroscopy from electroluminescence is expected to be a promising approach for decoding the orbital structures.

6.3.2. Vibration detection by plasmon-enhanced Raman scattering. The Raman spectrum has attracted extensive attention in the past few decades, mainly because it can effectively reflect the vibrational information of various types of molecules. Therefore, the corresponding Raman signal has become a 'fingerprint' for identifying molecular components [310–312]. The energy difference of the vibrational modes corresponding to the vibrations of different chemical bonds leads to the different alignment of the vibration energy levels. Due to the transition between the different vibronic levels, ground level and virtual level, the frequency difference of the emitted photons will be reflected in the Raman spectrum, which is specifically manifested as the Raman peaks of these modes locate at different positions of the Raman shift. The intensity of the Raman peak and the frequencies corresponding to various vibrational modes reflect the bond strength and the components of molecules, thereby becoming a powerful tool for detecting the characteristics of the target molecules.

Specifically, the Raman spectrum is a kind of scattering spectra, which reveals the information of molecular vibrations by analyzing the scattered light with different frequencies. Raman scattering, including Stokes and anti-Stokes scattering, and its scattering mechanism can be well interpreted by the quantum theory. Once the vibrational modes are excited, the energy levels of the molecules include not only the ground state and the excited state, but also a series of vibration energy levels. The polarization caused by the light on the molecules can be regarded as virtual photon absorption, indicating that the electron transitions from the ground level to the virtual level. The electron in the virtual state returns to a certain vibronic level and releases energy in the form of photons. When the energy of the radiated photon is less than that of the incident photon, this process is called Stokes scattering. Another case is that the electron transitions from the vibronic level to the virtual state, and then return to the ground level. In this way, the energy of the radiated photon is greater than the incident photon, which is called anti-Stokes scattering.

However, because Raman signals are extremely weak, it is very challenging to detect the Raman signals of the molecules, especially for single molecules. To overcome this, the plasmon can be used to enhance the Raman signals in the nanogap to achieve effective detection at the single-molecule level. In detail, owing to the interaction between the light and free electrons on the metal surface, the collective oscillation for electrons occurs, which can be defined as the generation of a new electromagnetic wave mode, that is, the formation of plasmons. Once the frequency of light matches the oscillation of electrons, the free electrons resonate with light on the metal surface, thereby forming a strongly enhanced electromagnetic field. The electromagnetic field can increase both the excitation and radiation rate of the scattering process and eventually enhance the Raman scattering, which is called surface-enhanced Raman scattering (SERS) [349–351]. The SERS enhancement factor of a free molecule can be approximated by [351]:

$$EF(\omega_0, \omega_{\rm R}, r_{\rm m}) = M_{\rm loc}(\omega_0, r_{\rm m}) M_{\rm Rad}(\omega_{\rm R}, r_{\rm m}), \qquad (3)$$

where  $M_{loc}$  represents the power enhancement factor for the local electrical field,  $r_m$  is the position where the molecule locates,  $M_{rad}$  is the power enhancement factor for the radiation case and  $\omega_R$  is the frequency of the inelastic Raman photons. When the frequency of Raman-scattering light is close to that of the incident light, the above equation can be approximately described as [351]:

$$EF(\omega_{0}, \omega_{\mathrm{R}}, r_{\mathrm{m}}) \approx \left| \frac{E_{\mathrm{loc}}(\omega_{0}, r_{\mathrm{m}})}{E_{0}(\omega_{0}, r_{\mathrm{m}})} \right|^{2} \cdot \left| \frac{E_{\mathrm{loc}}(\omega_{\mathrm{R}}, r_{\mathrm{m}})}{E_{0}(\omega_{\mathrm{R}}, r_{\mathrm{m}})} \right|^{2}$$
$$\approx \left| \frac{E_{\mathrm{loc}}(\omega_{0}, r_{\mathrm{m}})}{E_{0}(\omega_{0}, r_{\mathrm{m}})} \right|^{4}, \qquad (4)$$

where  $E_0(\omega_0, r_m)$  is the incident laser fields and  $E_{loc}(\omega_0, r_m)$  is the local enhanced electric field strength. The relative relationship between the intensity of Raman-scattered light and the intensity of the incident light can be approximately deduced from this equation.

As one of the most important contents of plasmon enhanced Raman scattering, the tip-enhanced Raman scattering (TERS) is an effective way to study the Raman characteristics of single molecules [350, 352]. When the light incident on the nanogap, three aspects of local surface plasmon resonance effect, lightning-rod effect and antenna effect contribute to the enhancement of the local electromagnetic fields. These enhancements greatly increase the sensitivity for the detection of Raman signals, making the in situ monitoring for single-molecule information become possible, such as the structural information, chemical composition, environmental information, etc. In addition, it has great potential to infer the mechanism of quantum transition of different vibronic levels from the TERS. For instance, based on the DFT calculations, the single meso-tetrakis(3,5-ditertiarybutylphenyl)porphyrin (H<sub>2</sub>TBPP) molecule exhibits different Raman spectra under different alignment angles (figure 37(c)) [352]. The change of molecular angle will lead to the appearance of Raman peaks for some vibrational modes and the decrease of the intensity of some peaks. The changes are attributed to the transition selection rules of the vibrational energy levels that govern the generation of the Raman signals. The probability of electron transition at these vibrational levels is affected by the change of molecular alignment, resulting in the modulation of Raman intensity corresponding to different vibrational modes. Consequently, SERS spectroscopy, based on the recognition of molecular vibrational modes, has become a sophisticated approach for characterizing the important information, and it plays a crucial role in revealing the internal interaction mechanism of single molecules.

#### 6.4. Thermal effects on vibration

Many intrinsic properties and quantum effects in single molecules can greatly affect the charge transport characteristics, such as thermal effects related to vibration. In this part, the thermal effects within single molecules are mainly discussed, including the use of the thermal energy to excite vibrons to change the charge transport characteristics, the vibrational heating of molecules excited by light or electric field and the thermoelectric performance related to vibronic effect on thermal conductance. The systematic study of the thermal effects will promote the rapid development of single-molecule functional devices based on the thermal modulation.

6.4.1. Thermally-induced vibron-assisted tunneling. The thermal effects can affect many properties of single molecules, such as conductance and thermoelectric effects. An important temperature dependent phenomenon of the single-molecule junctions is the transition of the charge transport mechanism from tunneling to hopping. This is because the thermal energy excites the vibron inside the molecule, which then couples with the electron to change the transport mechanism (figure 38(a)) [98, 353, 354].

The vibrons can substantially affect the transport mechanism depending on the electron-vibron coupling strength, which is defined as the ratio of the magnitude of vibronic coupling M to the energy parameter  $\sqrt{\Delta E^2 + (\Gamma/2)^2}$ [320, 354].  $\Delta E$  and  $\Gamma$  present the injection gap and the width of the orbital resonance arising from the electrode coupling, respectively. The weak electron-vibron coupling,  $\ll$  1, leads to coherent tunneling in the  $\sqrt{\Delta E^2 + (\Gamma/2)^2}$ junction. For the strong electron-vibron coupling, the incoherent transport mechanism induced by the vibrons occurs. In addition, the thermal energy plays a significant role in regulating the tunneling process. Essentially, this parameter can change the electron-vibron coupling strength, including the amplitude of the vibronic coupling or the magnitude of the injection gap. Therefore, the use of the thermal energy can effectively excite the vibrons, and then the vibrons participate in the modulation of the charge transport. The whole process is called thermal-induced vibron-assisted tunneling.

There are some examples of thermal-induced vibronassisted tunneling in single-molecule devices caused by thermal excited vibrons. Through bridging the single diarylethylene molecule with closed conformation to graphene electrodes, the temperature-dependent I-V curves can intuitively show the thermal-induced changes in the charge transport characteristics (figure 38(b)). When the temperature is lower than 90 K, the conductance remains constant; when the temperature is higher than 90 K, the conductance increases. The above phenomena can also be depicted by Arrhenius plots (figure 38(c)), in which the transition of the transport mechanism occurs around 90 K, indicating that the temperature-dependent transport changes from coherent tunneling to incoherent hopping. The conductance for the coherent transport hardly changes with temperature, while the conductance for the incoherent transport is greatly affected by temperature. The temperature induced change of transport properties is attributed to the thermal-induced electron-vibron coupling. Since the energy of the internal vibrational mode, that is, the twisting vibration of the diarylethene molecule, is close to the thermal energy corresponding to a specific temperature, the vibrational mode can be excited to generate vibrons. Ultimately, the enhanced coupling between electrons and vibrons leads to the appearance of the transport transition. The enhancement of the electron-vibron coupling strength origins from two aspects: one is that as the temperature increases,  $\Delta E$  decreases due to the thermal broadening of the electronic energies of both the molecule and the electrodes; the other is the increase in the magnitude of vibronic coupling M. As the change in  $\frac{M}{\sqrt{\Delta E^2 + (\Gamma/2)^2}}$ , the transport  $\Delta E$  and M lead to an increase in turns into an incoherent hopping. In addition, the strong coupling strength induces the inelastic process of electrons to generate additional conducting channels, leading to an increase in conductance. Therefore, the vibronic coupling in single-molecule junctions induced by thermal effects becomes an important mechanism for modulating charge transport and promotes the progress of single-molecule devices towards practical applications.

6.4.2. Vibrational heating in single-molecule junctions. The local heating in nanoelectronic components has a great impact on the performance and stability of the electronic devices. For single-molecule devices, a lower heat capacity indicates that the above parameters are more susceptible to heating, so it is of great significance to elucidate the local heating in singlemolecule junctions [355–358]. However, the precise characterization of thermal effects in single-molecule junctions is a great challenge. It has been shown in section 6.4.1 that the local heating transfers the thermal energy to the vibrational modes of molecules. Then, the excited vibrational modes may couple with electrons, resulting in the inelastic transport. On the contrary, local heating can be achieved by the thermal energy released through energy dissipation during the vibrational relaxation process [359]. Generally, there are two different ways for heating in single-molecule junctions. One is the scattering among the electrons. For instance, when a bias voltage is applied during the tunneling process of the electrons through single-molecule junctions, inelastic scattering can cause thermal excitation. The other is the release of the thermal energy caused by the relaxation of molecular vibrations [359].

In specific, the vibrations in the single-molecule junctions are mainly generated by DC and light irradiation [360, 361]. For instance, if a bias voltage is applied and a corresponding current flows through the molecules, the electrons will transfer energy to the vibrational modes. Under the irradiation of light, the chemical bonds of the molecules begin to vibrate after absorbing photons with a certain energy. Through measuring the effective temperature  $T_{\nu}^{\text{eff}}$ , which is the result of the equilibrium between heating and heat dissipation, the thermal energy change caused by the vibrations in single-molecule junctions can be realized [361–363]. The SERS spectroscopy is a feasible approach to measure the effective temperature of single



**Figure 38.** Thermal effects on molecular vibrations. (a) Thermal energy excited vibrons coupling with the tunnelling electron to change the transport mechanism. (b) and (c) Temperature-dependent charge transport characteristics of the diarylethylene single-molecule junction, which show the I-V curves (b) and the Arrhenius plots (c). (a)–(c) Reprinted with permission from [354]. Copyright (2017) American Chemical Society. (d) Time dependent Raman signals of two vibrational modes of the dodecanethiol junction. (e) Bias dependence of  $T_{\nu}^{\text{eff}}$  for different vibrational modes in the OPV3 single-molecule junction. (d) and (e) Reproduced from [359], with permission from Springer Nature. (f) and (g) Temperature dependence of the figure of merit for the three polyacene species (benzene: red line; naphthalene: green line; anthracene: blue line). The thermoelectric figure of merit considers the contribution of electrons (f) and both electrons and vibrons (g). Reprinted figure with permission from [371], Copyright (2010) by the American Physical Society.

molecules, because the magnitude of the effective temperature is determined by the intensity of Raman signals. The effective temperature is derived from the ratio of Stokes and anti-Stokes signals:

$$\frac{I_{\nu}^{\rm AS}}{I_{\nu}^{\rm S}} = A_{\nu} \frac{(\omega_{\rm L} + \omega_{\nu})^4}{(\omega_{\rm L} - \omega_{\nu})^4} \exp(-\hbar\omega_{\nu}/k_{\rm B}T_{\nu}^{\rm eff}).$$
(5)

For a certain vibrational mode,  $T_{\nu}^{\rm eff}$  is related to the parameters of the Raman response, which include the intensity of anti-Stokes signal  $(I_{\nu}^{AS})$  and the intensity of Stokes signal  $(I_{\nu}^{S})$ ;  $\omega_{L}$ and  $\omega_{\nu}$  represent the frequency of incident laser and Raman mode, respectively;  $A_{\nu}$  is a correction factor that describes the ratio of the anti-Stokes section and the Stokes section. Based on this method, it is possible to accurately obtain intuitive physical insights into the potential mechanism of the vibrational heating in single-molecule junctions. For instance, the Raman response of two vibrational modes (C-C stretch at 1099 cm<sup>-1</sup>, CH<sub>2</sub> or CH<sub>3</sub> deformation at 1475 cm<sup>-1</sup>) excited by the light irradiation in the dodecanethiol junction shows that the Raman signals exhibit almost periodic discontinuity with the change of time (figure 38(d)) [359]. The change of Raman signals as a function of time is attributed to the conformational change of the molecule, which greatly affects the vibrational relaxation as well as the vibrational mode. Eventually, the Raman signal and the corresponding effective temperature significantly change. According to equation (5), it can be concluded that the effective temperature varies from 300 K to more

than 2000 K. When the molecule switches between different configurations, the effective temperature will also change between the previous values. This indicates that the conformation changes can be intuitively reflected in the effective temperature measurements.

The effective temperature change caused by DC induced vibrational heating can also be extracted from the measured Raman spectrum. For example, the thermal effects induced by the current can extract the information about the molecule-electrode coupling [359]. The bias dependence of  $T_{\nu}^{\rm eff}T_{\nu}^{\rm eff}$  for different vibrational modes in the molecule consisted of a three-ring oligophenylene vinylene terminating in amine functional groups (OPV3) can be examined (figure 38(e)). When the bias voltage exceeds a certain value, the effective temperature of each vibrational mode increases linearly with the bias voltage. There is a voltage asymmetry in  $T_{\nu}^{\rm eff}T_{\nu}^{\rm eff}$  between the positive and negative sweeps, which is highly consistent with the asymmetry of measured I-V curves. In addition, the voltage asymmetry in  $T_{\nu}^{\text{eff}}$  of different vibrational modes is quite different. The asymmetry of the effective temperature of each vibrational mode depends on the asymmetry of the molecule-electrode coupling, which is attributed to the fact that the effective cross section of the vibration changes with the direction of the current. Consequently, the information of the molecule-electrode coupling can be characterized by extracting the effective temperature corresponding to the vibration heating in Raman signals.

In a word, vibrational heating reveals the important physical mechanisms in single-molecule junctions. At the same time, rational use of the thermal energy generated by the vibrational heating mechanism will become an effective way to control the performance of single-molecule devices in the future.

6.4.3. Vibronic effects on thermal conductance of singlemolecule devices. The thermal conductance can be used to measure the heat transfer ability of materials, and has a wide range of application, such as the construction of thermal insulation materials and thermoelectric materials [364–370]. In particular, due to the conversion between the thermal energy and the electrical energy, the thermoelectric performance is of great significance in the energy storage. In addition, exploring the thermoelectricity at the single-molecule level is important for understanding its intrinsic properties. Both electrons and vibrons can make contribution to the thermal conductance [371, 372]. Among them, the vibrons can greatly modulate the thermoelectric efficiency of single-molecule junctions, providing a possible way to construct practical single-molecule thermoelectric devices.

Theoretically, the Landau formula can evaluate the thermoelectric coefficient of a single-molecule system that only includes the contribution of electrons [371]. When considering the contribution of vibrons, the thermoelectric coefficient can be well described by the density-functional parametrized tightbinding model combined with the Green's function approach [373, 374]. The excited vibrons in the molecules release the thermal energy during the relaxation process, and finally form a thermal gradient between the electrode gaps, thereby generating thermal conductance. The thermal conductance for the vibronic part, denoted as  $\kappa_{ph}$ , can be expressed as:

$$\kappa_{\rm ph}(T) = \int_0^\infty \frac{\mathrm{d}\omega}{2\pi} \hbar \omega \frac{\partial f_{\rm B}(\omega, T)}{\partial T} T_{\rm ph}(\omega) \kappa_{\rm ph}(T)$$
$$= \int_0^\infty \frac{\mathrm{d}\omega}{2\pi} \hbar \omega \frac{\partial f_{\rm B}(\omega, T)}{\partial T} T_{\rm ph}(\omega), \qquad (6)$$

where  $T_{\rm ph}(\omega)$  represents the transmission function considering the vibrational modes. Consequently, the total thermal conductance  $\kappa$  in single-molecule junctions can be described as  $\kappa = \kappa_{\rm el} + \kappa_{\rm ph}$ , where  $\kappa_{\rm el}$  is the thermal conductance contributed by the electrons.

For a single-molecule junction, the thermoelectric efficiency can be evaluated by the thermoelectric figure of merit *ZT* [371].  $ZT = \frac{S^2TG}{\kappa ZT} = \frac{S^2TG}{\kappa}$ , where *S* represents the Seebeck coefficient (or thermopower), and *T* and *G* represent the temperature and the conductance of the molecular junction, respectively. A high *ZT* value indicates a high thermoelectric conversion efficiency. A large number of theoretical calculations show that the single-molecule junction inherently exhibits a higher thermoelectric efficiency [375–380]. However, when the thermal conductance from the vibrons is taken into account, the thermoelectric efficiency will be greatly reduced.

The thermoelectric efficiency before and after considering the contribution of the vibrons can be obtained from the theoretical calculations. For example, the temperature dependence of the ZT for the three polyacene species (benzene, naphthalene and anthracene) shows an obvious difference [371]. When only the electron contribution  $(ZT_{el})$  (figure 38(f)) or the contribution from both the electrons and vibrons (ZT)(figure 38(g)) are considered, the thermoelectric figure of merit shows a huge difference. Obviously, in comparison with  $ZT_{el}$ , ZT for each species has a significant decline. The thermoelectric figure of merit  $ZT_{el}$  of benzene and naphthalene are almost the same at room temperature, showing a very strong thermoelectric efficiency. However, the ZT of benzene is much lower than that of naphthalene at room temperature. Due to the narrow HOMO energy level of benzene, a low resonance transmission probability and a low current manifest, resulting in large thermopower S and  $ZT_{el}$ . Furthermore, the contribution from electrons to thermal conductance for the benzene molecular junctions is much smaller than the vibronic effects on thermal conductance, leading to a significant reduced ZT at room temperature.

In addition to the vibrons, other factors are possible to affect the thermoelectric properties of single-molecule junctions as well. For instance, through introducing semiconductor electrodes to connect with single molecules, the thermoelectric performance can be appropriately improved [372]. In addition, the chemical methods of introducing side groups can also improve the thermoelectric performance [371]. In a word, designing specific molecules and optimizing the thermal conductance corresponding to the vibronic contribution can greatly improve the thermoelectric characteristics, thereby guiding the further development of practical single-molecule thermoelectric energy storage devices.

#### 6.5. Single-molecule vibration dynamics

The vibration dynamics is a very important physicochemical property of molecules. For instance, the vibration of molecules plays an important role in activating the reactants and modulating the reaction path. A large number of studies have shown that the vibrational transfer occurs during the ultrafast vibration of molecules. Since understanding the intermolecular or intramolecular vibrational transfer mechanism is of great significance for revealing and regulating the ultrafast chemical reaction process, it is necessary to explore the vibration dynamics.

6.5.1. Vibrational coherence. The vibrational coherence refers to the vibration coupling between different vibrational modes. The vibrational coherence between chemical bonds occurs within or between molecules [381–384]. Due to the existence of vibrational coherence effects, a series of complex chemical reaction processes will be strongly affected. For instance, the vibrational coherence of solute and solvent can determine the mechanism and the distance scale of cooperative bimolecular chemical reactions, such as proton transfer [381].

Since the time scale of coherence is very short, usually on the femtosecond scale, the detection of vibrational coherence effects is full of challenges. In recent years, various timeresolved spectroscopy technologies based on ultrashort laser pulses, such as time-resolved infrared spectroscopy, transient
absorption spectroscopy and ultrafast coherent anti-Stokes Raman scattering, have contributed to the study of a large number of intermolecular or intramolecular vibrational coherence effects [381, 385]. For instance, two-dimensional electron spectroscopy can reveal the vibrational coherence between the molecules during the process of photosynthesis [386]. This vibrational coherence effect occurs between groups composed of heterogeneous chemical bonds at different positions of the molecule. In addition, the vibrational coherence time can affect the physical and chemical properties of the molecule. This parameter can be characterized by analyzing the coherent process between groups composed of similar chemical bonds at different positions. For example, the C-H bond of the ethanol molecule has abundant vibrational modes, which can be used to study the vibrational coherence between groups composed of similar chemical bonds [387]. Experimentally, the ultrafast dynamics of C-H bond vibrational modes in ethanol molecules can be explored by coherent anti-Stokes Raman scattering technology. There are three Raman activity modes for the C-H bond of ethanol molecules around the wavenumber of 3000  $\text{cm}^{-1}$ , which are symmetric stretching mode of CH<sub>3</sub> group ( $\nu$ (CH<sub>3s</sub>) at 2930 cm<sup>-1</sup>), antisymmetric stretching mode of CH<sub>3</sub> group ( $\nu$ (CH<sub>3as</sub>) at 2970 cm<sup>-1</sup>) and symmetric stretching mode of CH<sub>2</sub> group ( $\nu$ (CH<sub>2s</sub>) at 2880 cm<sup>-1</sup>). If only the  $\nu$ (CH<sub>3as</sub>) mode is excited, the intensity of this mode will decay rapidly within a certain time delay, and the intensity of  $\nu(CH_{3s})$  and  $\nu(CH_{2s})$  modes will appear and then gradually increase. By defining the time difference between the intensity of different vibrational signals reaching the maximum value as the vibrational coherence time, it is estimated that the coherence time between  $\nu(CH_{3as})$  and  $\nu(CH_{3s})$  is about 110 fs. The vibrational coherence between CH3 group and the adjacent CH<sub>2</sub> group through the C–C bond, and the corresponding time is about 90 fs.

In addition, many studies also focus on the vibrational coherence process from the intramolecular modes to the intermolecular modes, which may lead to the collective motion and enhance the local reactivity. At present, research on the vibrational coherence is based on an ensemble system with a large number of molecules. Further exploration of the vibrational coherence process at the single-molecule level will deepen the understanding of molecular ultrafast dynamics and promote its application in quantum information.

6.5.2. Vibrational energy transfer. The vibrational energy transfer means that the vibrational energy in one molecule will be lost as it is transferred to another molecule. It determines the path of the chemical reaction, the chemical reaction rate and the change of chemical structure. Specifically, the vibrational energies of the molecules are transferred from the excited atoms, ions or groups to other unexcited atoms, ions or groups. This process is also known as the redistribution of the vibrational energy, which exists in gas, solid and liquid systems, involving the redistribution of vibration–vibration energy [388, 389]. The mechanism of vibration–vibration energy. Physically, the phenomenon

of vibrational energy transfer can be well explained. When the energy is injected into the vibrational mode of a certain vibrational frequency, the equilibrium of the initial vibrational state in the molecules is broken, resulting in the adjustment of the vibrational energy of molecules with different vibrational modes to produce a new energy equilibrium state. Once the initial vibrational mode is excited, there will be a coherent superposition state between the local vibrational modes, and the energy resonance will also occur. The vibrational energy will be redistributed in the molecule through the energy resonance.

There are many paths of the vibrational energy transfer. For instance, the vibrational energy can be transferred from the vibrational mode with high-frequency to that with lowfrequency, or from a vibrational mode with low-frequency excited by the means of mode selection to the adjacent vibrational modes with high-frequency [390]. However, the energy transfer cannot occur between all the vibrational modes, which largely depends on the molecular structure and the vibrational state of the donor and acceptor vibrational modes. Additionally, the energy transfer efficiency between different vibrational modes is also very different, which varies with the change of the frequency difference between the vibrational modes. These discussions of the mechanism of vibrational energy transfer help to reveal the dynamics of the vibrational energy flux in molecules, and help to selectively modulate the vibrations to reveal the complex physical and chemical reaction process [391, 392]. For example, the photochemical synthesis is carried out by controlling the photochemical reaction in the process of energy transfer [393, 394]. In addition, the energy storage capacity of different vibrational modes in macromolecules can be analyzed according to the energy transfer efficiency [395].

In current, the study on the mechanism of the vibrational energy transfer is mainly focused on a large population of molecules, rather than the single-molecule scale. Thus, to push a further exploration of single-molecule vibrational energy transfer is important, because it is possible to explore the vibrational dynamics that are hidden by ensemble experiments.

### 7. Single-molecule structural and orbital properties

Molecules with unique functions are the basis of singlemolecule optoelectronic devices. Generally speaking, changing the molecular structure and orbital properties will affect molecular properties, thereby providing the possibility for molecules with unique functions. Exploring the molecular structure and orbital effects at the single-molecule level helps to clarify the intrinsic physical mechanism of single-molecule optoelectronic materials and single-molecule optoelectronic devices, and at the same time provides a basis for further realization of the application of single-molecule optoelectronic devices. Here, we focus on the structure and orbital properties of single molecules, including QI effects, superposition effects, rectification effects, molecular structure change effects, and intermolecular and intramolecular interactions. Among them, the molecular structure change effect induced by light stimulations is often used to construct single-molecule optoelectronic devices. Other structural and orbital properties of single molecules are expected to be applied in optoelectronic devices.

### 7.1. Single-molecule quantum interference effects

Recently, QI effects have attracted more and more attention in the field of molecular electronics. Based on QI effects, CT of molecular systems can be controlled, and the CT state between the high conductance state and the low conductance state can be further controlled. The QI effects provide new basic insights for future functional single-molecule devices, and are of great significance to the development of molecular devices and materials. Here, we clarify the concept, mechanism, theoretical and experimental research of QI effects, and summarize the application of QI effects. Especially in the application section, we predict the application of QI effects under light stimulation in optoelectronic devices.

7.1.1. Fundamentals of single-molecule quantum interference. At the single-molecule scale, similar to double-slit interference, interference also occurs when electrons with quantum properties are transported between different discrete MO of molecules. QI effects, as a unique quantum effect of singlemolecule electrical transport, have various applications, such as single-molecule switches and high-switching ratio transistor devices. When electrons transport through certain pathways, theoretically the phase coherence of electrons during the transmission process will lead to the QI effects. In fact, the theoretical research of the QI effects in molecular electronics has received extensive attention [3]. In an early report, the cyclic olefin system is proved to have unique QI effects [396]. In addition to the QI effects of acyclic molecular systems, benzene ring systems with different connection sites, and AQ derivatives have also been predicted theoretically. For the  $\pi$ -conjugated system, a qualitative description method theoretically is provided. Specifically, the QI effects in charge transport stems from the interference between the quantum wave functions of electrons, which propagate coherently through different discrete MO in single-molecule junctions. Therefore, the Green's function has the following form:

$$G_{ij}(E_{\rm F}) = \sum_{k} \frac{C_{ik} C_{jk}^*}{E_{\rm F} - \varepsilon_k \pm i\eta}$$
(7)

$$\approx \frac{C_{i\rm HOMO}C_{j\rm HOMO}^*}{E_{\rm F} - \varepsilon_{\rm HOMO} \pm i\eta} + \frac{C_{i\rm LUMO}C_{j\rm LUMO}^*}{E_{\rm F} - \varepsilon_{\rm LUMO} \pm i\eta}, \qquad (8)$$

where  $E_{\rm F}$  is the Fermi level,  $\varepsilon_k$  is the energy of the *k*th MO and  $\eta$  is an infinitesimal positive number.

It can be seen that MO are closely related to Green's function, and HOMO and LUMO are the most important MO. Based on this, the Green's function can be further expressed in the following form of equation (8). When the Fermi level of the electrode is between the energies of the molecule's HOMO and LUMO, the remaining MO contribute little to electron transport. Thus, Green's function is approximately equal to equation (8), which represents the transmission of the main transporting orbital (whether it is HOMO or LUMO) and the interference with another orbital. When the two terms of equation (8) have same signs, the absolute value of the Green's function increases, resulting in constructive QI; when the two terms of equation (8) have opposite signs, destructive QI will occur (figure 39(a)) [397].

Particularly, single molecules with destructive QI have attracted more attention, due to its important research significance in CT and energy transfer. Experimentally, the QI effects in charge transport through various molecules can be investigated by the single-molecule junction, and the measurement technology mainly includes STM-BJ, MCBJ and conductive probe atomic force break technology (cpAFM-BJ). It has been confirmed that some  $\pi$ -conjugated systems such as cross-conjugated AQs, single benzene, polycyclic aromatic hydrocarbons, and heterocyclic aromatic hydrocarbons are parts of the molecular building blocks with destructive QI effects (figure 39(b)). In summary, the QI effects of molecules are determined by the central group and their different connection sites. For example, for a single benzene ring system, when the bridge group is connected to the meta connectivity, the single-molecule junction shows an obvious destructive QI effect. However, the corresponding effect could not be obtained when the bridging group is connected in parasites.

7.1.2. Single quantum interference molecules. Constructive or destructive QI effects, as a unique effect of charge transport in single molecules, is of great significance for the preparation of novel high-performance single-molecule electronic devices with quantum effects. Therefore, the QI effects have attracted much attention both theoretically and experimentally.

In fact, QI properties of molecules are determined by both the central group and the connection site of the bridging group to the central group. As far, some  $\pi$ -conjugated systems have been experimentally confirmed to have QI effects. For example, by introducing a side group at a specific connection site on the single benzene ring, QI effects can be observed. Specifically, the molecular conductance of meta-configuration is significantly lower than that in para-configuration. That is, when the side groups form connection with the central benzene ring by the meta-configuration structure, the single-molecule junction will exhibit the destructive QI effect. For instance, regardless of whether the linkage position of thienyl rings is at 2 or 3 (figures 39(c) and (d)), when thienyl groups are connected to the meta position of the benzene ring, the molecule exhibits the destructive QI effect. However, when the thienyl rings are connected to the para position of the benzene ring, the destructive QI effect cannot be observed. Therefore, the QI effect are determined by the connection sites of benzene, regardless of the bridging groups [398].

Besides benzene ring, the molecules with an AQ center also possess QI effects (figure 39(e)). Due to the almost degenerate HOMO and HOMO-1 of AQ–DT and AQ–MT, electrons can transport through the molecule by two different pathways and produce a phase difference in the HOMO–LUMO gap, thus leading to the destructive QI effect and reducing molecular conductance (figure 39(f)). Whereas the anthracene (AC) unit does not have the destructive QI effect, because the energy



**Figure 39.** Single-molecule QI effects. (a) Fundamentals of the single-molecule QI. (b) Molecular building blocks with destructive QI effects. (a) and (b) Reprinted with permission from [397]. Copyright (2018) American Chemical Society. (c) The structures of a molecule with para-(blue) benzene units. (d) The structures of a molecule with meta-(red) benzene units. (c) and (d) [398] John Wiley & Sons. (c) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (e) Chemical structures of AQ–DT, AQ–MT and AC–DT molecules. (f) Electrons transport of AQ–DT. (e) and (f) Reproduced from [399], with permission from Springer Nature. (g) Molecular structures of 2,4-TP-SAc and 2,5-TP-SAc. Reproduced from [26], with permission from Springer Nature. (h) Three molecule junctions of carboranes. [401] John Wiley & Sons. (c) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

difference between HOMO and HOMO-1 is very large, so there is only one electron transport path. In order to verify the destructive QI effect of the AQ central molecule, a series of rigid  $\pi$ -conjugated molecular wires are designed by AQ and AC, respectively (denoted as AQ–DT and AC–DT). The twodimensional conductance histogram shows that the conductance of AQ–DT molecule with a cross-conjugated structure is nearly 2 orders of magnitude lower than that of the AC–DT [399].

In addition, the specific connection of the thiophene center has the destructive QI effect. For example, a single benzene ring connecting in 2,4 sites of thiophene central groups (2,4-TP-SAc) shows the destructive QI effect (figure 39(g)). In specific, a single benzene ring is connected to the thiophene ring through an alkynyl group. Obvious anti-resonance can be observed when the side group connects to 2,4 sites, proving the destructive QI effect of 2,4-TP-SAc. However, the molecule with 2,5 linkage side groups does not have the destructive QI effect. Furthermore, the QI effects of the molecule can be controlled by varying the voltage applied to the electrochemical gate, since the position of the molecular energy level changes with the voltage. For 2,4-TP-SAc, by controlling the voltage applied to the electrochemical gate, the switch ratio of high and low conductance is as high as 100 times. In contrast, the switch ratio of 2,5-TP-SAc molecular is generally unchanged [26].

In addition, the QI of para-oriented diphenyl benzene and meta-oriented diphenyl benzene can also be controlled by varying the voltage applied to the electrochemical gate. Specifically, the sign of two terms in equation (8) is opposite for para, and is the same for meta. Therefore, para-oriented diphenyl benzene shows the constructive QI effect, while metaoriented diphenyl benzene shows the destructive QI effect. Through further control of the gate voltage, the conductance of the pair-connected molecules with the constructive QI effect changes smoothly, while the conductance of meta-connected molecules with the destructive QI effect changes up to 200 times [400].

In addition to the  $\pi$ -conjugated system mentioned above, side groups attached to specific sites in other  $\pi$ -conjugated systems, such as pyrene center, anthanthrene center and azulene center, will also exhibit QI effects. Besides, the destructive QI effect in other systems have also been confirmed, such as carborane, an icosahedral cage structure based on a three-center-two-electron bond (3c-2e) having three isomers (figure 39(h)). In particular, para-connected, meta-connected and ortho-connected carboranes all exhibit an abnormally low conductance and destructive QI effect. Combining theoretical investigation, charge transport of the three connectivities are jointly contributed by the  $\pi$  channel and the 3c-2e channel, and the 3c-2e channels in three carborane junctions all exhibit the destructive QI effect. Since both the  $\pi$  channel and the 3c–2e channel show the destructive QI effect, metaconnected carborane junctions exhibit stronger destructive QI effect characteristics than other structures [401].

In addition, the QI effects of the central aromatic ring can be transformed through space. When the  $\pi$ -conjugated fragments of the molecule with the destructive QI effect are arranged face-on or edge-on and close enough to interact through space, the assembled tunneling junctions will show the destructive QI effect [402]. The fluorenone-based molecule with side chain groups linked at a particular site also has the destructive QI effect, and the destructive QI effect can be controlled by regulating the intramolecular pathway [403]. The specific connection site of the perovskite materials also has QI effects. By the coupling between Au and halogen, gold electrode will slide on Br atom in the perovskite quantum dot along the horizontal direction. At the end of the sliding process, an obvious conductance 'jump' with around one order of magnitude increase is observed, which proves that the constructive QI effect occurs in the single quantum dot junction [404].

7.1.3. Regulation and application of single-molecule quantum interference. The QI effects of single molecules have broad applications in the fields of electronic devices, such as single-molecule switches and field-effect transistors. Therefore, the regulation and further application of single-molecule QI effects are worth exploring.

Generally, changing the chemical structure of the molecule is one of the effective strategies to regulate the QI effects for single-molecule charge transport. Pyridine-based molecule with a meta-connected side group (M3) exhibit QI effects (figure 40(a)). Since the LUMO + 1 of M3 is lower than its LUMO energy, when the pyridine nitrogen of M3 is protonated/methylated, controlling the molecular QI effect can be realized (figure 40(b)). Specifically, when adding trifluoromethanesulfonate (MeOTf) to the M3 system, the pyridine nitrogen of a pyridine central group will methylate with forming M3-Me (figure 40(c)). The electrical characteristics based on STM-BJ reveal that the molecular conductance has changed from the low conductance state of M3 to the high conductance state of M3-Me. This proves that the conversion from the destructive QI effect to the constructive QI effect is due to the methylation of M3, but the process is irreversible. When introducing trifluoroacetic acid (CF<sub>3</sub>COOH) to M3, the pyridine nitrogen of a pyridine central group will be protonated and form M3-H, accompanied by the conversion from the destructive QI to the constructive QI (figure 40(c)). Furthermore, different from methylation process, the M3-H can return back to M3 by adding Na<sub>2</sub>CO<sub>3</sub> to M3-H, thereby realizing the conversion of the constructive QI to the destructive QI and realizing a molecular switch [45].

In addition, 2-hexyl-4-(hexyloxy)-3,6-bis(4-(methylthio) phenyl)pyrrolo [3,4-c]pyrrol-1(2H)-one (SPPO), as an isomer of diketopyrrolopyrrole molecules, has only one nitrogen atom substituted by an alkyl group, showing the QI effects. The free nitrogen of SPPO can be reversibly protonated and deprotonated upon addition of acid and base, respectively, resulting in the changing of QI effects

(figure 40(d)). Specifically, after protonation, the two pyrrole rings cut off the electronic coupling between the two linear conjugated substructures, thus forming a cross-conjugated resonance structure with the destructive QI effect. Furthermore, the conductance of SPPO-H<sup>+</sup> molecules will be dropped by an order of magnitude, thus successfully regulating the QI effects of SPPO molecules based on protonation [405].

As mentioned above, changing the structure of the molecular local site can control the QI effects of the molecule. Moreover, the QI effects of the molecule can also be regulated by changing the overall structure of the molecule. For example, there is a configuration change between dihydropyrene (dha) and vinylheptafulvene (vhf). Under ultraviolet radiation, the molecule changes from the almost planar dha-6 configuration to the bent vhf configuration with the destructive QI effect, accompanied by a decrease of molecular conductance (figure 40(e)). Another bent dha-7 configuration can also be transformed into the vhf configuration under ultraviolet irradiation, and exhibits the destructive QI effect and lower molecular conductance than that of vhf [406]. In addition, the QI effects can also be controlled by changing the molecular configuration through adjusting the substituent position on the central group. For instance, changing the position of the methoxy (OMe) substituent on the central phenylene ring, the destructive QI dip of the meta-substituted phenylene ethylene oligomer (M-OPE) will shift. Specifically, when an OMe group is introduced at position 1, the destructive QI dip of molecule will shift to a position with higher energy (figure 40(f)). However, introducing an OMe group at position 2 or 3, the destructive QI dip of molecule shifts to the direction with lower energy. Therefore, adjusting the position of substituents can control the destructive QI effect of molecules. Especially, when the OMe group is connected to the central phenylene ring at position 2 (M2), the configuration change of the OMe group will affect the QI effects of M2 (figure 40(g)). In detail, by rotating the OMe group into the molecular plane from the position perpendicular to the plane, the destructive QI effects disappear, leading to a high molecular conductance. For molecules with substituents attached at other positions, the configuration of the OMe group has no effect on the QI effects. Therefore, the configuration of the OMe group can be acted as a molecular current controller. Based on such a regulation function for QI effects, a molecular switch can be designed [407].

As a generalized configuration, dimer conformation also affects the QI effects of the molecules. The oligo-phenyleneethynylene molecule with a thiol anchor group at one side can form a  $p-\pi$  stacking dimer molecular junction through an intermolecular  $\pi$ -stacking interaction. As two electrodes of MCBJ are compressed or stretched, two molecules in the dimer move relative to each other, resulting in a configuration change, thereby changing the QI effects of the dimer. In addition, due to the periodic QI effects, the conductance of the dimer molecular junction exhibits quasi-periodic fluctuations (figure 40(h)). Specifically, if the stacking of the two molecules is different, the QI effects of  $\pi$ -stacking dimeric molecules can be affected by changing molecular frontier orbital coupling [408].



**Figure 40.** Single-molecule QI effects. (a) Schematic diagram of a single-molecule junction modulated by atomically precise gating. (b) Transmission function of the molecule. (c) Chemical structures of M3, M3-H, M3-Me and OPE3. (a)–(c) Reprinted with permission from [45]. Copyright (2021) American Chemical Society. (d) Resonance structures of SPPO and SPPO-H<sup>+</sup>. Reprinted with permission from [405]. Copyright (2018) American Chemical Society. (e) Example diagrams of dha-6, dha-7 and vhf. No interference is expected at the Fermi energy for dha-6 because all diagrams without onsite loops have the same sign. For dha-7, all diagrams contain the same onsite loop, so the destructive interference is expected at the Fermi energy. For vhf, diagrams with onsite loops on N shift the interference away from the Fermi energy. Reproduced from [406]. CC BY 4.0. (f) Magic-ratio model of molecular junctions. (g) Transmission coefficients of the molecule. (f) and (g) [407] John Wiley & Sons. (c) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (h) Simulations of the electronic transport properties of a dimer. Reproduced from [408], with permission from Springer Nature. (i) The regulation schematic of AQ. Reprinted with permission from [410]. Copyright (2015) American Chemical Society. (j) Schematic illustration of a vertical molecular tunneling field effect. Reproduced with permission from [411]. (c) American Association for the Advancement of Science. CC BY-NC 4.0.

The position of molecular energy levels will shift with the change of molecular configuration, thereby adjusting the QI effects. An electrochemical gate is an effective way to regulate the relative position between the Fermi level of the electrode and the molecular transport orbit by changing the potential, thereby adjusting the molecular QI effects. For example, a single benzene ring connecting in 2,4 sites of the thiophene central group exhibits the destructive QI effect. The position of the molecular energy level moves with the applied electrochemical gating, which can adjust the QI effects [26]. Similarly, by varying electrochemical gate field, the QI effects can also be effectively regulated [400].

As described above, QI effects can be effectively and reversibly regulated by adjusting the energy level position, thereby realizing a single-molecule transistor with high on/off ratio and high performance [26, 400]. Due to the QI effects, phenyl-acetylene-macrocycle has a wide range of strong antiresonance near the Fermi level of the electrodes, and shows an excellent performance of FETs based on theoretical calculation [409]. In addition, AQ has the destructive QI effect. By adding extra electrons to AQ through gating, the redox state of AQ can be changed. After the two-step reduction, the cross-conjugated AQ becomes linearly conjugated, causing the destructive QI to disappear (figure 40(i)). Therefore, the QI effects of AQ can be controlled by the gate, and the conductance changes by an order of magnitude [410].

Furthermore, applying an electric field parallel to the direction of the molecule can also control the QI effects, thereby performing stable switch operations at room temperature and constructing efficient and stable quantum tunneling FET devices. For example, using pseudo-p-bis ((4-(acetylthio)phenyl)ethynyl)-p- [2,2]cyclophane (PCP) with a [2,2]cyclophane QI center to assemble monolayers, a vertical molecular tunneling field effect device based on the gold film/SAM/single layer graphene/ionic liquid gate stack structure can be constructed (figure 40(k)). Specifically, the ionic liquid gate electric field can be applied to each molecule in parallel through penetrating the graphene layer, causing the energy level of the PCP molecule to shift. This leads to high on/off ratio ( $\sim$ 330) for quantum tunneling field-effect devices, which is an order of magnitude higher than the system without destructive QI effects [411].

Furthermore, SAMs with an anthanthrene core can be used to construct vertical molecular tunneling field-effect devices. By changing the position of the connection point between the anthanthrene and the electrode, the generation and disappearance of the destructive QI effect can be accurately controlled. In specific, the side group attaching to the 7,2' position of the anthanthrene core is denoted as molecule 1, which shows the constructive QI effect. The side group of molecule 2 with -SAc terminal groups and molecule 3 with pyridine terminal groups are both connected with 1,5' sites, which lead to the destructive QI effect. Therefore, through changing the connect site from 1,5' to 7,2', due to the disappearance of the destructive QI effect, the conductivity of molecule 1 increased by  $\sim$ 34 times than that of molecule 2. Such a difference can be enlarged to more than 170 times with further control of the molecule-electrode interface by different terminal groups. Under the superposition of QI effects and molecule-electrode interface effects, the switching on/off ratio for the lowest conductance SAM can reach up to 306, which is an order of magnitude higher than that of molecule without adjustment. In a word, it is very effective and feasible to improve the performance of molecular devices based on the QI effects [412].

Theoretically, QI effects in quantum systems can be induced towards desired states by electronic excitation of light. For instance, photoexcited electrons transit between atomic energy levels, and the QI effects could change the total transition probability, thereby affecting the molecular energy level state after photoinduction and changing the performance of optoelectronic devices [413]. In addition, the configuration of photochromic molecules will change under light induction, which leads to the changes in molecular tunneling energy levels, further realizing the interconversion of constructive QI effects and destructive QI effects [406]. This combination of QI effect and photo-stimulation is of great significance for the construction of high-performance optoelectronic devices.

#### 7.2. Single-molecule superposition effects

Single-molecule superposition effect, as a unique charge transport effect, is of great significance for understanding the fundamental principles and electron transport characteristics of optoelectronic devices. Here, we clarify the mechanism and application of two classic superposition effects, namely superposition of parallel paths and space conjugated multichannel conductance.

72.1. Superposition of parallel paths. The superposition effects in a single-molecule circuit with two parallel elements significantly improve the molecular conductance, instead of following the Ohm's or Kirchhoff's law. The study of superposition effects is of great significance to the preparation of molecular devices, such as transistors and quantum logic gates.

According to Ohm's or Kirchhoff's circuit laws, the net conductance of two parallel elements in a circuit is the sum of their respective conductance. Therefore, it would be predicted that the conductivity of a molecule with two parallel paths will be twice as high as that of a molecule with a single path. However, when the scale of the electronic circuit is reduced to the electronic phase coherence length, quantum effects play a dominative role in charge transport. Under the combined effect of the constructive QI and the complex transmission characteristics of electrons in the two transmission channels, the molecular conductance can be increased by more than two times [3].

However, due to the quantum effect, the charge transport mechanism of molecular circuits is still an open issue. The study of charge transport in single-molecule multi-channel systems, especially in parallel path systems, is helpful to understand the charge transport mechanism and is of great significance for exploring the superposition laws of molecular circuits. For instance, the acyclic structure with single-channel and the macrocyclic structure with parallel paths are constructed to explore the properties of electron transport. In comparison with di-anilinyldibutatrienylacetylene with a single pathway and graphene molecular fragment hexabenzocoronene (HBC), paradianilinyl-carbo-benzene (carbo-benzene A) with parallel paths possesses superior conductivity. Specifically, due to the existence of parallel paths in single-molecule junctions, carbo-benzene A has a fairly small HOMO-LUMO gap, resulting in increased transmission and exhibiting a higher conductance (figure 41(a)) [414].

In addition, some other systems follow the conductance superposition law as well, such as the single-molecule circuit system with parallel paths. By constructing two kinds of molecules, one is a single-channel backbone molecule and the other is a parallel dual-channel backbone molecule, the conductance superposition law is investigated. In this case, the bonding and antibonding combinations of the frontier MO form the molecule backbone orbitals, which are coupled with the electrodes. For the molecule with parallel dual channels, this coupling is larger due to the superposition effects caused by the constructive QI effect of two channels, and its LUMO is closest to  $E_F$  (figure 41(b)). Therefore, the low-bias conductance of a dual-channel molecule under the Fermi energy transmission is twice more than that of one backbone, so its conductivity value is higher than twice [415].

In addition to the constructive QI effect, the electrostatic interaction between two channels also affects the molecular electrical transport process. For example, dual-channel intramolecular circuits based on a charged cyclophane are constructed, and the law of electron transmission is explored in depth. Specially, two identical extended viologen (ExBIPY<sup>2+</sup>) units, each connected to a phenyl sulfide anchor, can synthesize a dual-channel cyclophane. Because of the strong electrostatic interaction in the dual-channel system, the LUMO moves to the Fermi level of Au, which results in a near-resonance charge transport and greatly increases the conductance of the dual-channel system (figure 41(c)) [416].

72.2. Space conjugated multichannel conductance. Space conjugation, in which the electron cloud forms an overlap through spatial delocalization of a  $\pi$ -electron cloud, can effectively affect charge transport. In a  $\pi$ - $\pi$  stacking system, electrons can be transported in a conjugate space, which is of great significance for the preparation of high-efficiency optoelectronic devices [417]. Based on this, two pyridines are connected as terminal groups to two biphenyls connected by vinyl groups, constructing



**Figure 41.** Single-molecule superposition effects. (a) Structures of carbo-benzene A. Reproduced from [414], with permission from Springer Nature. (b) Model and schematic energy level diagram for the double-backbone junction. Reproduced from [415], with permission from Springer Nature. (c) Schematic diagram of an intramolecular circuit across a tetracationic double-channel cyclophane. Reprinted from [416], Copyright (2020), with permission from Elsevier. (d) Electron transport mechanism of f-4Ph-4SMe, f-4Ph-2SMe-A, and f-4Ph-2SMe-B. Reproduced with permission from [419]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0. (e) Schematic illustration of a mechanical single-molecule potentiometer based on o-PP-2SMe. Reproduced from [63]. CC BY 4.0. (f) Schematic diagram of the conductance enhancement of through-space conjugated molecular wires based on HPB derivatives. Reprinted from [421], Copyright (2021), with permission from Elsevier.

two folded molecules with intramolecular  $\pi$ - $\pi$  stacking interactions, respectively (Z)-1,2-diphenyl-1,2-bis(4'-[pyridin-4-yl)-(1,1'-biphenyl)-2-yl]ethene (f-TPE-PPy) and (Z)-1,2-diphenyl-1,2-bis{4'-[(E)-2-(pyridin-4-yl)vinyl]-(1,1'-biphenyl)-2-yl}ethene (f-TPE-PEPy). The  $\pi$ -stacked biphenyls in the molecules achieve effective orbital overlaps and electronic couplings, so that the strong spatial conjugation dominants electron transport and enhances the molecule conductance. In comparison, two folded molecules with a weaker  $\pi$ -orbital overlap between vinyl bridge and biphenyl exhibit a lower molecular conductance [418].

The  $\pi-\pi$  stacking system also has QI effects, which in turn affects the electron transport mechanism. Therefore, different single-molecule parallel circuits are constructed to investigate the QI effects in a  $\pi-\pi$  stacking system for electron transport. In specific, three types of molecular circuits are built by controlling the number and connection sites of methylmercapto (SMe) anchor groups on the molecular backbone (figure 41(d)). These structures all have  $\pi-\pi$  stacking characteristics. Through introducing methylmercapto anchor groups to the ends of two p-quaterphenyl chains (f-4Ph-4SMe), the molecule exhibits the highest conductivity due to the co-effect of through-bond and through-space. However, the destructive QI between the two p-tetraphenyl chains of the molecule with only one methylmercapto group connected to each p-tetraphenyl chain (f-4Ph-2SMe-B) seriously affects the conductance, thus achieving an extremely low conductivity [419].

Furthermore, the angle of  $\pi - \pi$  stacking can be effectively controlled, thereby regulating the CT mechanism in the stacked  $\pi$  system. For instance, a series of orthopentaphenylene (o-PP) derivatives consisting of five orthoposition linked phenyl rings are constructed with different anchor groups, including methylthio (SMe), cyano (CN) and pyridines (Py), respectively. The  $\pi - \pi$  stacking characteristics generated by the biaryl groups with face-to-face anti-parallel arrangement affects charge transport through space conjugation. In particular, the degree of space conjugation can be controlled by changing the conformation of o-PP-2SMe by the mechanical force (figure 41(e)). Specifically, for o-PP-2SMe with an antiparallel folding structure, the through-space dominates the CT mechanism. For co-parallel folding structure, both through-space and through-bond participate in the electrons transport process. Expectedly, o-PP-2SMe with the fully stretched structure has almost no through-space transport mechanism. By controlling the space conjugate, the change of molecular conductance can reach two orders of magnitude [63].

In addition to  $\pi - \pi$  stacking, strong space conjugated molecules can transfer electron by space conjugated multichannels as well. For instance, a new single-molecule wire is constructed by combining the hexaphenylbenzene (HPB) core with through-space conjugation and an oligophenylene backbone with through-bond. The space conjugation of a HPBbased single-molecule wire can be regulated by introducing methoxy groups. Specifically, the introduction of methoxy groups into the four peripheral phenyls of the molecule can enhance the electron density and promote the electronic coupling interaction between adjacent phenyls. Therefore, as the number of introduced methoxy groups increases, the twisting angle of the oligophenylene backbone increases, leading to a gradual increase in the spatial conjugation of the molecule. The conductance of HPB-SM, HPB(OM)-SM, and HPB(OM)<sub>3</sub>-SM with different number of methyl groups is larger one by one and is larger than that of p-oligophenylene based on a linear reference molecule [420].

Such a spatially conjugated multichannel transmission mechanism can be further regulated by introducing denser  $\pi$ -electron cloud groups. For example, thienyl rings with denser  $\pi$ -electron clouds are introduced into the HPB-based single-molecule wire. When the benzenes are substituted by thienyls, because the  $\pi$ -electron cloud of the thienyl ring is denser, a stronger interring coupling is achieved and spatial conjugation is enhanced (figure 41(f)). Furthermore, with the gradual addition of the benzene ring, the contribution of the conjugation space to electron transport increases. Finally, the energy level of the molecule approaches the Fermi level, which improves the conductivity of the molecule [421].

### 7.3. Single-molecule rectification effects

Rectification effects are a unique CT phenomenon that can be used to construct molecular rectifiers. Exploring the rectification effect is beneficial to gain an in-depth understanding of molecular charge transport and facilitate the development of optoelectronic devices. Here, we focus on the rectification effects caused by the asymmetry structure of the molecules.

73.1. Single asymmetric molecules. Molecular rectifiers are the basic components of molecular devices, which have broad applications in the field of molecular electronics. The asymmetry of the used molecule is the decisive factor for the rectification performance.

In fact, a donor-acceptor structure is the basis structure for realizing the rectification function. For traditional rectifiers, the unidirectional conductivity of P-N junctions consisted of an N-type doped donor and a P-type doped acceptor is used to achieve the rectification. It is foreseeable that because the molecule contains both a donor and an acceptor, when electrons pass through the molecule from two opposite directions, they will exhibit completely different conductance, thereby realizing the rectification function. This means that the molecule will show the rectification properties as a P-N junction. Based on this, Ratner et al firstly proposed the concept of molecular rectifier in 1974. They designed a molecule with a tetrathiofulvalene donor and a tetracyanoquinodimethane acceptor, which proves the theoretical feasibility of the molecular rectifier (figure 42(a)) [23]. Specifically, the molecule can be divided into three parts: a tetrathiofulvalene donor, a saturated 'sigma' covalent bridge and a tetracyanoquinodimethane acceptor. When the molecule is connected to the electrodes, the HOMO of the donor and the LUMO of the acceptor are close to  $E_{\rm F}$  of the connected electrodes. When the bias voltage is reversed, the current through the molecule is also different, thereby realizing the rectification performance. Such an asymmetric molecular model containing donor and acceptor is called the AR model.

After verifying the feasibility of the molecular rectifier, molecular rectifiers based on the AR model have been extensively studied. For example, an asymmetric molecule containing the bithiophene donor, conjugated phenylacetylene bridge and NDI acceptor, exhibits reverse polarization rectification properties (figure 42(b)) [422]. In addition to using different donor groups and acceptor groups, certain groups with different substituents can also be used as donors and acceptors to construct asymmetric molecules. By fluorinating the phenyl group on the outside of one end, an asymmetric molecule with phenyl-ethynyl-phenyl donor system and fluorobenzene-ethynyl-phenyl acceptor system is constructed, and the bridge unit is biphenyl C-C bond (figure 42(c)). Through connecting the molecules to metal electrodes by sulfur anchor groups, the asymmetric bias dependence of the conductance indicates that the single molecule has rectifier properties [24].

Asymmetric molecules without bridge groups also have rectifying properties. For instance, based on the dipyrimidinyl–diphenyl asymmetric molecule which contains an electron-rich biphenyl segment and an electron-deficient bipyrimidyl segment, a reversible rectification diode can be observed in an Au/dipyrimidinyl–diphenyl/Au junction, proving that the molecule has the rectifier properties (figure 42(d)) [423].

In addition to the asymmetric molecule composed of a donor  $\pi$ -system and an acceptor  $\pi$ -system, an asymmetry molecule with alkyl carbon as one end and  $\pi$ -conjugation group as the center can also exhibit rectification properties. For instance, the asymmetric molecule of  $S(CH_2)_{11}$ -4-methyl-2,2'-bipyrid-4'-yl and S(CH<sub>2</sub>)<sub>11</sub>Fc both exhibit rectification properties, and the rectification efficiency is related to end groups (figure 42(e)) [424]. In addition, a fullerene acceptor is also used to construct asymmetric molecules with rectifying properties. For example, an asymmetry molecule with a fullerene acceptor and didodecyloxybenzene donor has rectification properties (figure 42(f)) [425]. An all-hydrocarbon asymmetry molecule composed of fullerene and diamantane also shows rectification properties as well. In detail, due to positively charged terminal hydrogen atoms on the diamondoid, when applying bias voltage with different directions by the STM tip, it will exhibit different types of electrostatic interactions, resulting in rectification properties (figure 42(g)) [426].

For systems with a symmetrical molecular backbone, introducing asymmetric end groups at both ends, can also construct asymmetrical molecules to achieve the rectification function. For instance, amine groups and thiol groups as anchor groups are attached to two ends of 1,4-disubstituted benzene molecules to construct an asymmetric configuration. Due to the asymmetric coupling between the two ends of the



**Figure 42.** Chemical structures of asymmetric molecules with rectification effects. (a) Initial model D- $\sigma$ -A proposed by Aviram and Ratner. Reprinted from [23], Copyright (1974), with permission from Elsevier. (b) Chemical structure of the molecule, which contains the bithiophene donor, conjugated phenylacetylene bridge and NDI acceptor. Reprinted with permission from [422]. Copyright (2011) American Chemical Society. (c) Chemical structure of the asymmetric molecule with phenyl-ethynyl-phenyl donor system and fluorobenzene-ethynyl-phenyl acceptor system. Reproduced with permission from [24]. (c) NationalAcademy of Sciences. (d) Chemical structure of the dipyrimidinyl–diphenyl molecule. Reprinted from [423], Copyright (2013), with permission from Elsevier. CC BY-NC-ND. (e) Chemical structure of the S(CH<sub>2</sub>)<sub>11</sub>-4-methyl-2,2'-bipyrid-4'-yl molecule. Reprinted with permission from [424]. Copyright (2014) American Chemical Society. (f) *Ab initio* (B3LYP/3-21G<sup>\*</sup>) geometry-optimized structure of the dyad showing the bridge and donor benzene rings to be planar (shading codes: dark grey = carbon; light grey = hydrogen; black = oxygen). Reproduced from [425] with permission from the Royal Society of Chemistry. (g) Structure of a Dia–C<sub>60</sub> molecule. Reproduced from [426], with permission from Springer Nature.

molecule and the electrode, an asymmetric relative displacement between the frontier molecular orbital and the Fermi level of the electrode is caused, which leads to the rectification properties of the molecule [427].

73.2. Rectification effect and application of single-molecule devices. As mentioned above, asymmetric molecules can be used to construct molecular rectifiers due to their rectifying characteristics. Exploring the rectification mechanism of asymmetric molecules is essential for realizing efficient and stable molecular rectifiers.

Based on theoretical calculations, Ratner *et al* proposed the mechanism of molecular rectifiers based on D- $\sigma$ -A molecule structures. Here, the electrode connected with the donor is denoted as  $M_d$ , and the electrode connected with the acceptor is denoted as  $M_{\rm a}$ . The energy level structural diagram of the single-molecule device is shown in figures 43(a) and (b). When a forward bias is applied, which means that the electrode  $M_d$  is connected to the positive and the electrode  $M_a$  is connected to the negative, the energy level of the  $M_d$  will drop and the energy level of the  $M_a$  will rise. At a certain voltage, the energy level of the  $M_d$  is near to the HOMO of the donor, and the energy level of the  $M_a$  is also in the same range as the LUMO of the acceptor. Meanwhile, the LUMO of the acceptor is higher than the HOMO of the donor. In this case, the energy levels of  $M_a$  and  $M_d$  show resonant tunneling with the frontier MO of donor and acceptor, respectively, thus generating a large tunneling current (figure 43(a)). At reverse voltages, the energy

level for the  $M_d$  electrode will rise and that for the  $M_a$  electrode will drop, resulting in a large energy difference between the LUMO of the donor (as well as the HOMO of the acceptor) and the energy level of the electrode. Therefore, electrons can hardly transport through molecules (figure 43(b)). Therefore, the rectification function can be achieved by this finely designed asymmetric molecular system [23].

Based on the above theory, a series of asymmetric molecules are constructed to realize the rectification performance. For example, two phenyl–ethynyl–phenyl  $\pi$ -systems are connected by C-C bond, and a D-A asymmetric structure is constructed through fluorinating the phenyl group at one end of molecule. Specifically, due to the steric repulsion between two methyl groups in ortho position of the C-C bond, the molecule can be separated into two weakly coupled quantum dots denoted as F-dot and H-dot. Among them, F-dot shows an asymmetric polarizability and has a larger polarizability at negative biases. When F-dot displays a larger polarizability, a larger forward current will be obtained. Therefore, the molecular junction exhibits a lower current at negative biases, thus having the rectification performance [24]. In addition, due to the different dipole strength of Au-S bond on the two sides of the molecule, the SAM devices based on dipyrimidinyl-diphenyl asymmetric molecules also show the rectification performance. Furthermore, at high temperatures, the barrier between bottom electrode and molecule is lower than



**Figure 43.** The mechanism of a molecular rectifier. Energy level shift with (a) an applied voltage and (b) a reverse applied voltage. (a) and (b) Reproduced with permission from [23]. (c) Elsevier. CC BY-NC-ND 4.0. (c) Schematic diagram of the local DOS under finite biases. Due to the electric field present in the junction at finite biases, the energy of the levels changes as a function of their coupling with the leads. The forward polarization tends to reduce the intramolecular dipole and pulls the levels out of the bias window (yellow dashed line). The reverse polarization increases the intramolecular dipole and pushes the HOMO inside the bias window. Reprinted with permission from [422]. Copyright (2011) American Chemical Society. (d) Energy level diagrams (with respect to the vacuum) of the AuTS-SAM<sub>2</sub>//Ga<sub>2</sub>O<sub>3</sub>/ EGaIn junctions at 2.0 V (left), 0 V (middle), and -2.0 V (right). Reprinted with permission from [430]. Copyright (2017) American Chemical Society.

that between top electrode and molecule, thereby showing an asymmetric bias dependence of the conductance [423].

However, molecules with a D–A structure also exhibit a reverse polarization rectification under similar mechanism. For instance, the single molecule, composed of a bithiophene donor, a NDI acceptor, a conjugated phenylacetylene bridge and a nonconjugated end group, exhibits reverse polarization rectification properties. Specifically, in the single-molecule junction, a resonant energy level with 2 eV away from the Fermi level can be observed at the bias window of 2 eV (figure 43(c)). For a negative bias, the intramolecular dipole is increased by reverse polarization, thereby pushing the resonant level into bias window to achieve a higher conductance. On the contrary, since the resonant level is pulled out of bias window in positive biases, the molecular junction shows a lower conductance (figure 43(c)). Therefore, the molecular junction shows the opposite rectification behavior [422].

In addition, the MO of D–A structure molecules, such as HOMO/LUMO, are formed under the combined action of the two parts of the molecule. The mismatched contribution of the donor and the acceptor to the MO will also lead to rectifying characteristics. In a C<sub>60</sub>-didodecyloxybenzenedyad system, the LUMO of the molecule is located on the C<sub>60</sub> acceptor. Notably, both the HOMO and LUMO + 7 of the molecule are located on the donor didodecyloxybenzene. Therefore, when applying a forward bias matched with potential drop, electrons

can easily tunnel from the  $C_{60}$  acceptor to the didodecyloxybenzene donor [425].

The rectification properties can also be realized by the interfacial interaction between molecules and electrodes. For example, rectification mechanism is explored in the 1,4-disubstituted benzene molecule. Amine and thiol as anchor groups are connected with two ends of the molecule, respectively. Due to the asymmetric coupling between the two ends of the molecule and the electrode, an asymmetric shift between the frontier molecular orbital and the Fermi level of the electrode is caused, therefore realizing the rectification property [427].

With the development of molecular electronics, molecular rectifiers based on electrostatic force mechanisms have also been explored. For instance, the rectification mechanism of diamantane– $C_{60}$  conjugate (Dia– $C_{60}$ ) asymmetric molecules are considered based on an electrostatic force. Specifically, there are positively charged hydrogen atoms at the diamon-doid surface in the diamondoid–fullerene hybrid molecules. In the STM measurement, when the negatively charged STM tip approaches the molecule, the electrostatic attraction reduces the distance between the molecule and the STM tip, thereby enhancing electron tunneling. However, when the STM tip with the positive bias is close to the molecule, the fullerene will rotate away from the STM tip due to the electrostatic repulsion, leading to the decrease of current [426].

In addition, when molecules have different charge transport mechanisms under different bias directions, rectification also can be realized. Such rectification mechanisms are explored by the typical system based on alkanethiolates with Fc head groups. The SAM assembled by a molecule consisted of alkanethiol and Fc head group  $(S(CH_2)_{11}Fc)$  is covalently attached to the template-stripped Ag, and the EGaIn (eutectic alloy of Ga and In) is used as top-electrode. In positive biases, charge transport is limited by the tunneling through the  $(CH_2)_{11}$ . In negative biases, the current density depends on the initial step of hopping, that is, the electron transports during the process of Fc converting to Fc<sup>+</sup>. Therefore, the system shows the different current densities under different bias directions [424]. Furthermore, the rectification mechanism is analyzed from the perspective of molecular energy levels. In detail, for a S(CH<sub>2</sub>)<sub>11</sub>Fc system, the HOMO level of Fc is slightly lower than the Fermi levels of two electrodes. Under a positive bias, the Fermi levels of top electrode and the HOMO level of Fc both decreases. Due to the HOMO level is not in the energy levels of two electrodes, charge transport cannot be realized. On the contrary, in the negative bias, the difference between HOMO of Fc and the Fermi level of top electrode increases, thereby the electron can be transported [428]. Even at a high frequency, the rectification properties of the device can also be realized. For example, a rectifier device is constructed based on the ferrocenyl undecanethiol (FcC<sub>11</sub>), and its operating frequency is as high as 17.8 GHz[429].

Furthermore, the introduction of additional energy level on the basis of Fc energy level will also achieve rectification. For example, a PTM acceptor is connected to the electron donor Fc unit. Due to the large potential drop on the insulating alkyl chain, Fc-PTM units are decoupled from the bottom electrode. However, the PTM unit shows the conjugation property because of the large HOMO-LUMO gap, so the potential drop across the PTM unit of the molecule is small. Therefore, although the Fc unit is separated from the top electrode owing to the presence of PTM, Fc is still coupled with top electrode because of the large intramolecular coupling between Fc and PTM. Similar with the rectification mechanism of the S(CH<sub>2</sub>)<sub>11</sub>Fc molecule, the Fc-PTM molecule has a rectification function. Moreover, PTM can switch between radical and nonradical forms, resulting in the change of rectification efficiency. In this case, the rectification mechanisms are different with the mechanism of Fc-PTM. Specifically, when the PTM is in the radical state, a SUMO is localized on the PTM radical and provides a HOMO-LUMO gap tunneling pathway (figure 43(d)). Therefore, when reversing the bias direction, the current density of the radical state PTM varies less than that of the nonradical state PTM, showing a lower rectification efficient [430].

Moreover, controlling the energy level alignment among HOMO, LUMO of the molecule and the Fermi level of the electrode in molecular junctions will also affect the rectification effect. In  $M-S(CH_2)_{11}S-BTTF//EGaIn$  junctions, the rectification mechanism is dominated by the energy level located on the BTTF unit. However, due to the interface electronic coupling and the location of the intrinsic Fermi level of the

electrode, the different top electrode will change the energy level alignment in molecular junctions, thereby controlling the rectification function [137].

In addition to the molecular structure, the asymmetry of MO can also cause rectification. For example, the molecular orbital of hydroquinone (HQ) is asymmetric, in which the LUMO of HQ is positioned on the right of the molecule. Therefore, due to the high electron transport barrier, the electrons can hardly pass through the HQ in low biases. As the bias is increased, the coupling between the molecule and the right electrode is weakened, and the charge distribution on the right electrode is reduced, resulting in an increase in current. Furthermore, oxidized quinone (Q) can be obtained via redox reactions. Since LUMO of Q is a delocalized orbital and close to the Fermi level, the molecule lost the rectification function [431].

In fact, the rectification effects can also be controlled by light. For the donor–acceptor system, the rectification effect mainly depends on the energy level of the electrode and the frontier MO of the donor and acceptor. With the induction of light, the charge separation process of optoelectronic devices may change, thereby regulating the molecular rectification effect, which is of great significance for realizing the functionalization of single-molecule optoelectronic devices [432].

#### 7.4. Single-molecule structural change effects

The structural change effect of molecules will affect the molecular orbital properties, which will further change the properties of the molecule. Studying the single-molecule structural change effects is helpful to clarify the internal physical mechanism of single-molecule optoelectronic devices, and is of great value to the development of practical molecular electronics in the future. Here, we summarize the structural change effects of molecules, including stereoelectronic effects, tautomerization, isomerization, nanomechanical movements, motion of single molecular machines and the changes in the single-molecule structure during chemical reactions.

7.4.1. Single-molecule stereoelectronic effects. Stereoelectronic effect reflects the influence of the relative spatial orientation of electronic orbitals on chemical and physical properties of the molecule. Exploring the mechanism of stereoelectronic effect at the single-molecule level is of great significance for the applications in the fields of chemistry, biology and materials.

Recently, series researches are focused on revealing the inherent stereoelectronic effect of single molecules. For example, due to the stereoelectronic effect of permethyloligosilanes, the conductance of single-molecule junctions based on permethyloligosilanes exhibits high and low states. Specifically, the permethyloligosilanes backbone with methylthiomethyl linkers are connected to Au electrodes, forming Au-molecule–Au single-molecule junctions. The strong  $\sigma$  conjugation in the oligosilane backbone and the spatial characteristics of the sulfur-methylene  $\sigma$  bonds lead to the stereoelectronic effect of the molecule. Therefore, three dihedral configurations are existed in the Au-molecule–Au system (O–O, A–A and O–A states), corresponding to two states of a high conductance and a low conductance (figure 44(a)). Among them, the A–A state and the O–A state have similar tunnel coupling between the contact interface and the sulfur-methylene  $\sigma$  bonds, resulting in similar low conductance. Furthermore, stereoelectronic effect can be controlled by lengthening or compressing the single-molecule junction [62].

In addition, as the basic unit of organic materials, biphenyl also has stereoelectronic effect. The study of the stereoelectronic effect in biphenyl has attracted much attention. Taking the 2,7-bis([1,10-biphenyl]-4-yl)-9h-fluorene arene system as an example, the influence of the stereoelectronic effect on the electrical properties are theoretically studied. The rotation of the benzene ring at both ends of the molecule results in a change in the dihedral angle, which affects the superposition of the  $\pi$  orbitals of the phenyl rings, thereby affecting the molecular conductance. Therefore, the stereoelectronic effect causes the changes of molecular conductance [433].

Experimentally, the stereoelectronic effect of biphenyl is also investigated. For example, in order to explore the stereoelectronic effect of biphenyl, a single-molecule junction is constructed by covalently connecting hexaphenyl aromatic chain molecule to nanogapped graphene electrodes. Because the torsion of the benzene rings at both ends produces different dihedral angles, different degrees of conjugation are produced at both ends of the molecule, thereby changing the molecular conductance. Specifically, there are two different dihedral angles between the two outer benzene rings at both ends of the triphenyl unit, corresponding to strong conjugate states (high conductance) and weak conjugate states (low conductance) (figure 44(b)) [434].

In addition, for a triphenyl system, degenerate stereoelectronic states can be distinguished by introducing side groups. In specific, an azobenzene unit as a branch is connected to the central ring of the terphenyl molecule, so that the original degenerate stereoelectronic states of the triphenyl system can be distinguished. Therefore, by monitoring the current characteristics of the single-molecule junction in real time, four stable stereoelectronic states are detected (figure 44(c)). Moreover, since azobenzene can undergo a reversible structure change with a specific wavelength of light, such fine stereoelectronic effect can be further controlled [435].

In addition, the stereoelectronic effect can also affect the QI effect of the molecule, thereby affecting the electron transport of the molecule. For example, the meta-substituted phenylene ethylene oligomer (M-OPE) system have the destructive QI effect. Changing the configuration of the methoxy (OMe) substituent at the 2 position on the central phenylene ring will lead to stereoelectronic effect, thereby changing the molecular conductance. Specifically, when the OMe group is rotated from perpendicular to the plane, the destructive QI effect of the molecule is destroyed, resulting in a larger molecular conductance (figure 44(d)) [407].

As mentioned above, the stereoelectronic effect reflects the influence of the relative spatial orientation of electron orbitals on the chemical and physical properties of molecules, which can be modulated by light. In principle, the structure of certain molecules, such as photochromic molecules, will change upon photoexcitation. They exhibit optoelectronic properties and can be used to construct optoelectronic devices [435].

7.4.2. Single-molecule tautomerization. Tautomerization refers to intramolecular proton transfer in a molecule, which results in a change in functional groups, leading to molecular isomers. In these cases, two configurations can transform between each other. The study of tautomerism is of great significance to the construction of single-molecule devices and the rational application of molecules in the fields of chemistry, biology and materials.

Keto-enol tautomerism, as the most classic tautomerization in organic chemistry, is the tautomerization process that acidic  $\alpha$ -protons of the keto form (ketone and aldehyde) transfer to the enol form. Based on the configuration changes of keto-enol tautomerism, a reversible single-molecule switch can be realized. For instance, due to the transfer of H-atom between the carbon to the oxygen center, the molecule involving a ketoenol unit between two thioanisole anchors has two isomers of the keto form (A) and the enol form (B) (figure 45(a)). Among them, the conductivity of the ketone form is lower than that of the enol form because the methylene group cuts off the conjugation the phenyl groups. Furthermore, such configuration transformation can be adjusted by a bias voltage. In specific, the keto form is thermodynamically stable with a relatively high barrier, and the thermal barrier will decrease during charge injection. As the bias voltage increases, the potential energy surface (PES) of the molecule is reached under the action of this thermal transition. Correspondingly, due to the thermodynamic driving force, the molecule can be transformed from insulating keto form to the conductive enol form, resulting in conductivity transition [436].

In addition, due to the migration of hydrogen atoms in the molecular cavity, molecule with a framework structure also have tautomerism. Naphthalocyanine, as a typically molecule with tautomerization, have huge potential application prospects in single-molecule devices. For example, based on hydrogen tautomerism of single naphthalocyanine molecules, a single-molecule switch can be constructed (figure 45(b)). Specifically, two hydrogen atoms in a molecular cavity of a single naphthalocyanine bond with N atoms at position 1, 3. Through applying a bias voltage by the STM tip above the molecule, the tunneling electrons in the STM junction will increase the LUMO resonance, thereby inducing the transfer of two hydrogen atoms to N atoms at position 2, 4. Since the LUMO images of these two tautomers are significantly different, the tautomerization properties can be directly monitored [437].

Similar with naphthalocyanine, a metal-free phthalocyanine molecule (H<sub>2</sub>Pc) also has two hydrogen protons in the center, showing tautomerization properties. There are two isomers of H<sub>2</sub>Pc, denoted as tautomer A with hydrogen protons at the position of 1, 3 and tautomer B with hydrogen protons at the position of 2, 4 (figure 45(c)). Under high bias voltages, tip-induced tautomerization is triggered. In detail, the symmetry mismatch between the Ag substrate and the H<sub>2</sub>Pc molecule



**Figure 44.** Stereoelectronic effects at the single-molecule level. (a) Three dihedral configurations: A–A (purple), O–A (yellow), and O–O (green) from the perspective of the sulfur-methylene  $\sigma$  bond in the Au–Si<sub>4</sub>–Au system. Reproduced from [62], with permission from Springer Nature. (b) Schematic diagram of conformational transition of terphenyl units between strongly-conjugated and weakly-conjugated states and corresponding hexaphenyl aromatic chain single-molecule junctions. Reprinted with permission from [434]. Copyright (2017) American Chemical Society. (c) The molecular structures with different PR\_L and PR\_R orientations in *cis* forms. Reproduced with permission from [435]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0. (d) Two conformations of the molecular tap M<sub>2</sub> (shown as the free thiol). Reproduced with permission from [407]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0.

will break the energetic degeneracy of two tautomers, and only tautomer A can be observed. In addition, due to the repulsion of hydrogen protons, the STM tip close to the molecule may change the energy barrier of two tautomers. Therefore, when a high bias voltage is applied, the tautomerization of  $H_2Pc$  can be induced by tunneling electrons [438]. In addition, when the tunneling current does not pass through the  $H_2Pc$  molecule, the molecule can be excited by high-energy tunneling electrons, causing tautomerism [439].

In addition to tunneling electrons, hot electrons can also affect the tautomerism of  $H_2Pc$ . Specifically, hot electrons are provided by injecting electrons into the Cu(111) substrate with a few nanometer distance from the molecule, which can be further controlled by the design of Ag nanostructures at the atomic level. When Ag atoms act as a barrier, exponential decay of hot electron current between the STM tip and the  $H_2Pc$  molecule can be observed, thereby reducing the probability of an excited molecule. However, when using an elliptical Ag nanostructure, hot electrons will be focused, which is conducive to the formation of an excited molecule, thereby increasing the probability of molecular tautomerism [440]. Porphycene is an isomer of porphine, and is also a typical molecule with tautomeric properties, which have two hydrogen atoms in its rectangular inner cavity. Based on the positions of H atoms, there are three distinct tautomers. Similar to naphthalocyanine, the isomerization of porphycene molecules can also be induced by injecting tunneling electrons into porphycene molecules through the STM tip. In detail, when a bias voltage is applied, the inelastic electron tunneling can induce the vibrational excitation of a N–H stretching mode. The vibrational energy further induces the migration of hydrogen atom, leading to the process of tautomerization (figure 45(d)) [441].

Furthermore, changing the adsorption states of molecules on the substrate surface will affect the potential energy of molecules, thereby controlling the tautomeric of porphycene. For instance, due to the interaction of the non-hydrogenated nitrogen atoms with the Cu atoms underneath, the formation of *cis*-1 porphycene is stably adsorbed on the surface of copper Cu(110) (figure 45(e)). Similarly, the vibrational excitation caused by inelastic electron tunneling will induce hydrogen migration of the molecules after applying the voltage by the STM tip. Placing a Cu atom near the single porphycene



**Figure 45.** Tautomerization of different molecules. (a) Configuration changes of keto-enol tautomerism. (b) Schematic diagram of the hydrogen tautomerization reaction of naphthalocyanine. (a) and (b) From [437]. Reprinted with permission from AAAS. (c) Structural model of a freestanding H<sub>2</sub>Pc molecule. The hydrogen switching between two degenerated ground states is indicated by red arrows. The energy landscape of this tautomerization process is sketched under the molecule. Reprinted with permission from [438]. Copyright (2016) American Chemical Society. (d) Schematic diagram of the tautomerization process of porphycene. Reprinted figure with permission from [441], Copyright (2013) by the American Physical Society. (e) Potential well deformation by a single copper atom. Reproduced from [442], with permission from Springer Nature. (f) Chemical structure of *trans* and *cis* tautomers of a porphycene molecule that can be selectively converted on a Cu(111) surface by STM-(e<sup>-</sup>) or by thermal ( $k_BT$ ) excitation. The H atom transfer is indicated by the arrows. Reprinted with permission from [443]. Copyright (2015) American Chemical Society. (g) Molecular structure of *cis* porphycene, which can be reversibly switched between the two mirror reflected configurations. Curved arrows depict hydrogen transfer during tautomerization. (h) Schematic diagram of the tip-induced tautomerization experiment. (g) and (h) Reproduced from [444], with permission from Springer Nature. (i) Four tautomers of free-base tetraphenyl-porphyrin which have one hydrogen atom in the inner cavity. Reproduced from [445], with permission from Springer Nature.

molecule, the process of hydrogen migration can be further controlled by adjusting the relative position between the Cu atom and porphycene. In specific, when the distance between the Cu atom and the molecule exceeds the adsorption distance, it has no effect on the molecular isomerization. When the Cu atom is within the molecular adsorption range, the configuration that is hydrogen atoms close to the metal atom side shows the lowest energy because of direct attractive electronic interaction, therefore the hydrogen atoms tend to move closer to the metal atoms, leading to tautomerism. However, when the Cu atom is placed at the closest position, the surface-related electrical repulsive interaction will induce the opposite deformation of double-well potential, so the hydrogen atoms tend to move away from the Cu atom. Therefore, the position of the metal atom will affect the formula barrier of the two tautomers, thereby regulating the tautomerism [442]. Furthermore, the trans porphycene is most stable on the Cu(111) substrate surface. With voltage pulses, due to the vibrational excitation

through inelastic electron scattering, porphycene configuration will convert to *cis*-1. In addition, the process of *cis*-1-*trans* could be triggered through hot carriers by heating the sample from 5 to 30 K (figure 45(f)) [443].

In addition, the mechanical force can also induce porphycene tautomerization. Specifically, using the Cu tip of STM to contact the molecule, the external force exerted by the metal tip on the molecule will weaken the N–H bond and strengthen the migration of hydrogen in the molecular cavity, thereby inducing  $cis \leftrightarrow cis$  porphycene tautomerization (figures 45(g) and (h)) [444].

In addition, porphyrin based on porphine also exhibits tautomeric properties. For example, free-base tetraphenylporphyrin (2H-TPP) also can be used to construct singlemolecule switches. Specifically, a 2H-TPP molecule with two hydrogen atoms in the inner cavity has two tautomers, corresponding to two conductive states of a high conductance state and a low conductance state. By removing a hydrogen atom from the inner cavity of 2H-TPP by deprotonation, the remaining hydrogen atom can transfer between the four nitrogen positions through the inelastic electron tunneling excitation, leading to the four-level conductance (figure 45(i)). Based on this feature, a four-level conductance switch can be realized [445].

74.3. Single-molecule photoisomerization. The structure of photochromic molecules will change under the action of certain wavelength light, accompanied by the changes of molecular absorption spectrum and molecular conductance. Usually, such change is reversible in solution. Based on this structural changes, photochromic molecules have huge applications in molecular electronics.

Diarylethene, a typical photochromic molecule, which is mainly composed of two thiophene rings connected by carbon-carbon double bonds, has two reversible structures of non-conjugated open state and conjugated closed state. Among them, the non-conjugated open isomer is a bent configuration, and the thiophene ring is twisted out of the plane from the cyclopentene ring, so the  $\pi$  electron delocalization is confined to each half of the molecule. On the contrary, the conjugated closed state is nearly a planar configuration, and the  $\pi$  electrons delocalization are distributed throughout the molecule (figures 46(a) and (b)) [7]. When exposed to ultraviolet light, diarylethene can change from a non-conjugated open state to a conjugated closed state, and the molecular conductance changes from a low state to a high state accordingly. Due to the photoisomerization properties, diarylethene is of great significance in the field of single-molecule devices.

For example, a single photochromic molecular switch is constructed by connecting diarylethene derivative molecule into Au electrodes. Under visible light, the molecule configuration changes from the conjugated closed state to the non-conjugated open state, changing the molecular conductance from a high conductance state to a low conductance state. However, under ultraviolet light, the diarylethene derivative molecule cannot return to the conjugated closed state. This is due to the highly hybridization of the molecular orbital and the electrodes, which quenches the photoexcited state of the closed-state diarylethene molecule (figure 46(c)) [446]. In specific, when the non-conjugated open state molecules are excited and begin to transform to the conjugated closed state, the interaction between the molecules and the Au electrodes makes the excited-state molecules return to the ground state, that is, photo-excitation occurs, resulting in energy dissipation. To realize the reversible configuration change of diarylethene molecule in single-molecule device through light regulation, a series effort has been done. For example, SWCNTs are used to replace metal electrodes to construct single-molecule devices (figure 46(d)). However, due to the strong coupling between the molecule and SWCNT electrodes through amide bonds, the excited-state energy of closed-state diarylethene transfers to SWCNT electrodes, resulting in the photochemistry process to only change from the open state to the closed state [447].

In order to further adjust the energy level arrangement and interface coupling of the molecule-electrode interface, graphene is used instead of metal/SWCNTs as electrodes, and reasonably designed side groups and bridging groups are introduced at the same time. For instance, the hydrogenated group with the electron-donating effect can increase the energy level of the molecule. For fluorinated cyclopentene, the energy level of the molecule shifts down due to the electron-withdrawing effect of fluorine. Therefore, the introduction of electronwithdrawing/electron-donating substituents to molecules can effectively regulate the molecular energy level (figure 46(e)). However, it is still unable to achieve reversible configuration switching through light control. In order to further weaken the interface conjugation between the graphene electrodes and the molecule, a methylene  $(CH_2)$  group is introduced between the terminal amine group and the functional centers on both sides. The presence of methylene groups effectively reduces the delocalization of  $\pi$ -electrons. But in single-molecule junctions, the reversible configuration changes between the open state and closed state still cannot be achieved [448]. Furthermore, three methylene (CH<sub>2</sub>) groups are introduced between the diarylethene functional center and the terminal amine group. The quenching of the excited molecule caused by the electrode is reduced, and the reversible photoisomerization process of diarylethene molecules is successfully achieved, thus realizing a reversible single-molecule switch (figure 46(f)) [12].

In addition, electron withdrawing side-groups can also control the interface coupling. For oligo(phenylene ethynylene) (OPE)-embedded difurylperfluorocyclopentenes, sidegroup will also adjust the interface conjugation between Au electrodes and the molecule. Specifically, the electronwithdrawing ability of the CF<sub>3</sub> side group leads to a decrease in the energy level of molecule, a decrease in the energy level broadening of  $\Gamma$ , and an increase in the molecular energy level  $E_0$  [449].

In addition, diarylethene can also be used as ligands to control the properties of the central molecule. For example, introducing diarylethene derivative phen\* ligands into Fe(II) complexes, the structure of diarylethene derivative phen\* ligands can be controlled by specific wavelength of light, thereby affecting the ligand field. Due to the changed electronic coupling between Fe(II) and the ligand, the changed ligand field will further regulate the SCO of Fe(II) [450].

Furthermore, azobenzene is also a typical photochromic molecule, which contains two benzene rings connected by N = N double bonds and exhibits a photo-induced *cis-trans* isomerism effect under ultraviolet light or visible light. Among them, *cis* isomerism is a bent configuration and *trans* isomerism is a planar conformation (figure 47(a)). The change of the molecular structure will cause changes in molecular energy levels, thus, the *cis* isomer and *trans* isomer of azobenzene exhibit different conductance, which provides a basis for judging the changes in the molecular structure of azobenzene. For azobenzene-based molecules connected to Au electrodes by alkanethiol anchoring groups, the photoisomerization of azobenzene-based molecules has been explored by conducting atomic force microscope (C-AFM). Specifically,



**Figure 46.** Single-molecule photoisomerization. (a) and (b) Typical photochromic molecules. (c) Potential energy curves of the molecular switch along the switching coordinate. (a)–(c) Reprinted figure with permission from [446], Copyright (2003) by the American Physical Society. (d) Diarylethene connected to SWCNT electrodes and corresponding configurational changes under light. Reprinted with permission from [447]. Copyright (2007) American Chemical Society. (e) Chemical structures of three specially designed diarylethene molecules. Reproduced with permission from [448]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0. (f) Single-molecule junctions of diarylethene molecule with three methylene groups between the diarylethene backbone and the terminal groups. From [12]. Reprinted with permission from AAAS.

under ultraviolet light irradiation, the azobenzene molecule changes from a planar *trans* configuration to a bent *cis* configuration. Due to the reduction of the barrier length of the *cis*-configuration molecule, the molecular conductance will increase [451]. Based on nanogapped graphene electrodes, similar phenomenon can also be observed. Specifically, a single azobenzene molecule is covalently connected to nanogapped graphene electrodes through amide bonds. Under alternative irradiation of ultraviolet light and visible light, the conductance of single-molecule junction is found to switch between the two states repeatedly, which proves the reversible switching of azobenzene between *trans* configuration and *cis* configuration (figure 47(b)) [452].

When azobenzene is introduced as a central group, the configuration of the molecule can be controlled by light. For instance, both ends of the azobenzene molecule are covalently connected to the OLT chain. When the molecule is exposed to ultraviolet light, the configuration of the azobenzene side chain group changes from *trans* to *cis*, that is, from the planar conformation to the bent conformation. The twisting of the azobenzene ring will cause the twisting of the OLT chain, which induces a mechanical constraint in the OLT chain, thereby resulting in the change of the molecular conductance (figure 47(c)) [453]. Furthermore, when azobenzene is introduced into the terphenyl species connected between nanogapped graphene electrodes through amide bonds, the

electric field-induced isomerization of azobenzene can be realized due to the change of dipole moment in the direction of the main chain caused by the azobenzene configuration change (figure 47(d)). Specifically, when a negative voltage is applied, the cis structure of azobenzene is stable, while at the positive voltage direction, the azobenzene molecule is regulated to a trans structure. Therefore, the configuration of azobenzene can be regulated by electric fields [454]. Furthermore, introducing the azobenzene unit as a side group into the central ring of the terphenyl molecule will cause the asymmetry of the molecular structure. Therefore, the fine conformations caused by the stereoelectronic effect can be detected. Specifically, different angles between the benzene ring on both sides and the central benzene ring can lead to stereoelectronic effect, which in turn lead to different conductance of single-molecule devices. When azobenzene is in the *cis/trans* state, there are four stable conformations [435].

In addition, the single-molecule conductance of other molecules with photoisomerization properties has also been studied. Similar to azobenzene, the benzene rings of 4,4-(ethylene-1,2-diyl)dibenzoic acid will be twisted under specific wavelengths of light, realizing the reversible conversion between two states of *E* and *Z* isomers. Due to the close proximity between phenyl rings and gold substrates, the bent structure of the *Z* isomer increases charge transport between two electrodes, resulting in the higher conductance of *Z* isomer than that of the *E* isomer (figure 47(e)) [455].



**Figure 47.** Single-molecule photoisomerization. (a) Structures of *trans* and *cis* isomers of azobenzene. (b) Chemical structural changes of molecules based on azobenzene with UV/visible light irradiation. (a) and (b) Reproduced with permission from [452]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0. (c) Structure changes of the molecule with azobenzene units under certain wavelength of light. Reprinted with permission from [453]. Copyright (2017) American Chemical Society. (d) Single-molecule junctions of azobenzene as side group of bridging molecules. And dipole projection on the molecular backbone (the actual charge transport pathway). The arrow denotes the direction of the dipole projection groups. Reproduced from [455]. CO BY 4.0. (e) Structure of the *E* and *Z* isomers of 4,4'-(ethene-1,2-diyl)dibenzoic acid. Reprinted with permission from [455]. Copyright (2010) American Chemical Society. (f) The molecular structures of dha-6, vhf, dha-7 and the conversions observed in molecular junctions. Reproduced from [406]. CC BY 4.0.

Dimethyldihydropyrene (DHP), taking pyrene as the parent compound, is a typical photochromic molecule with two isomers that can realize the conductance switching function. When exposed to ultraviolet light, a weakly-conjugated cyclo-phanediene (CPD) configuration will change to a conjugated DHP configuration, accompanied by a change in conductance (figure 46(a)). When DHP is connected with Au electrodes by a pyridine anchor group, the molecular conductance changes between high and low with specific wavelengths of light, realizing the reversible conversion between CPD configuration and DHP configuration in a single-molecule junction [456].

Dihydroazulene also exhibits photoisomerization properties, and the C–C bond of a central group of dihydroazulene will break and twist (figure 46(a)). Specifically, the dha-7 configuration has similar properties with the dha-6 configuration, and both of them can be changed into the vhf configuration under ultraviolet irradiation. While the vhf configuration can return to the dha-6 structure after heating (figure 47(f)). Therefore, three conformations can be observed during the photothermal reaction of the dha/vhf system [406]. Norbornadiene (NB) is a bicyclic hydrocarbon. When exposed under UV light, it will transfer to the metastable quadricyclane (QC) form, exhibiting photoisomerization. However, the QC form only can return to the NB form with heat treatment. Using STM to measure the electrical properties of a molecule consisted of norbornadiene central group and oligo(phenylene ethynylene) arms end-capped with SAc anchor group, the conductance of the NB form can be found to be higher than that of QC form. Therefore, single-molecule switch can be realized [457].

Spiropyran derivatives (SP), consisted of an indoline part, a chromene part and a linked bond of C–O, have also shown light-controlled isomerization properties (figure 46(a)). The SP-1 configuration and the merocyanine form (MC-1 configuration) can transform between each other under the irradiation of specific wavelength of light. By assembling a single SP-1 molecule on Au electrodes, the reversible transform between SP-1 and MC-1 states can be achieved by light induction [458]. Moreover, the conductance of Au/SAM/Ga<sub>2</sub>O<sub>3</sub>/EGaIn tunneling junction composed of single SP films will be changed under the control of light, which proves that the configuration of SP molecules can still remain reversible transformation in the device [459]. Furthermore, using a combination of exposure of acid and UV, SP will change to the MC form. Without exposure to an acid, the SP state will be maintained. Moreover, configuration changes lead to changes of the molecular conductance, thereby achieving a memory function [460].

74.4. Single-molecule electroinduced isomerization. The change of molecular configuration can directly affect the physical and chemical properties, while the controllable regulation of molecular configuration is important to realize single-molecule functional device. Among them, an electro-induced method is one of the useful strategies to regulate molecular configuration, including redox, inelastic collision, electric field force and other mechanisms.

Molecular motors can mechanically move under external stimulation, thereby performing tautomerization. The isomerization of molecular motors induced by electric fields is explored in single-molecule junctions. For instance, the molecular motor consisting of vinyl group axis and anthracene group is connected to the nanogap metal electrodes through bidentate mercaptothiophene linking groups. In particular, the hydrogen atoms on the end of two sides of anthracene group are substituted by methoxy groups and cyano groups, respectively, constructing a dipole rotor. The oscillating electric field generated by the back-gate electrode can induce the rotation of the dipole rotor. Therefore, the molecule can repeatedly switch between two stable states, corresponding to two conductivity states. Therefore, the molecular configuration can be controlled by an electro-induced effect to further control the molecular conductivity [461].

Diarylethene is a typical photochromic molecular system, with two reversible structures in the open state and the closed state. In addition to light stimulation, diarylethylene can also be switched between the two configurations by electrical stimulation. For instance, the isomerization of 1,2-bis(2-methyl-5-((Z)-(2-cyano-2(pyridin-4-yl)vinyl))furan-3-yl) hexafluorocyclopentene (C5F-4Py) on the Au(111) surface have been studied by electro-induced effects. Initially, the C5F-4Py molecule adsorbed on the Au surface with the non-conjugated open state can change to the conjugated closed state by applying voltage pulses through the STM tip. In addition, the configuration of C5F-4Py will switch to the open state (figure 48(a)) [462].

In addition, the configuration change of azobenzene can also be controlled by electric fields, which has two reversible structures of a planar *trans* configuration and a bent *cis* configuration. For example, the 3,3,5,5-tetra-tert-butylazobenzene molecule (TBA) can induce reversible isomerization on Au(111) through electric fields in the STM junction. Specifically, the dipole moment makes the azobenzene molecule exhibit polarizability. Due to the presence of four substituted tert-butyl groups in TBA, the electronic coupling can be reduced and the surface movement can be promoted. Therefore, the PES associated with the configuration is deformed under the action of an electric field, resulting in a reduction of isomerization barrier [463].

In other molecular systems, electro-induced structural changes have also been realized. For instance, cumulene derivatives formed by a linking backbone of carbon atoms through  $\pi$ -bonds has a *cis*-isomer and a *trans*-isomer. When an electric field is applied, the resonance structure of the polar zwitterion that can rotate freely around the terminal C–C bond is enhanced, which reduces the rotating barrier and the energy required for the molecular isomerization. In addition, since *trans*-isomer has a larger field-induced dipole moment than *cis*-isomer, the configuration distribution of the final product is determined by the electric field conditions (figure 48(b)) [464].

74.5. Single-molecule mechanical isomerization. Force is also an effective means to regulate molecular isomerization. In fact, the mechanical force is usually used to adjust subtle molecular isomerism at the single-molecule level. For instance, cyclohexane has two chair isomers corresponding to different conductance. Through the –SMe or –SAc anchor groups to construct cyclohexane single-molecule junctions, two typical conductance characteristics can be observed during the retracting and approaching of the STM tip, which proves the transformation of the two isomers (figure 48(c)). In specific, the binding energy between Au electrodes and anchor groups is strong, which can overcome the interconversion barriers between two chair isomers. Therefore, the two chair configurations can be converted under the force generated by the binding energy of electrodes and anchor groups [72].

In addition, the molecule can also be transformed between the two configurations of unfolding/folding under the action of force. For instance, the molecule with two phenyl rings spaced by a diketone chain can be unfolded/folded along the central C–C bond under the action of force (figure 48(d)). This is due to the smaller energy barrier of conformation interconversion than the binding energy between the molecule and Au electrodes. Specifically, when the molecular junction is compressed, the molecule can fold around the C–C bond. On the contrary, the molecule will unfold when stretched [465].

A similar force-induced configuration change process can also be realized in stacker molecules. For example, 1,4,5,8naphthalenetetracarboxylic diimide and 1,3,6,8-pyrenetetrol connected via a short aliphatic chain can be mechanically unfolded/folded [466]. In addition, reversible unfolding/folding can also be achieved by force, such as orthopentaphenylene (o-PP). There are three conformations for ortho-pentaphenylene derivatives (o-PP-2SMe) consisting of five ortho-positionlinked phenyl rings and methylthio (SMe) anchor group, respectively, antiparallel folding structure, coparallel folding structure and fully stretched structure. With the movement of the STM tip, the configuration of o-PP-2SMe is changed under the tensile force. In detail, when the STM tip is retracted, the molecule is fully stretched, and when the STM tip is close, the molecule folds [63].

Furthermore, for systems with more complex structures, the structural changes can also be realized under mechanical forces. For example, a single DNA molecule will also stretch



**Figure 48.** Single-molecule electroinduced isomerization and mechanical isomerization. (a) Configurational and conductance changes of diarylethene by electrical stimulation. Reprinted with permission from [462]. Copyright (2016) American Chemical Society. (b) Illustration of single-molecule junctions with DFT-optimized structures of *cis*-isomer and *trans*-isomer. Reproduced from [464]. CC BY 4.0. (c) Chemical structures of cyclohexane, which have two chair conformational isomers. Reproduced with permission from [72]. (c) Elsevier. CC BY-NC-ND 4.0. (d) Unfolding/folding illustration of thr molecule with two phenyl rings spaced by a diketone chain. Reprinted with permission from [465]. Copyright (2020) American Chemical Society. (e) Configurational changes of Fc–Lip under the mechanical force. Reprinted with permission from [468]. Copyright (2017) American Chemical Society.

under the mechanical force applied by STM. The configuration of DNA changes with the movement of the STM tip. Specifically, the bases at the ends are strongly distorted, while the bases in the middle are almost unaffected, which affects the piezoresistance of DNA [467].

Moreover, the molecular structure change induced by the mechanical force may lead to the change of the redox state. For instance, the cyclopentadienyl (Cp)–Fe–Cp distance in 1,1'-ferrocenyl diester (Fc–Lip) with special sandwich structures will change under the mechanical force. Specifically, a Fc–Lip molecule mechanically stretches with the retraction of Au tip, and a larger Cp–Fe–Cp distance is obtained. As the increase of the metal–ligand bond length, the electron transfer reaction is driven to oxidation, which changes the redox state of the Fc–Lip molecule (figure 48(e)) [468].

74.6. Single-molecule nanomechanical movements. The nanomechanical motion of a molecule will change the molecular structure, thereby affecting molecular charge transport and other properties. Based on this, single-molecule memristors, single-molecule memories and other applications can be realized.

Endohedral fullerene, a typical molecule possessing nanomechanical motion characteristics, has been extensively studied due to its unique properties. Due to its stable carbon shell, fullerene can be used as an encapsulation container for atoms, ions or molecules. Through constructing a suitable endohedral fullerene, the molecular mechanical motion can be manipulated, thus realizing functions such as memory. Here, the focus is on the mechanical motion of the endohedral fullerene induced by the electric field force.

By controlling the single-molecule nanomechanical motion, the switch function can be realized. For instance, the triangular Sc<sub>3</sub>N clusters in the icosahedral C<sub>80</sub> fullerene cage are driven by tunneling electrons to rotate among the three pairs of enantiomers, thereby achieving the switching function (figure 49(a)). In this system, Sc<sub>3</sub>N stably adsorbs at a certain site in the C<sub>80</sub> cage, and the inelastic scattering of the tunneling electrons excites the stretching vibration of the Sc<sub>3</sub>N. Correspondingly, the energy used to overcome the barrier is redistributed in the endohedral fullerene by intramolecular vibration, driving the rotation of the Sc<sub>3</sub>N clusters between the three pairs chiral conformations [469].

In addition, the nanomechanical motion can also be carried out by applying an electric field to induce the rotation of the polar molecules in the fullerene cage. For example, the orientation of polar molecules MX (M stands for alkali



**Figure 49.** Single-molecule nanomechanical movements. (a) Schematic illustration of Sc<sub>3</sub>N nanomechanical movements in a C<sub>80</sub> cage. Reprinted with permission from [469]. Copyright (2011) American Chemical Society. (b) Mechanism illustration of polar MX nanomechanical movements in a C<sub>70</sub> cage. Reprinted with permission from [470]. Copyright (2019) American Chemical Society. (c) Schematic illustration of an electric field regulating the movement of Gd atoms in a C<sub>82</sub> cage. Two coloured arrows represent the direction of the dipoles. Reproduced from [471], with permission from Springer Nature. (d) *I*–*t* spectrum suggesting the movement of Li atoms in C<sub>60</sub>. Reproduced from [472]. CC BY 4.0.

metal, X stands for halogen) in  $C_{70}$  (MX@ $C_{70}$ ) can be changed by introducing oriented external electric fields (figure 49(b)). Specifically, for initial MX and MX@ $C_{70}$ , when a weak electric field with an opposite direction of the intrinsic dipole moment of MX is applied, the energy of the local minimum decreases. Therefore, the switching barrier is reduced, leading to the rotate of polar molecules within the fullerene [470].

In addition to adsorption at specific sites in fullerenes, the movement between different adsorption sites of the inclusion compound in the fullerene cage can also produce nanomechanical movements. For example, the Gd atom has the two most stable adsorption sites adjacent to the  $C_{82}$  cage, which results in two dipole states with different directions of Gd@C<sub>82</sub>. When introducing an electric field, the coercive field due to the intrinsic ferroelectricity of Gd@C<sub>82</sub> will provide the energy to decrease the transformation barrier between two states, thereby realizing the movement of a Gd atom in the  $C_{82}$  carbon cage (figure 49(c)). Moreover, because of the different molecular states of Gd@C<sub>82</sub>, there are high and low conductance corresponding to the positions of the Gd atom, which can be used to realize the memory storage function [471].

Furthermore, the special cage structure of fullerenes allows multiple adsorption sites to be provided. Therefore, the movement of endohedral complexes at multiple adsorption sites of the fullerene cage can also achieve the mechanical movement of single molecules. Based on this feature, under the induction of an electric field, Li atoms can move in multiple adsorption sites in the inner fullerene Li@C<sub>60</sub>, forming 14 different Li-cage molecular states. Specifically, super atom molecular orbitals (SAMOs) are fullerene-centered diffuse orbitals, so the resonant tunneling through SAMOs is more conducive to activate the movement of Li atoms. Because  $p_{x,y}$ -SAMO ( $p_{x,y}$ indicates the shape of p orbital) is decoupled from Au(111), the efficiency of hot electron transfer to the electrode will be reduced through the resonant tunneling of SAMOs with an electric field. Furthermore, due to the coupling between the vibration modes of  $p_{xy}$ -SAMO and Li, Li atom is more likely to be activated and move in the carbon cage. Therefore, different molecular states can be proved by the conductance changes of Li@C<sub>60</sub> (figure 49(d)) [472].

7.4.7. Motion of single-molecule machines. Molecular machines are usually supramolecular systems, whose components can move relative to each other under external stimulations, such as heating and electrochemistry, thereby converting chemical energy into mechanical energy. Mechanically interlocking molecules are a typical class of molecules that can be used to assemble molecular machines, mainly

including molecular motors, rotaxanes and catenanes, and have a wide range of applications in the preparation of single-molecule memories and single-molecule switches.

Specifically, catenanes is a complex topological structure composed of two or several entangled cyclic annular parts. Under a specific external stimulation, the controllable relative movement can occur between the cyclic annular components. For example, using bistable [2]catenane-based molecule to construct a single-molecule device, the reversible switch can be achieved (figure 50(a)). Specifically, a tetracationic cyclophane with two bipyridinium units is interlocked with a crown ether, forming [2]catenane. Moreover, the crown ethers contain TTF units and 1,5-dioxaphthalene ring system in opposite positions. In the movement process, the TTF unit and the electron-deficient tetracationic cyclophane are initially combined through non-covalent forces. After TTF unit is oxidized to the positively charged state, the Coulomb repulsion between the TTF and the tetracationic cyclophane may cause the crown ether to rotate to the position of 1,5-dioxaphthalenering. When TTF gets an electron, the whole system will return to the original state, realizing the reversible change of the system. Therefore, due to the bistable properties of [2]catenane, singlemolecule devices with switching or memory function can be constructed [473].

Rotaxane is also a kind of a supramolecular system, which is formed by a cyclic molecule as a host threaded onto a dumbbell-shaped linear molecule as a guest. In the rotaxanes, the cyclic component can shuttle back and forth between the specific site of the linear component under certain conditions. For instance, in a [2]rotaxane, the electron-deficient tetracationic cyclophane with two bipyridinium units can stably thread between the two electron-rich TTF and dioxynapthalene groups of the molecular axis due to the  $\pi - \pi$  interaction, thus realizing the memory function (figure 50(b)). In detail, the binding energy of TTF and tetracationic cyclophane is significantly greater than that of dioxynapthalene, and the TTF group can form a stable supramolecular interaction with the tetracationic cyclophane through mechanical bonds under certain external conditions. However, when the TTF group is oxidized, the combination between TTF and tetracationic cyclophane will be destroyed, and the tetracationic cyclophane will move to the site of dioxynapthalene. Through regulating the state of TTF group by electrochemistry, the tetracationic cyclophane will reciprocate between the two binding sites of TTF and dioxynapthalene on the molecular axis. Therefore, the [2]rotaxane molecule can act as the information memory unit to construct single-molecule devices [474].

Furthermore, the molecular stretching and contracting behavior can be achieved through the construction of molecules with multiple rotaxane units. An efficient metal supramolecular rotaxane polymer is constructed, which is composed of [c2] daisy chains with perfect wormlike chains (figure 50(c)). There are two binding sites on the rotaxane axis, which are the secondary ammonium and triazolium ions. The binding constant of dibenzo-[24]crown-8 ether and secondary ammonium ion is different from that of triazolium ions. Firstly, the macrocycle is located in the position of the secondary ammonium ion. After deprotonation, the macrocycle moves to the site of the triazolium ions. Therefore, the molecular stretching and shrinking behavior can be achieved [475].

As a typical molecular machine, molecular motors can rotate in one direction. For example, the molecular motor consists of a five-arm rotor and a ruthenium atomic ball bearing with vertical positioning, which can be driven by STM to rotate in a clockwise or anticlockwise direction. Specifically, the molecular motor is fixed on the surface of Au substrates through a stator with a thioether group. However, since one of the arms has no Fc end groups, the rotor of the molecule has an asymmetric structure. Therefore, the rotation energy potential of the molecular motor is asymmetric. By applying the tunneling voltage through STM, the energy of inelastic electron tunneling can excite the rotation of the molecular motor. Furthermore, the rotation direction can be controlled by selecting the subunits of inelastic electron tunneling (figure 50(d)) [476]. In addition, some small molecules with special structures can also be driven to perform the directional rotation under tunneling current through STM, such as butyl methyl sulphide (BuSMe) and N-heterocyclic carbenes (NHC) [477, 478].

7.4.8. Single-molecule structural changes during chemical reactions. Exploring the transformation of the molecular electronic structure and geometric structure during chemical reactions will help to understand the process of chemical reactions and integrate complex functions produced by molecules into single-molecule devices. Therefore, it is necessary to study molecular properties and single-molecule dynamics by the single-molecule detection technology.

In fact, the changes in the molecular structure generally reflect in the conductance of the molecules. Through modifying reactive groups in the molecule of the single-molecule device, the reaction in the molecule of the single-molecule device can be monitored, providing a strategy to study chemical reactions. Some nitrogen-containing molecule, for example polyaniline, will undergo protonation/deprotonation reactions by adjusting the pH. When the group on the molecule is protonated/deprotonated, the conductance of the molecule will change. Therefore, such a reaction process can be monitored by detecting the molecular conductance. In specific, polyaniline chains are covalently connected to SWCNTs through amide bonds to construct single-molecule devices. Adjusting the pH, polyaniline chains can be protonated or deprotonated, accompanied by changes in molecular conductance (figure 51(a)) [91]. In addition, the pyridine nitrogen in pyridine-based molecules with meta-connected side groups (M3) showing QI effects can also be protonated under acidic conditions, which enhances the molecular electrical transport capacity. When Na<sub>2</sub>CO<sub>3</sub> is added to the system, the pyridine nitrogen will undergo a process of deprotonation, thereby decreasing the molecular conductance. Through the alternate treatment of alkali and acid, a reversible cycle can be realized and single-molecule switching can be achieved [45].

In addition, central molecules in single-molecule devices can undergo proton transfer with external molecules, and the process of proton transfer can be controlled by reversibly controlling of external molecules. For example, 1,3-azulene



**Figure 50.** Structural changes of single-molecule machines. (a) Structural changes of bistable [2]catenane. From [473]. Reprinted with permission from AAAS. (b) Chemical structure of the molecular motor composed of an ruthenium(II)-based complex. From [473]. Reprinted with permission from AAAS. (c) Chemical structure of the bistable [2]rotaxane. Reproduced from [474], with permission from Springer Nature. (d) Schematic illustration of an integrated translational motion of a supramolecular polymer chain. Reproduced with permission from [475]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0.

derivatives (1,3Az) are connected into Au metal electrodes through SMe anchor groups. In order to controllable introduction of protons, spiropyran photo-switchable media and ring-opened merocyanine (MCH) are also introduced into the system. Under blue light (400–460 nm), the H<sup>+</sup> atom released by MCH is received by 1,3Az, forming 1,3Az-H. The process of protonation enhances the conjugation and shrinks the HOMO–LUMO gap of azulene, resulting in a higher conductance of azulene derivatives. Furthermore, the H<sup>+</sup> atom can be lost by 1,3Az-H and be received by photo-switchable spiropyran. Therefore, the molecular conductance returns to a low conductance state. Based on this feature, a photo-induced single-molecule switch is realized (figure 51(b)) [479]. As mentioned above, the changes of the molecular structure during chemical reactions can be reflected in molecular conductance. Monitoring the changes of molecular conductance during chemical reactions will help to reveal the internal mechanism of chemical reactions, possessing great significance in basic research and practical application. For example, a single molecule with a 9-fluorenone center is covalently connected to nanogapped graphene electrodes to construct a singlemolecule junction. By introducing NH<sub>2</sub>OH into the system, the nucleophilic addition reaction can undergo between the carbonyl group in the molecule and NH<sub>2</sub>OH. As the resulting product has a different structure from the original molecule, the electrical conductance is different (figure 51(c)) [480].



**Figure 51.** Structural changes during the chemical reaction. (a) Structural changes of polyaniline which undergo protonation/deprotonation reactions. From [91]. Reprinted with permission from AAAS. (b) Structural changes of intermolecular proton transfer of the non-photoresponsive 1,3Az, controlled by the photoswitchable medium MCH under blue light irradiation. Reproduced with permission from [479]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0. (c) Single-molecule junction of a 9-fluorenone center molecule. Reproduced from [480]. CC BY 4.0. (d) Single-molecule junction of a NHC molecule. Reproduced with permission from [482]. (c) Elsevier. CC BY-NC 4.0.

Besides, the functional group containing 9-phenyl-9-fluorenol is integrated into the nano-gapped graphene electrodes. Under the catalysis of protic solvent, the reversible reaction of a 9-phenyl-9-fluorenol molecule can occur. Through real-time monitoring of the dynamic reactions process, the significant conductance changes of the sample molecules during the chemical reversible reaction process are tracked and collected, proving the changes in molecular structure during the reaction process [481].

In addition to direct chemical reactions, the structure change during a catalytic process can also be explored. For instance, by covalently connecting N-heterocyclic carbene (NHC) with a catalytic activity into graphene electrodes, single-molecule devices can be constructed. During the catalytic process, three current conductance can be observed, corresponding to the three relatively stable structures derived from the NHC catalyst. This also demonstrates that there are three kinds of molecular structures based on NHC in the catalytic process (figure 51(d)) [482].

### 7.5. Intermolecular and intramolecular interactions

Intermolecular and intramolecular interactions are of great significance for the construction of reliable molecular electronic devices with required functions. Here, we focus on three extensively studied interactions, respectively, which are  $\pi$ -stacking interactions, hydrogen-bonding interactions and host-guest interactions.

7.5.1.  $\pi$ -stacking interactions.  $\pi$ -stacking interactions are a kind of weak interactions exhibiting between  $\pi$ -electron conjugated systems. Exploring the mechanism of  $\pi$ -stacking interactions is of great significance for the design of multifunctional single-molecule devices. Recently, a lot of works focus on the charge transport properties of molecules with  $\pi$ -stacking interactions. It is found that intramolecular  $\pi$ stacking interactions can effectively improve the charge transport capability of molecules. For instance, series oligomers with an increasing number of anthracene units are designed to construct a single-molecule junction, which is connected to metal electrodes by amine groups (figure 52(a)). Under the combination of intramolecular hydrogen bonding and aromatic interactions, the oligomers are folded. There are  $\pi - \pi$  conformations between anthracene groups of folded molecules, thereby showing intramolecular  $\pi$ -stacking interactions. Due to  $\pi$ -stacking interactions, HOMOs of the folded molecule shows large densities on the anthracene units, that is, it is located on the anthracene group. Therefore, an effective pathway for CT is provided, resulting in a high conductance [483].

In addition,  $\pi$ -stacking interactions can induce molecules to form dimers, showing unique conductance properties. For instance, oligo-phenylene ethynylene molecules show bimolecular interaction. Specifically, due to  $\pi$ - $\pi$  stacking interactions between the phenyl rings, oligo-phenylene ethynylene molecules with one anchor group can form a dimer



**Figure 52.**  $\pi$ -stacking interactions at the single molecule level. (a) Schematic representation of the folding and anchoring processes of oligomers with anthracene groups. Reproduced from [483]. CC BY 4.0. (b) Staggered  $\pi$ - $\pi$  stacking configuration of a pair of OPE-monothiol. Reproduced from [484], with permission from Springer Nature. (c) Schematic diagram of single-stacking junctions of terphenyl. Reprinted with permission from [486]. Copyright (2020) American Chemical Society. (d) The electronic transport properties of a dimer. Reproduced from [408], with permission from Springer Nature.

(figure 52(b)). Moreover, because of both ends of the dimer with an anchor group, the obvious molecular conductance of the dimer can be detected. The electrical characteristics measured by MCBJ show that the conductance of dimers decreases by an order of magnitude than that of a single molecule [484].

Furthermore,  $\pi$ -stacking interactions between molecules of a dimer can also be regulated through chemical control. For example, the stacking between molecules will be hindered and  $\pi$ -stacking interactions will be weakened after introducing huge tert-butyl substituents into the benzene ring of oligophenyleneethynylenes [485]. In addition, an electric field can affect the stacking pattern of two molecules in the dimer, thereby affecting the properties of the dimer. For instance, under the action of an electric field, the dihedral angles of terphenyl groups decrease, which reduces the steric hindrances and facilitates the stacking of terphenyl molecules, thereby enhancing  $\pi$ -stacking interactions (figure 52(c)) [486].

In addition to the electric field, the mechanical force can also regulate the stacking model of the dimer. For example, an oligo-phenylene-ethynylene molecule with a thiol anchor group at one end can form a dimer through intermolecular  $\pi$ -stacking, and the stacking model of the dimer can be further controlled by the mechanical force through MCBJ. Specifically, when the tip moves away from the substrate, the degree of dimer stacking will change due to the relative movement of two molecules in the dimer, thereby changing the electronic structure. Therefore, a periodic QI effect is observed (figure 52(d)) [408]. Furthermore,  $\pi$ -stacking interactions can also affect other molecular properties, such as the thermoelectric performance. For instance, by adjusting two adjacent C<sub>60</sub> molecules to form a dimer,  $\pi$ -stacking interactions between the molecules will enhance the thermoelectric performance [487].

7.5.2. Hydrogen-bonding interactions. Hydrogen-bonding interactions are the electrostatic interactions between the hydrogens on the strong polar bond (X–H) and the high electronegative, lone-electron pair or partially negatively charged M atom, which can be denoted as X–H···M. It exists widely in nature, having a great significance in chemical reactions and biological behaviors [488]. Furthermore, the study of hydrogen-bonding interactions is contributed to the design of functional molecules, thus promoting the development of single-molecule functional devices.

So far, some studies have been conducted to explore the characteristics of hydrogen bonds at the single-molecule level. For example, the visualization of hydrogen bond formation in 8-hydroxyquinoline (8-hq) molecular assemblies on a Cu(111) substrate has been achieved by noncontact AFM (NC-AFM). In specific, through accurate analysis of the configuration of hydrogen bonds, the local bonding information of the molecule can be obtained, such as the dehydrogenated 8-hq and Cu assembly via O(N) –Cu bonds [489].

The regulation of hydrogen bonds will affect molecular properties and the chemical reaction process, so it is of great significance to explore the strategy of regulating hydrogen bonds. For instance, photochromic oxazine molecules are adsorbed on the Cu substrate, and the different intermolecular hydrogen-bonding configurations make the molecules exhibit different adsorption shapes. With STM lateral manipulation, the intermolecular hydrogen-bonding configuration changes, which proves that the hydrogen-bonding configuration can be regulated [490].

In addition, hydrogen-bonding interactions can act as a channel for electron transfer, therefore affecting the electrical properties of molecules. For example, the molecular length of glutathione disulfide (GSSG) is twice of glutathione (GSH),



**Figure 53.** Hydrogen-bonding interactions at the single molecule level. (a) Chemical structures of glutathione disulfide (GSSG) and glutathione (GSH). (b) Schematic diagram of charge transport of glutathione disulfide through hydrogen bonds. (a) and (b) Reproduced from [491] with permission from the Royal Society of Chemistry. (c) Chemical structures of 1H-imidazole and benzimidazole, and the crystal structure of 1H-imidazole. Reproduced from [492]. CC BY 3.0. (d) Device structure of the single supramolecule junction with multiple hydrogen-bonding dimers and hydrophobic alkylene spacers. Reprinted with permission from [494]. Copyright (2019) American Chemical Society. (e) Schematic diagram of each transition process between the five structures. Reproduced from [495]. CC BY 4.0.

but its molecular conductance is higher (figure 53(a)). This is because the GSSG molecule has two molecular chains that contain a proton atom (H, provided by hydroxyl group) and an electronegative atom (O, provided by carbonyl group) at the ends in the same direction, which are connected by hydrogen bonds. Specifically, although hydrogen bond is hard to form due to the long distance between the proton atoms and electronegative atoms in two molecular chains in a single GSSG molecule, the H<sub>2</sub>O molecule can act as both hydrogen donor and hydrogen acceptor. Therefore, the ends of two molecular chains can be connected by hydrogen bonds through H<sub>2</sub>O to form a charge transport channel, thereby showing a higher conductance (figure 53(b)) [491]. In addition, single molecules can be connected together to form a multimer through hydrogen bonds. 1H-imidazole (1,3-diazole) is a small molecule that has both strong hydrogen bond donor and strong hydrogen bond acceptor. Under a anhydrous environment, 1H-imidazole can be linked by hydrogen bonds to form a polymer chain. Therefore, in addition to the conductance of a single 1H-imidazole, the molecular conductance of dimers and trimers connected by hydrogen bonds is also observed. However, under an environment containing water, 1H-imidazole-H<sub>2</sub>O supramolecules will be formed through hydrogen bond interactions (figure 53(c)). Therefore, the conductance of molecular junctions containing the H-bonded water is monitored [492].



**Figure 54.** Host-guest interactions at the single molecule level. (a) Chemical structures of a host molecule wire with a pendant crown ether and the dicationic guest. (b) Schematic representation of guest molecules passing through the host hollow ring in the single-molecule junction. (a) and b) Reproduced with permission from [4]. (c) American Association for the Advancement of Science. CC BY-NC 4.0. (c) Chemical structures of a host molecule wire with a macrocyclic side group and the guest. (d) Device structure and electrical characterization of the cyclocyclo-dextrin single-molecule junction. (c) and (d) Reproduced with permission from [500]. (c) Wiley-VCH GmbH, Weinheim. CC BY-NC 4.0.

Multiple hydrogen bonds can also be used to construct supramolecular systems. For example, through four cooperative hydrogen bonds, several supramolecules are constructed based on pyrimidinedione (UPy) derivatives, which have different aurophilic anchor groups, such as pyridine, amine and thiol. The electron transport properties of supramolecules can be attributed to the quadruple hydrogen bond interaction [493]. Hydrogen bonds can also cooperate with hydrophobic groups to construct supramolecular systems. For instance, a single supramolecule with the stability in water can be assembled by introducing hydrophobic alkylene spacers with different lengths between the poly(ethylene glycol) (PEG) and 2-ureido-4[1H]-pyrimidinone (UPy) groups (figure 53(d)). Specifically, due to the hydrogen bonds interaction of water, supramolecules assembled based on hydrogen bonds are unstable in water. By introducing hydrophobic groups, the synergetic effect between hydrogen bonds and hydrophobicity will improve the stability of the supramolecule in water, which is beneficial to the design of functional molecular machines [494].

In addition, the study of hydrogen bond dynamics is conducive to the in-depth understanding of the transformation of the molecular structure and the construction of singlemolecule functional devices. By constructing single-molecule junctions, the process of isomerism caused by hydrogen bond rearrangement can be monitored at the single-molecule level in real time. For example, a quadruple hydrogen bond dimer of ureido pyrimidine-dione (UPy) has been covalently connected into graphene electrodes to construct a single-molecule junction. Due to the intermolecular proton transfer and lactam-lactam tautomerism, the hydrogen-bonding structure in the dimer is rearranged. Specifically, in the molecule, the H atom coordinated with the blue O atom migrates to the red N position, so that structures 1 and 2 undergo tautomerism. In addition, the H atom will migrate from the red N position to the blue O position, changing the tautomer 4 to tautomer 5. In addition, due to the intermolecular proton transfer, the configuration transform among structures 2, 3, and 4 will be achieved (figure 53(e)). Therefore, there are multiple configurations of the molecule in the rearrangement process of hydrogen bonds, which are manifested as multiple molecular conductance states [495].

75.3. Host-guest interactions. Host-guest interaction, that is, the process of host molecules and guest molecules being selectively combined through non-covalent interactions to form host-guest complexes, is generated when the structure is complementary and the energy matches. In fact, such

non-covalent interactions may include multiple interactions, such as hydrogen-bonding interactions, ionic bonds, van der Waals interactions and electrostatic interactions. The study of host-guest interactions has an important scientific significance for single-molecule functional devices based on molecules with specific functions [496–499].

The strategy of synthesizing supramolecules based on hostguest interactions has been widely used in molecular electronics, chemistry and other fields. However, the mechanism of host-guest interactions is still unclear. Single-molecule devices provide a powerful platform for studying the mechanism of host-guest interactions. For example, the formation mechanism of [2]pseudorotaxane host-guest complexes consisted of electron-rich crown ether and a dicationic guest is studied by a single-molecule device. In detail, the change of the molecular structure during the host-guest interaction process can be reflected in the molecular conductance (figure 54(a)). Based on the I-t curves, two conductance states are observed, corresponding to the formation and dissociation process of the complex. In specific, enthalpy will drive the formation of a host-guest complex, corresponding to a high conductance state. On the contrary, the dissociation processes of the supramolecule correspond to a low conductance state (figure 54(b)). Therefore, due to enthalpy-driven complexation, the host-guest complex will dissociate as the temperature increases, and the corresponding high conductance state decreases [4].

In addition, for host-guest complexes based on  $\alpha$ cyclodextrin, the host-guest interactions can be affected by the charge of the guest molecule. For instance, a conjugated molecular wire with a macrocyclic side group and a permethylated  $\alpha$ -cyclodextrin (PM- $\alpha$ CD) is covalently connected to graphene electrodes, constructing a stable single-molecule junction (figures 54(c) and (d)). Meanwhile, the end of alkyl chains as guest molecules are modified with carboxy terminal group and amino terminal group, respectively. After treatment in acid solution, the two ends of the alkyl chain are negatively and positively charged. When the negatively charged end of the guest enters PM- $\alpha$ CD, perturbed HOMO (p-HOMO) of pseudorotaxane is close to the Fermi level of the electrode, so a higher conductance can be observed. When the positively charged end enters PM- $\alpha$ CD, the *p*-HOMO of pseudorotaxane is far away from the Fermi level of the metal, so a low conductance state is observed. Furthermore, such a change of conductance state depends highly on temperature changes. The study of host-guest interactions provides a new perspective for precise control of single-molecule devices [500, 501].

## 8. Summary and outlook

In conclusion, the electronic devices are the basis of optoelectronic devices, and they share similar mechanisms. Understanding the electronic and optoelectronic devices from the perspective of mechanisms is essential to facilitate their applications. In detail, the physical phenomena and mechanisms involved in single-molecule electronic and optoelectronic materials and devices are clarified in this review. Specifically, the fundamentals of single-molecule electronic devices, which are the basis of single-molecule optoelectronic devices, are introduced, including the design, fabrication and inherent charge transport mechanisms of the devices. In addition, from the perspectives of charge effects, spin effects, exciton effects, vibration effects, structure and orbital effects, the molecular material basis, physical mechanism, manipulation and application of singlemolecule optoelectronic nanodevices are systematically summarized in detail. In particular, single-molecule optoelectronic materials are summarized, which generally have optoand electro-activities, including semiconductor molecules, photo-isomeric molecules, redox molecules and magnetic molecules.

Although single-molecule devices have made great progress both in experiment and theory, there are still some issues that need to be investigated and discussed in the future. As we all know, when the system scales down to the single-molecule level, quantum effects play a dominant role in electron transport and other characteristics, such as spin and vibration. However, the mechanism and detail of molecular electron transport, especially when external regulations are introduced, have not yet been fully resolved. Typical open questions and possible solutions are listed below.

- (a) The mechanism and regulation of excited states of molecules and the interaction between the excited state and electrodes/external fields are the key issues. Specifically, the intrinsic nature of molecules such as the excited state generated by light may be quenched due to the interaction between molecule and electrode. Especially in the optoelectronic device, the retention of molecular excited states is crucial because the exciton determines the functionality of the device. To solve this problem, the energy transfer and CT mechanisms of the excited state need to be further explored. For example, the combination of femtosecond laser and ultrafast electrical measurement can be used to detect energy transfer and CT dynamics of molecular excited states, helping to further control excitons in single molecules. Furthermore, in order to prolong the excited state lifetime of molecules, precise design of the device structure and control of the exciton state are required. For instance, the electron occupation of the hole in the exciton state can be introduced to suppress spontaneous emission.
- (b) For the CISS effect mentioned in section 4.1.4, its origin is still unclear. It has been suggested that it originates from spin-orbit coupling (SOC), but the SOC in the chiral molecules seems to be too small to be the sole origin of the observed spin filtering. Therefore, another consideration has been proposed, that is, the CISS is inherited from the metal surface, because essentially all experiments revealing CISS effects are conducted with chiral molecules placed on heavy metals, which have a large intrinsic SOC. Therefore, whether the effect is derived from the spin polarization induced by the strong spin orbital of the metal electrode at the interface or the spin–orbit

coupling of the chiral molecule itself is still an open question. Graphene-based single-molecule devices provide the possibility to clarify the origin of the CISS effect. In specific, highly stable single-molecule devices based on specific chiral molecules and nanogap graphene electrodes should be constructed. The sensitive, comprehensive detection technology should be developed to achieve real-time detection of the current spin polarization of chiral molecules, so that the influence of electrode-molecule coupling, spin-orbit coupling of electrode materials and the chiral characteristics of molecules on the CISS effect can be studied. Furthermore, through asymmetrically designed electrodes, the magnetic electrode can generate spin-polarized electrons that can pass through single-molecule junctions, helping to explore the origin of the CISS effect.

- (c) The transition between singlet and triplet is also a key issue, which corresponds to the emission of fluorescence and phosphorescence, affecting the emission efficiency of single-molecule electroluminescence. Furthermore, the singlet and triplet states are spindependent, which provides a new perspective for tuning the types of excited states. Specifically, the spin properties of single molecules, such as multi-radical systems, can be regulated through circularly polarized light and magnetic field, resulting in transitions between different excited states.
- (d) In single-molecule optoelectronic devices, the mechanism for conductance enhancement or photocurrent generation is still controversial. Specifically, whether the photo-induced current enhancement observed in single-molecule junctions should be attributed to photon-assisted tunneling or plasmon-induced 'hot electrons' remains inconclusive. Non-metallic electrodes without the plasmon-induced 'hot electron' effect can be used as control systems for single-molecule devices to distinguish the conductance enhancement mechanism. Furthermore, the effect of 'hot carriers' thermally relaxed from high-energy 'hot electrons' on the photocurrent is worth exploring as well.
- (e) In single-molecule devices based on photoisomeric molecules, the key factors affecting the electronic characteristics deserve further elucidation. Specifically, the photoisomeric molecules in the devices can undergo the structural change under light irradiation. It is still uncertain that the factor to hinder the molecular photoinduced structural change in the device should be attributed to energy transfer between molecule and electrode or the limitation of the spatial structural change of the molecule itself. A possible solution is to design spacers with different rigidity and conjugation degrees to study the effects of molecular spatial structural changes and molecule/electrode interface coupling in the photoisomerization process. Furthermore, the energy transfer and CT processes should be further studied in combination with other new technologies, such as ultrafast optics.

Although significant achievements have been made during the development of single-molecule optoelectronic devices, many key issues still remain. For instance, the physical mechanisms mentioned in this paper, especially the charge effects, spin effects, exciton effects and vibration effects, still need to be investigated in depth. How do charge, spin, exciton and vibron affect electron transport in the single-molecule device? How do we manipulate the charge performance to further regulate device functions? How to effectively control the spin state in single-molecule devices has always been a problem. Can excitons and vibrons exist in the single-molecule devices for an enough time to be effectively monitored? In particular, can the dynamic processes of excitons and vibrons be clarified at the single-molecule level? How the electrodes in the devices affect excitons and vibrons in single molecules? All the above require further exploration.

Therefore, it is extremely important to develop disruptive device construction techniques, expand the current research systems, technologies and dimensions, explore working mechanisms in depth and realize new applications. In specific, to fabricate more efficient, stable and compatible single-molecule devices, new optimization techniques need to be developed to achieve precise nanogap electrodes and controllable molecule/electrode interface connections. Secondly, infrared, terahertz or microwave band lights should be introduced to explore the photoelectric interaction processes. To observe the ultra-fast photoelectron processes and chemical bond change processes of single molecules in these devices, it will be necessary to develop an ultrafast detection technology. In addition, the polarized light can be used to control specific physical properties of single-molecule devices, such as spin. Controlling some special environments, such as ultracold and strong magnetism, may bring some interesting new phenomena. In addition to improving the research techniques, the existing research systems should also be expanded. For example, the process of photoelectron transfer in biological protein systems, such as chlorophyll, should be explored. It should be noted that a measurement technique that combines a femtosecond laser technology and ultrafast electrical monitoring should be developed to reduce the temporal scale. Monitoring transient biological processes will bring many interesting discoveries. Thirdly, further in-depth exploration of physical mechanisms such as charge effects, spin effects, exciton effects, vibration effects, and structure and orbital effects at the single-molecule level will help to guide the development of single-molecule devices. These require elucidation of the underlying physical mechanisms and cleverly designed experiments. In the end, through understanding the quantum laws of single molecules, single-photon sources, high-sensitivity quantum sensors, quantum memories, quantum computations and other functional quantum devices can be realized. Of course, this must be based on overcoming the key problems, such as the environmental interference of spin memory devices and the energy quenching of single photon sources. We have enough reasons to believe that single-molecule optoelectronics has a bright future through strong collaborations among scientists from different disciplines.

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### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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