

Recent Advances in Photochemical Reactions on Single-Molecule Electrical Platforms

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The photochemical reaction is a very important type of chemical reaction. Visualizing and controlling photo-mediated reactions is a long-standing goal and challenge. In this regard, single-molecule electrical detection with label-free, real-time, and in situ characteristics has unique advantages in monitoring the dynamic process of photoreactions at the single-molecule level. In this review, a valuable summary of the latest process of single-molecule photochemical reactions based on single-molecule electrical platforms is provided. The single-molecule electrical detection platforms for monitoring photoreactions are displayed, including their fundamental principles, construction methods, and practical applications. The single-molecule studies of two different types of light-mediated reactions are summarized as below: i) photo-induced reactions, including reversible cyclization, conformational isomerization, and other photo-related reactions; ii) plasmon-mediated photoreactions, including reaction mechanisms and concrete examples, such as plasmon-induced photolysis of S-S/O-O bonds and tautomerization of porphycene. In addition, the prospects for future research directions and challenges in this field are also discussed.

1. Introduction

For a long time, photochemical reactions have been considered as a powerful approach to initiate various organic transformations under mild conditions and have been widely used in organic syntheses.^[1–5] Photomediated chemical reactions are initiated by absorbing light energy to trigger an excited state pathway.^[6–8]

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Generally, the light must have a specific wavelength to effectively produce the excited state and achieve the desired reaction. Light excitation contributes to a change in the electronic configuration of the compound. Since the chemical properties basically depend on the electronic structure, the chemical reactivity at the photochemical excited state is significantly different from that of the ground state. Monitoring the photoexcitation process with intermediates/transition states helps to understand the intrinsic photochemical reaction mechanism and pathway.^[9,10] In particular, the research at the single-molecule level can explore the detailed information hidden in the ensemble-averaged experiment, which is essential for finding out the reaction mechanism.[11-15]

Several single-molecule detection techniques that can reveal information about the behavior of individual molecules during photoreactions have

been developed.^[16] For instance, various optical strategies, such as fluorescence microscopy,^[17,18] optical tweezers,^[19–21] fluorescence resonance energy transfer,^[22,23] and surface plasmon resonance enhancement,^[24] have been used to detect single-molecule photoreactions. These optical methods are suitable for studying systems that have the inherent fluorescence or can be fluorescently labeled. On the other hand, the single-molecule electrical platform has the characteristics of label-free, realtime, in situ, etc., which can monitor the dynamic process of photoreactions at the single-molecule level.^[25,26] Furthermore, the electrical platform can capture intermediates and visualize the reaction pathways of photoreactions, playing a significant role in further understanding the intrinsic mechanism.

In this review, we focus on single-molecule photochemical reactions based on the single-molecule electrical platforms, which provide new insights for understanding the pathways and mechanisms of photochemical reactions. We first introduce single-molecule electrical platforms that can be used to study single-molecule photochemical reactions. According to the photoreaction conditions involved, two major categories of lightmediated reactions are further introduced: i) different types of light-induced reactions, including reversible cyclization reactions, conformational isomerization, and other light-related reactions; ii) plasmon-driven photoreactions, including reaction mechanisms and concrete examples. Finally, the prospects for future research directions and challenges in this field are also discussed.







Figure 1. Scanning tunneling microscope technique. a) Schematic view of probing single molecules with an STM tip. b) Schematic diagram of the STM tip with a constant LDOS to probe the single adsorbed molecule with a featured LDOS. The Fermi energy of the molecule is tied to E_F of the substrate upon adsorption. c) STM spectra and images for single CoPc (top) and CuPc (bottom) molecules. The filled regions in the d/dV spectra indicate molecular states that contribute to the STM images of the central molecules, respectively. Reproduced with permission.^[30] Copyright 2006, World Scientific Publishing Co. Pte. Ltd.

2. Single-Molecule Electrical Platforms

In recent years, the rapid development of nanotechnologies, especially those based on the single molecule, is of great significance for monitoring and manipulating molecules at the single-molecule level. Single-molecule electrical platforms are capable of transducing molecular characteristics, such as conformation changes, charge effects, and molecular interactions, into electrical signals.^[26] The electrical signals correlated with molecular states can be further used to analyze intermediates/transition states and visualize pathways of chemical reactions. We mainly focus on the single-molecule electrical technologies that have been applied in the detection of single-molecule photoreaction, including low-temperature scanning tunneling microscope, metal break junctions, and carbon electrode-based single-molecule junctions. The principles and practical applications of these strategies are discussed in detail.

2.1. Scanning Tunneling Microscopic Technique

Scanning tunneling microscope (STM) is a powerful technique for detecting and manipulating single atoms and single molecules with high spatial resolution.^[27] In particular, STM provides a platform to manipulate and detect single molecules absorbed on the substrate through the STM tip.^[28,29] In the application of STM, low-temperature STM imaging can intuitively characterize the important properties of single molecules. By applying a bias voltage to the tip of the STM and detecting the tunneling current, the morphological characteristics of single molecules on the surface of metal or semiconductor substrates can be provided (Figure 1a).^[30] It should be noted that the tunneling current is not directly related to the atomic structures of the single molecule, but is related to the distribution of the local density of states (LDOS) near the Fermi energy level (E_{r}) (Figure 1b). According to the principle of electron tunneling, the tunneling current is proportional to the convolution of the LDOS of the sample in the energy range. Therefore, assuming that the LDOS of the tip within the bias energy near the Fermi surface is constant and the geometric effect of the molecule is ignored, the STM image should theoretically be superimposed from the LDOS of the molecule from $E_{\rm F}$ to the bias voltage in a constant

current mode. In this regard, STM can be used to image single molecules on the atomic scale and study the properties of single molecules in terms of structure determination and electronic identification.

For instance, STM images of cobalt(II) phthalocyanine (CoPc) and copper(II) phthalocyanine (CuPc) adsorbed on the Au(111) surface have been studied (Figure 1c).[31] Although the two metal phthalocyanine molecules have the same organic molecular structure except for the different central metal ions, their STM images and spectra are quite different. The STM image of a CoPc molecule displays bright protrusion at the position of the Co atom, while the position of the Cu atom shows a hole. As it is known, the electron density and the local density of surface states near the Fermi level have a great effect on the STM image. The different imaging results are interpreted as that Co(II) with d⁷ configuration has significant d-orbital characteristics near the Fermi energy level, resulting in the tunneling enhancement, while d⁹ orbital of Cu(II) contributes little. Low-temperature STM has been also applied to probe the electronic properties of 5,10,15,20-tetraphenylporphyrin (AuTPP) molecules absorbed on the Au(III) surface in an ultrahigh vacuum environment. High-resolution constant current STM images of the single AuTTP molecule could be obtained under different bias voltages. The results show that the appearance of AuTPP is almost biasindependent in the voltage range of -1.3 V to +0.2 V, showing a saddle-shaped configuration. Although the STM image of AuTTP changes significantly at +0.9 V, the four bright protrusions centered over the mesocarbon atoms of the macrocycle become dominant with weaker contributions of the pyrroles. According to the tunneling spectrum, the high-resolution STM images at -1.3 V and +0.9 V could be interpreted as being dominated by contributions mainly from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. STM imaging is a powerful approach for monitoring and detecting single-molecule reactions with the characteristics of directness and visualization.

2.2. Single-Molecule Break Junction Techniques

Single-molecule break junctions, where single molecules serve as charge transport channels, can be fabricated by breaking metal



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Figure 2. Single-molecule break-junction techniques. a) STM break junction technique used to form Au-single molecule–Au junctions. Reproduced with permission.^[34] Copyright 2006, Nature Publishing Group. b) Conductance of a molecular junction formed between a gold STM tip and a gold substrate as the tip was pulled away from the substrate. Reproduced with permission.^[35] Copyright 2003, American Association for the Advancement of Science (AAAS). c) Operation principle of the mechanically controllable break junction: the formation and the size control of the nanogap are realized by bending the substrate through a three-point bending configuration. d) Current–voltage characteristics for MCBJ devices that were exposed to the pure solvent (top) and a solution of [Zn(5,15-di(p-thiolphenyl)-10,20-di(p-tolyl)porphyrin)] (ZnTPPdT) molecules (bottom). Reproduced with permission.^[38] Copyright 2013, Nature Publishing Group.

contacts in the presence of target molecules. Break junction techniques, including scanning tunneling microscope break junction and mechanically controllable break junction, usually aim to characterize electronic properties of single molecules trapped in two metal electrodes.^[32,33]

In the scanning tunneling microscope break junction (STM-BJ), the formation of metal-molecule-metal junctions is achieved by repeatedly moving the STM probe tip into and out of contact with the metal substrate in a solution with target molecules. The STM tip can be precisely regulated by a piezoelectric transducer. When the STM tip is close to the substrate, the end groups of the molecule can be connected to both the tip and the substrate electrodes, thereby forming a single-molecule junction (Figure 2a).^[34] Repeated displacement of the approaching/withdrawing tip from the substrate allows the construction of high statistical histograms, which can be used to analyze the probable conductance value of the molecule (Figure 2b).^[35] Therefore, the chemical reactions can take place and be monitored in a single-molecule junction based on the STM setup by recording different conductance characteristics. For instance, the STM-BJ method has been used to study nanocatalytic electrooxidative coupling in a series of anilines by in situ monitoring the single-molecule formation of azobenzenes. The break junction measurements are performed in an ionic environment using an insulated Au STM tip with an exposed area of $\approx 1 \,\mu m^2$ and an Au substrate with an area larger than 0.5 cm². The redox reactions could occur through tuning the electrochemical potential in an electric double layer, which is generated around the small tip area after applying a potential bias to the tip. The conductancedisplacement traces of the junction are measured at different tip bias voltages. When +100 mV tip bias is applied, only a short conductance plateau of 0.15 nm can be observed at 10^{-2} G₀, which proves the formation of an aniline-based junction. Increasing the tip bias to +600 mV would result in a new, longer plateau at the lower conductance of 9×10^{-3} G₀. The results indicate the new formation of the junction, which is verified as the synthesis of azobenzene derivatives.[36]

The mechanically controllable break junction (MCBJ) technique has been used to fabricate the nanogap with subangstrom precision to establish single-molecule junctions.^[37] The schematic illustration of an MCBJ setup is depicted in Figure 2c, which consists of a flexible substrate and a fixed metallic wire as a nanoelectrode.^[38] The metallic wire is fixed on the flexible substrate, and then a force is applied to the center of the substrate through a piezoelectric control push rod to bend the substrate. The wire is stretched and eventually ruptured to form an adjustable nanosized gap. The tunneling current can serve as a feedback control signal. After the nanogap is fully opened, it will trigger the push rod to move down, causing the nanogap to close.^[39] Since the MCBJ is employed to measure the conductance of single-molecule junctions based on benzene-1,4-dithiol, the application of the MCBJ technique has been extended to the field of molecular electronics. In addition to the measurement of single-molecule conductance properties based on the MCBJ (Figure 2d), reactions can be monitored at the single-molecule level. In situ formation and real-time detection of organometallic oligomer chains have been demonstrated by using the MCBJ approach in a liquid environment.^[40] In this experiment, a nanosized gold wire is broken in the presence of the target molecular solution to construct gold-molecule junctions. After repeatedly breaking and forming single-molecule junctions, different junction configurations would be addressed. The current through the single-molecule junction is monitored and used to determine the formation of organometallic oligomer chains. In addition, the MCBJ setup can be integrated with other test systems, such as Raman spectrometer, to get access to the fingerprint information of molecules.^[41] The advantage of the MCBJ setup is its high mechanical stability. However, the MCBJ technique is not suitable for characterizing the force and surface morphology, because it is still unknown for the atomic configurations and local shape of the electrodes. STM-BJ and MCBJ techniques provide complementary platforms for the formation and characterization of single-molecule junctions. Because of their similar working principles, conductance measurements of the same molecular system in similar environments are expected to show good agreement.

2.3. Carbon Electrode Based Single-Molecule Junctions

In addition to metal electrode-based single-molecule junctions, various nonmetal electrodes are also employed to construct single-molecule platforms, which have powerful operability and application. Among them, single-molecule junctions based on carbon electrodes, including single-walled carbon nanotubes (SWNTs) and graphene, have attracted more and more attention due to their unique features. Both SWNTs and graphene are composed of sp²-hybridized carbon atoms arranged in honeycomb sheets, which have the compatibility with organic/biological molecules. In addition, unlike the high mobility of atoms in the gold electrodes, carbon electrodes are atomically stiff and can form robust covalent bonds (e.g., amide linkages) or non-covalently contacts (e.g., π - π stacking interactions) at the molecule–electrode interface, with high stability and defined binding geometries.^[42]

SWCNT is a 1D nanowire with configuration-dependent electrical properties. Since the energy arrangement between the electrode and the molecule is adjustable, this provides an opportunity to construct a single-molecule junction based on the SWCNT electrode.^[43,44] SWCNT electrode-based single-molecule devices with covalent bonding can be constructed by using a lithography-



defined oxidative cutting method to generate terminal carboxylic groups at the edge of the nanogap (**Figure 3a**).^[45] More specifically, SWCNT is covered with a layer of polymethyl methacrylate (PMMA), and then high-resolution electron beam lithography (EBL) is applied to provide an ultrasmall (less than 10 nm) window precursor. Oxygen plasma ion etching is used to etch away exposed SWCNT to generate nanogap electrodes with carboxylic groups, which can covalently connect with the single molecule modified with amines through an amidation reaction to form a stable single-molecule junction. It should be noted that the size of nanogaps could be precisely regulated by varying degrees of oxidation, that is, by changing exposure time under oxygen. This method could achieve $\approx 20\%$ to 25% yield of single-molecule junctions under optimized conditions.

Graphene, a 2D zero-bandgap semimetal carbon material, has played a vital role in many fields.^[46] In addition, graphene has weaker gate response characteristics than SWCNTs, ensuring that the features of central molecules are not obscured when responding to the gate. Based on the feedback-controlledelectroburning method, nanogap graphene electrodes can be prepared, in which anthracene terminated molecules can be employed to bridge graphene electrodes via $\pi - \pi$ stacking interactions (Figure 3b).^[47] Specifically, the feedback-controlledelectroburning is performed as a voltage ramp applied to the graphene layer, accompanied by the current recording. When the current drops, the voltage is swept back to zero. Immediately afterward, a new voltage sweep is started and the process is repeated, thereby gradually narrowing the graphene electrode. The electroburning process is induced by Joule heating with large current densities, which helps carbon atoms react with oxygen at high temperatures. The electroburning method is less controllable, which leads to an unclear electrode configuration. Dash-line lithography (DLL) strategy has been developed to fabricate graphene point contact arrays with nanogaps less than 10 nm (Figure 3c).^[48] This method aims to obtain carboxylic acidterminated graphene nanogap electrodes, which provide a robust connection between target molecules and electrodes. In short, a piece of large-area single-layer graphene with high quality grown by chemical vapor deposition is transferred onto a Si/SiO₂ substrate, and then PMMA is spin-cast on the surface of graphene. Then, a designed CAD file with a 5 nm width dash line, where line A is exposed to an electron beam (e-beam) and separated by B (see Figure 3c), is used to open indented windows in PMMA by using ultrahigh-resolution EBL. After that, oxygen plasma ion etching is applied to etch away the exposed graphene through the open PMMA window. Finally, narrow gap between the indent graphene point is formed by exploiting the gradual etching and undercutting of the PMMA. The carboxylic acid groups on the edge of graphene electrodes can react with molecules containing amine terminals through amide linkages to form stable singlemolecule junctions.

3. Photoinduced Reactions

Due to the advantages of low cost, noninvasiveness, easy addressing, and high efficiency, light is considered as an ideal means to control organic reactions. Photochromic molecules under light stimulation can exhibit two or more mutually convertible states through the electronic excitation process.^[49,50] www.advancedsciencenews.com

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Figure 3. Carbon electrode-based single-molecule junctions. a) Schematic representation of cutting SWNTs into carboxylic acid-functionalized point contacts. Reproduced with permission.^[45] Copyright 2006, AAAS. b) Schematic representation of depositing a single molecule into a few-layer graphene nanogap, formed by feedback-controlled electroburning. Reproduced with permission.^[47] Copyright 2011, American Chemical Society. c) Schematic representation of cutting graphene by DLL-defined oxygen plasma oxidative etching to form indented graphene point contact arrays that are functionalized with carboxylic acids. A design CAD file with a 5 nm width dash line (A, 150 nm; B, 40 nm) is used for the cutting process. Reproduced with permission.^[48] Copyright 2012, Wiley-VCH GmbH.

Generally, photochemical reactions of photochromic molecules contribute to different conformational or electronic states, which show promising opportunities for building logical devices and memories at the molecular level.[51,52] Here, according to the features of photochromic molecules, photochemical reactions are divided into two categories, referred to as reversible cyclization reactions and conformation isomerization reactions (Figure 4). Reversible cyclization of photoresponsive molecules involves the formation and breaking of chemical bonds, including diarylethenes,^[53] spiropyrans,^[54,55] dihydropyrenes,^[56] dihydroazulenes,^[57] and norbornadienes.^[58] Photochromic molecules, including azobenzenes,^[59] styrenes, and acyl hydrazine,^[60] can undergo photoisomerization reactions. The molecular structure will be rearranged under the stimulation of light, resulting in a change in molecular conductance, which can be detected by single-molecule electrical platforms.^[61,62] Therefore, when the molecular junction is exposed to light, different conductance can be obtained and used as an indicator for monitoring the photoreaction process. The study of photochemical reactions by single-molecule electrical platforms provides opportunities to explore the mechanism of photoreactions and visualize photochemical processes at the single-molecule level, and further enrich their applications in the fields of synthesis, catalysis, and functional devices. $^{\left[63-66\right] }$

3.1. Reversible Photocyclization

In the photochemical reaction, photoresponsive molecules, such as diarylethenes, spiropyrans, dihydropyrenes, dihydroazulenes, and norbornadienes, exhibit chemical bond formation and breakage under light illumination, which is considered as reversible cyclization reactions. When a photochromic molecule acts as a bridge to connect electrodes in the single-molecule device, the biggest challenge is quenching of the photoexcited state of the molecule during the photochemical reaction, which obstructs the study of the intrinsic photochemical process. Theoretical studies have indicated that the strong electronic coupling between the electrode and the molecule at the interface may be the cause of the quenching of the molecular excited states.^[67] Another factor is the relative position between the Fermi level of the electrode and the energy level of the excited molecule. Hence, we will focus on the factors that affect the photochemical reaction in single-molecule devices and discuss the strategies to solve these problems.





Figure 4. Two kinds of photochemical reactions based on their reaction features.

One of the typical reversible cyclization reactions is based on the diarylethene molecule, which has received the most attention and has been extensively studied in single-molecule devices.^[53,68] Diarylethene displays two conformations and undergoes reversible photocyclization between an open-ring state and a closed-ring state under a specific wavelength of light. When a diarylethene molecule in a closed state is connected to two gold electrodes through an Au-S bond to form a single-molecule junction, the molecule can transform into the open state by exposing the molecular junction to light with a wavelength in the range from 500 to 700 nm. However, due to the attachment of the molecule to gold, the photochemical reaction in the junction with metal molecules is irreversible. Specifically, the Fermi energy level of gold is close to the energy level of the excited state of the diarylethene molecule in its open state, which leads to the quenching of the excited state, thereby inhibiting the ring-closing process of the molecule.^[69,70] A strategy has been developed by using SWNT electrodes instead of metal electrodes to form the diarylethene-based single-molecule electronic devices by covalently bonding.^[71] The photochemical reaction of diarylethene can achieve from an open state to a closed state, which is the opposite of the gold-break junction. However, the photoexcited closed state is quenched due to the strong interface coupling between the conjugated molecule and the electrode, and the reversible reaction cannot occur.

To study the intrinsic process of the photochemical reaction, the problem of quenching the excited state during the reaction should be solved by adjusting the molecule-electrode interface coupling.^[72] In order to realize the reversible photochemical reaction in the single-molecule junction, many efforts have been made. For instance, inspired by molecular engineering design that can be used to regulate the energy level alignment and electronic coupling of the molecule-electrode interface, diarylethenes with different side groups and anchoring groups are designed to tune the energy level alignments, and further used to form graphene-based single-molecule junctions.^[73] The fluorinated unit is used to substitute the hydrogenated cyclopentene of the diarylethene. Due to its electron-withdrawing property, it reduces the electron density on the central alkene unit and increases the molecular conductance. The introduction of methylene groups (CH₂) between the terminal amine group and the functional center can decrease electron delocalization, resulting in the decoupling of the electronic interaction between the molecule and the electrode. Despite these efforts, the reversible photochemical reaction of diarylethenes has still not been achieved in graphene-based single-molecule junctions. In order to further reduce the molecule-electrode coupling, three methylene (CH₂) groups are designed and incorporated into each side of the diarylethene molecule. At this time, the reversible photochemical reaction of diarylethene is achieved, and the

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Figure 5. Single molecule reversible photocyclization reactions. a) Schematic representation of graphene–diarylethene–graphene single-molecule junction. Reproduced with permission.^[74] Copyright 2016, AAAS. b) Schematic representation of DHP/CPD single-molecule junction. Reproduced with permission.^[77] Copyright 2013, American Chemical Society. c) Schematic representation of the photochemical and thermal relaxation reaction between norbornadiene (NB) and quadricyclane (QC). Reproduced with permission.^[78] Copyright 2017, American Chemical Society. d) Molecular structures of spiropyran derivatives and schematic illustration of the reversible single-molecule reaction in response to UV radiation. Reproduced with permission.^[80] Copyright 2014, American Chemical Society. e) Schematic representation of MCBJ measurement of photoconversion of dihydroazulene under in situ UV irradiation. Reproduced with permission.^[84] Copyright 2017, Nature Publishing Group.

photochemical process is in situ monitored by the graphenebased single-molecule junction (**Figure 5**a).^[74] Specifically, combined with theoretical simulations, it is proved that structural modification would weaken the molecule-electrode coupling strength, thereby avoiding the quenching of the molecular excited state. Experimental results show that when exposed to ultraviolet (UV) and visible (vis) light radiation, the molecular conductance between the high-conductance state and the lowconductance state is reversible. This indicates that the reversible photochemical reaction of a single diarylethene molecule has been achieved, and the intrinsic photochemical process has been successfully monitored at the single-molecule level. The above strategies have proved that molecular engineering has the potential to regulate photochemical reactions in single-molecule devices.

Dihydropyrene (DHP) is an ideal photochromic molecule, which can be converted into cyclophanediene (CPD) by breaking the chemical bond under the stimulation of visible light.^[56,75,76] This reaction process is reversible under UV radiation or thermal activation. By using the MCBJ technique, the reversible photochemical reaction of the bispyridine-substituted DHP molecule

can be monitored (Figure 5b).^[77] Specifically, a single DHP molecule with two pyridine rings on the opposite side is designed and connected to gold electrodes. The conductance-distance traces show the evolution platform of $10^{-6.5}$ $G_0 \leq G \leq 10^{-1}$ G_0 in the experiment, which is determined to be the closed form of the isomer DHP. Irradiating the DHP solution in a liquid cell of the MCBJ stage with visible light for 30 min results in in situ formation of the open isomer CPD. At the same time, no plateaus can be observed in the corresponding conductancedistance traces of single-molecule junctions with the photogenerated CPD species. The conductance change may be caused by the degree of conjugation of molecular structures. In comparison with CPD, DHP shows a polycyclic π -conjugated unit. This photochemical reaction leads to an excellent on/off ratio, which may serve as a promising candidate for fabricating addressable molecular building blocks.

Norbornadiene (NB) is a bicyclic hydrocarbon that undergoes photoisomerization into the metastable quadricyclane (QC) form under light stimulation.^[58] The quadricyclane form can relax back to the norbornadiene form by thermal activation. This photochemical reaction of the norbornadiene molecule has been

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studied through the STM-break junction platform (Figure 5c).^[78] Specifically, in order to study the photochemical properties of NB, the UV-vis absorption spectrum of NB is measured in toluene. The absorption wavelength starts around 460 nm. Due to the extended π conjugation in NB, it has a significant red shift compared to unsubstituted norbornadiene. Irradiating the toluene solution of NB with visible light causes its photoisomerization to QC, and the isosbestic point in the absorption spectrum indicates that the photoconversion reaction is complete. Since the configuration of NB has a π -conjugated unit, it provides a conductive pathway for electrons to pass through the molecule, leading to a higher conductance. Upon photoexcitation, the central NB molecule undergoes intramolecular [2 + 2] cycloaddition, rehybridizing the orbitals from sp² to sp³, and finally generates the photoisomer product QC. The electron transport through QC is dominated by the σ system with less conjunction pathway, which displays a lower conductance state. It is worth noting that QC can return to NB through thermal relaxation, and thermal conversion can be determined through experiments involving temperature.

Spiropyran (SP) is a well-studied photochromic molecule that can break the heterolytic C-O bond and transform from the closed-ring SP isomer to the open-ring zwitterionic merocyanine (MC) isomer under an external stimulus, including light, mechanical force, acid-base, metal ions, and temperature.^[54,79] Due to the sp³ spiro center between the chromene and the indoline moieties, the stable SP form absorbs in the UV region. However, the MC form absorbs in the visible region. The MC form has a planar configuration with extended π -conjugation, while the conjugation structure in the closed SP form is destroyed. The superior photochemical properties of spiropyran molecules are expected to be used in the development of spiropyran-based molecular devices and the study of their photochemical reaction processes. For instance, spiropyran molecule has been used as a molecular bridge to establish a single-molecule junction for studying its photochemical reaction at the single-molecule level (Figure 5d).^[80] The two ends of the spiropyran molecule contain -NO₂ groups, which have a good affinity with the gold surface to form a stable connection with the gold electrode. The SP in the mesitylene/dichloromethane solvent mixture is in a colorless form with a maximum absorption at 362 nm and is transformed into the blue merocyanine form, which has a new maximum absorption value at 610 nm under UV irradiation. The red shift of the absorption spectrum may be due to the increase in conjugation when SP is converted to MC. However, MC relaxes back to SP with a faster relaxation time after turning off the UV radiation. This is due to the presence of another -NO₂ group on the indoline side of SP, which makes the N⁺ in the open MC state more electrophilic. The STM-BJ technique is further used to measure the photochemical reaction based on the spiropyran molecule. Two conductance states at $\approx 0.023 G_0$ and $\approx 0.051 G_0$ can be observed in the dark, and a high conductance level at ≈ 0.15 G_0 appears under UV light irradiation. The higher conductance at $\approx 0.15 G_0$ is attributed to the MC state, which is caused by the smaller bandgap, the complete delocalization of frontier orbitals and the extended conjugation along the entire molecule. This photochemical reaction is reversible. When the UV radiation is turned off, the conductance peak at $\approx 0.15 G_0$ disappears.

The spiropyran molecule can also be used as a photocatalyst to provide a proton under light illumination. On this basis, a photoinduced proton-transfer strategy (PIPT) is designed to realize a reversible single-molecule reaction based on the azulene, and the MCBJ technique is used to study it.^[81] Specifically, the ringopened cyanine serves as a photoacid, releasing proton when the ring is closed and returns to the spiropyran form under blue light irradiation. At the same time, azulene derivatives will accept the proton released by merocyanine, and will lose the proton during the transformation of spiropyran to merocyanine in the dark. The PIPT strategy opens a new way to realize the reversible reaction of non-photoresponsive molecules and apply it to novel molecular materials and devices.

(DHA)/vinylheptafulvene The dihydroazulene (VHF) system can undergo significant structural changes upon irradiation.^[57,82,83] The photothermal reaction process of the photochromic dihydroazulene/vinylheptafulvene system has also been studied by the MCBJ measurement (Figure 5e).^[84] The single-molecule junction based on the DHA-6 molecule is obtained by attaching it to gold electrodes through Au-S bonds, and a conductance can be observed in the range of $10^{-3.0}$ – $10^{-4.5}$ G₀. Under UV irradiation, a new conductance around $10^{-4.5}$ – $10^{-6.0}$ G_0 appears, which can be assigned to VHF. The photoreaction process of DHA-6 is also explored by in situ UV irradiation, and the reaction kinetics is further studied by statistical analysis of the changes in the percentage of DHA-6 over time. It is found that the conversion from DHA-6 to VHF could not be completely accomplished after 120 min of UV irradiation, which is caused by the nonradiative decay of plasmon in the nanogap and the inevitable heating effect of irradiation. This indicates that other potential factors affecting the detection of photochemical reactions at the single-molecule level should be considered in the future design of the reaction. Although VHF could not relax back to DHA-6 through light stimulation, external heating at ≈ 60 °C should be applied to achieve the reversible ring-closing process. It is worth noting that another possible reaction may in principle generate DHA-7. From the perspective of conductance-displacement characterization, DHA-7 can form DHA-6 through VHF under UV illumination, but this process is reversible regardless of light or heat. Conductance measurement also shows that the conductance of DHA-7 is lower than that of DHA-6 and VHF. Theoretical simulations reveal that the conductance of the DHA-7 molecule with destructive quantum interference is significantly smaller than that of the DHA form with shifted quantum interference and the DHA-6 form without quantum interference. More importantly, in addition to the simple application as a molecular switch, the adjustment of reaction kinetics, potential barriers, and final product ratios in novel environments can be studied by single-molecule junctions.

3.2. Photoinduced Conformational Isomerization

Conformational isomerization is one of the most important types in photochemical reactions, which involves changes in the molecular structure without forming or breaking chemical bonds.^[59] Azobenzene molecule is a typical example, which has attracted more and more attention due to its chemical stability and tunability. Azobenzene is an aromatic azo precursor containing two benzene rings bridged by the N=N bond. After absorbing light, it can reversibly undergo a conformational change between *trans* and *cis*. The *trans* azobenzene exhibits a nearly planar conformation, while the *cis* form adopts a nonplanar conformation, with its phenyl rings twisted to minimize steric repulsion.^[85] Regarding the photoisomerization process of azobenzene, the involved electronic excited states and reaction pathways have been controversial for a long time.^[86,87] Generally, it is recognized that the isomerization mechanism follows $n-\pi^*$ and $\pi-\pi^*$ excitation.^[88] Upon $\pi-\pi^*$ excitation of the *trans* isomer under UV light, it undergoes a conical intersection to decay to the S₀ ground electronic state, resulting in *trans*-to-*cis* isomerization. However, the *cis*-to*trans* conversion is triggered by visible light, which corresponds to the energy gap of the $n-\pi^*$ transition.

The isomerization reaction of azobenzene can be studied at the single-molecule level by the low-temperature STM technique.^[89-91] However, the photoisomerization process of azobenzene can be suppressed because the strong coupling at the molecule-substrate interface results in a shorter life of the excited state on the metal surface. Therefore, in order to realize the reversible photochemical reaction of azobenzene molecules on the metal surface, it is necessary to avoid the quenching of the photochemical process. For instance, tert-butyle "legs" (TB: C_4H_9) are introduced to the azobenzene backbone to avoid quenching.^[92] The reversible photochemical reaction of azobenzene molecules on the gold surface can be observed. STM has been used to image the features of azobenzene molecules on Au(111) before and after the reversible cycle of mechanical structures between cis and trans states under light irradiation. Specifically, the constant current line scan of the azobenzene molecule shows that the TB-functionalized molecule is progressively taller than the naked azobenzene molecule. The experimental results prove that the TB-leg functionalization method could lift photomechanical molecules from the surface and provide a new strategy for overcoming quenching. Furthermore, it should be noted that the substrate-mediated process rather than the direct photoisomerization of the azobenzene occurs. Light is first absorbed by the d-band of the metal, and then isomerization of the molecule is initiated by electron transfer from the molecule to the hole generated in the d-band. A thin insulating layer of NaCl can also be used to decouple the molecules from the metal substrate. For instance, the direct photoisomerization of 4,4'dihydroxyazobenzene (DHA) can be achieved on a thin insulating sodium chloride (NaCl) layer on Ag(111) (Figure 6a).^[93] Specifically, the reaction process has been studied by STM at 5 K. The STM image of the trans configuration shows a double protrusion, while the cis configuration shows a protrusion after UV light (365 nm) illumination (Figure 6a). The possible mechanism of the UV light-induced isomerization is through the direct absorption by molecule rather than an indirect process. The wavelength dependence measurement is used to elucidate the isomerization process, in comparison with the absorbance spectra of the DHA in liquid phase, the wavelength of the UV filter (350 nm) matches the π - π * absorption peak of the *trans*-configuration, and the π - π^* transition is followed by the rotation of N=N bond (Figure 6b). In addition, the presence of the 0.56 nm thick NaCl spacer layer is expected to reduce the transfer probability of photoexcited electrons of the substrate to a negligible value, and the energy of UV light (365 nm, 3.4 eV) is not sufficient to excite Ag(111) d-band electrons with the band edge of 4 eV below the Fermi energy. The experimental results show that trans-to-cis isomerization occurs through the rotation pathway, while the inversion pathway of *cis*-to-*trans* isomerization is efficiently suppressed. The theoretical calculation shows that the electrostatic repulsion between the OH group and the Cl anion may be the reason for suppressing the inversion pathway. This suggests that the atomic details of inert surfaces should be considered, as they can have a significant impact on the nanoscale function of single molecules.

The photochemical reaction of azobenzene has also been explored on the single-molecule junction platform, which shows stable and reliable characteristics.^[94] For instance, the photochemical reaction of azobenzene has been studied in a grapheneelectrode-based single-molecule device (Figure 6c).^[95] As expected, the azobenzene unit undergoes a conformation change from a trans state to a cis state under UV irradiation, resulting in a decrease in the conductance state. This decrease in conductance is due to the larger HOMO-LUMO energy gap of the cis state and/or the poorer energy level alignment with the Fermi level of the electrodes. The reverse photoreaction from the cis form to the trans form can realize conductance recovery (Figure 6d). The stability and reversibility of the photoreaction can be tested by monitoring the current changes of the same device in real time under a series of ultraviolet and visible light irradiation under a constant bias voltage. Taking advantage of the large changes in geometric and electronic structure in the process of reversible photochemical reactions, azobenzene molecules can be used in the fields of information processing and digital storage devices.^[59] Through further molecular design, a reversible azobenzene single-molecule reaction can be realized in the device by utilizing light and electrical fields as external stimuli (Figure 6e).^[96] Specifically, the azobenzene moiety is introduced as a side chain of the molecular bridge to avoid the quenching of the molecular excited state, and the backbone CH₂ groups are replaced by benzene rings to enhance charge transport. Both experimental and theoretical studies have shown that different sourcedrain bias voltages or UV/vis light irradiation at low bias voltages can easily trigger the switching behavior (Figure 6f). This concept of in situ chemical gating provides a new perspective for the practical creation of multifunctional single-molecule optoelectronic devices. It also provides a new perspective for monitoring photochemical reactions in single-molecule devices without the quenching of the excited state.

Dynamic covalent chemistry involves reversible chemical reactions that form/break dynamic covalent bonds under external stimuli. Acyl hydrazine is a typical example, which can reversibly break and regenerate C=N bonds in response to different acid-base environments, as well as the transformation of C=N bonds under light and heat stimulation.^[60,97] By using STM-BJ and eutectic Ga-In (EGaIn) technique, a single dynamic acyl hydrazine bond is used to construct customized molecular devices for studying photothermal and acid-base mediated reactions (Figure 7a).^[98] Specifically, the photothermal isomerization reaction is confirmed by single-molecule conductance measurements with a fixed bias of 100 mV. After 30 min of the UV light (365 nm) stimulation of the acyl hydrazone bondconjugated (E) 4-pyridinecarbaldehyde isonicotinoyl hydrazone (E-PCIH), the presence of a significant low conductance of the *cis* isomer (Z-PCIH) is located at $10^{-5.8\pm0.23}$ G₀ (0.1 nS). The conductance change is attributed to the isomerized C=N bond in the acyl hydrazone, and the reversible reaction can be achieved by

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Figure 6. Single-molecule photoinduced conformational isomerization. a) Ball-and-stick models of the *trans*-isomer (left upper) and the *cis*-isomer (left bottom) of the 4,4'-dihydroxyazobenzene molecule. STM image of a *trans*-isomer and a *cis*-isomer on a NaCl double layer on Ag(111) (right). b) Absorption spectrum of *trans*- (black line) and *cis*- (black dotted line) dihydroxyazobenzene in a 1,4-dioxane and spectrum of Hg lamp with different filters. Gray: UV filter. Light gray: vis filter. The upper inset shows corresponding orbitals for native azobenzene. The lower inset shows simultaneous atomic resolution of the chlorine lattice imaged with functionalized tip. Reproduced with permission.^[93] Copyright 2012, American Physical Society. c) Photoinduced reactions in the graphene–azobenzene junction under ultraviolet and visible light irradiation. d) Time trace of the drain current for the same device showing the reversible photoswitching events under irradiation with UV light and visible light. Reproduced with permission.^[95] Copyright 2013, Wiley-VCH GmbH. e) Schematic representation of a single-azobenzene device to achieve reversible isomerization reaction under optical/electrical stimuli. f) Dipole projection on the molecular backbone (upper). Real-time measurements (bottom) of reversible switching between *cis* and *trans* forms of TTDA upon exposure to UV and visible light irradiations, respectively. Reproduced with permission.^[96] Copyright 2019, Nature Publishing Group.

operation under thermal stimulation (Figure 7b). These observations emphasize the opportunity to access unique molecular devices by introducing the concept of dynamic covalent chemistry, which has great potential for designing responsive molecular electronics and nanomachines at the single-molecule scale.

Overcrowded alkenes can achieve chiral switching through external stimuli and act as molecular motors. The photochemical reaction occurs based on the *cis-trans* photoisomerization around the central C–C double bond, which is the basic driving force for molecular rotation. The overcrowded alkenes have been used to functionalize solid-state devices (Figure 7c).^[99] Owing to the asymmetric stereochemistry around the double bond, the system undergoes a unidirectional 360° rotation. The rotation cycle goes through four distinct steps: two photochemical steps and two thermal steps, resulting in the P (right-handed)/M (left-handed) chirality inversions during 360° molecular rotation. Since the spin-polarization in the chirality-induced spin selectivity effect depends on the chirality of the molecule, the spin-polarization direction of electrons passing through the molecular motor should be switched by light irradiation or thermal treatment, which can be proved by spin-valve-like measurements with a clear up-spin selectivity for M-*trans* device and down-spin selectivity for P-*cis*







Figure 7. a) Photochemical reactions of acyl hydrazone in the STM-BJ. b) Reversible ON–OFF conductance transition of *E*-PCIH and *Z*-PCIH triggered by UV at 365 nm and heat at 65°. Reproduced with permission.^[98] Copyright 2021, Wiley-VCH GmbH. c) Single-molecule switch based on a chiral motor molecule. The spin-polarization direction of the current switches with the inversion of the chirality. d) MR curves for the devices fabricated individually with M-*trans* isomer (blue plot), M-*trans* isomer after irradiation with visible light for 5 min (sky blue plot), and P-*cis* isomer (orange plot). Sky blue plots show MR after photoirradiation. Reproduced with permission.^[99] Copyright 2019, Nature Publishing Group.



Figure 8. Photo-driven single carbocation reaction. a) Schematic representation of the photoinduced reaction to form carbocation in STM-BJ. b) Schematic representation of the energy level structures for charge transport before and after the formation of a carbocation. Reproduced with permission.^[100] Copyright 2019, The Royal Society of Chemistry.

device (Figure 7d). This opens up a new way for the development of next-generation organic optical/thermal spintronic devices in combination with molecular machines.

3.3. Other Photo-Driven Reactions

Photoinduced reactions involving unstable intermediate or active species, such as radicals and carbocations, have also been studied at the single-molecule level. For instance, the photo-driven reaction of malachite green leucoethanol (MGOH) molecules, which are precursors of carbocations, has been studied at the single-molecule level by using the STM-BJ technique (**Figure 8a**).^[100] Specifically, in the presence of 302 nm UV light, MGOH effi-

ciently produces malachite green carbocations (MG⁺) and hydroxide ions. To confirm the formation of the carbocations, the UV–vis absorption spectra of MGOH before and after UV irradiation are tested. The MGOH has a peak at 299 nm before irradiation. Two peak bands appear at 416 and 610 nm after irradiation, the intensity of which increases with the increase of the illumination time, corresponding to the characteristics of triphenylmethane carbocation. This is because the photo-driven reaction of MGOH causes a slight structural change, in which the orbital hybridization of the central carbon atom changes from sp³ to sp². Single-molecule electrical measurements are further performed to study this photochemical process. A low conductance at $\approx 10^{-4.97}$ G_0 can be observed before illumination, and

a higher conductance of $\approx 10^{-3.43}$ G_0 is displayed with 302 nm light illumination. The low conductance and high conductance correspond to single-molecule junctions with MGOH and carbocation, respectively. This photo-triggered formation of carbocation narrows the HOMO–LUMO gap and enhances the transmission close to the Fermi level (Figure 8b), resulting in a significant increase in molecular conductance with high reversibility. The photo-driven carbocation can enhance the charge transport in the triphenylmethane single-molecule junction, opening the way for the design of photochemical reactions and the study of dynamic processes. The capture of active species, such as radicals, carbocations/carbanions, and excited intermediates, can help to deepen the understanding of photochemical reaction pathways and mechanisms, but achieving this goal based on the existing single-molecule platforms is still a long-term challenge.

4. Plasmon-Mediated Reactions

In the past decade, plasmon-induced chemical reactions on metal nanostructures have received increasing attention due to their efficient use of light energy to control chemical reactions.[101-104] Due to the unique and tunable optical properties of plasmonic nanomaterials, plasmon-induced chemical reactions show different mechanisms and have potential advantages over traditional photochemical reactions.^[105-107] Surface plasmon are the collective oscillation of conduction electrons in metallic nanostructures, such as Au, Ag, and Cu nanomaterials.^[108] Since the oscillation frequency of electrons matches that of light waves, the localized surface plasmon resonance will be excited. It can overcome the optical diffraction limit by concentrating electromagnetic radiation to a small area on the metal surface and enhancing the local field. Therefore, the molecules adsorbed on the metal nanostructures are induced to undergo photochemical reactions, such as photodissociation and photodesorption of the molecules. The study of plasmon-mediated chemical reactions at the single-molecule level will help to understand their mechanisms and promote their applications. In particular, STM technology is a prominent experimental method to study the potential mechanisms of plasmon-mediated reactions on metal surfaces, because the reaction process of single molecules can be observed by analyzing the current traces. This section first discusses the excitation mechanism of plasmon-induced reactions, including indirect hot-electron transfer mechanism,^[109] charge transfer mechanism,^[110] and direct intramolecular excitation mechanism.^[111] After that, typical plasmon-mediated reactions based on the STM technology with different excitation mechanisms are discussed.

4.1. Mechanism of Plasmon-Mediated Reactions

The illumination of a plasmonic nanostructure triggers a series of subsequent processes. Specifically, the localized surface plasmon (LSP) is resonantly excited by light to generate a strong electric field near the metal surface, immediately along with the generation of hot electrons and holes through nonradiative decay of the LSP. Then, the energy distribution of the hot carriers in the metal evolves through electron interaction, electron– electron scattering and electron–phonon scattering, and finally heat is dissipated to the surrounding medium through thermal conduction. The strong electric field, electron–hole pairs, and heat generated in this process can serve as high-efficiency excitation sources for initiating the chemical reaction.^[106] The excitation mechanism and energy transfer pathway determine the plasmon-induced photochemical reaction of the molecules adsorbed on the metal nanostructures (**Figure 9**).^[111]

In the indirect hot-electron transfer mechanism (Figure 9a), electron-hole pairs are generated in the metal nanostructures due to the nonradiative decay of the localized surface plasmon. The excited carriers redistribute energy through the electron-electron scattering processes, forming a hot Fermi-Dirac distribution.^[109] Hence, hot electrons above or at the LUMO energy level can transfer to those orbitals of the adsorbed molecules through a three-step process. As a result, a transient negative ion state of the absorbed molecule, that is the molecule with the high-energy electron, is generated and survives on the metal surface for tens of femtoseconds, which is long enough to initiate a chemical reaction. The other resonance excitation process is the charge transfer (Figure 9b). If the energy of the localized surface plasmon is consistent with the energy gap between the metal state and the LUMO of the molecule, the charge transfer from the metal state near the Fermi level to the LUMO can be induced through a one-step process. Importantly, evidence from numerous surface-enhanced Raman spectroscopy studies has confirmed that electrons excited by the plasmon are transferred to molecules adsorbed on the metal surface. Because the electron transfer process increases the electron density in the empty molecular orbitals and generates new features in the Raman spectrum. Therefore, the charge transfer mechanism can also be used to explain the chemical enhancement effect of surface-enhanced Raman scattering. By contrast, unlike the case of indirect hot electron transfer and charge transfer, the direct intramolecular excitation mechanism (Figure 9c) does not involve the transient negative ion state, because there are separated holes and electrons in the molecule. It is proposed that the direct transition of the high-energy electrons from HOMO to unoccupied orbitals is excited by plasmon resonance with the same energy as the HOMO-LUMO gap, and there is no excited state electron distribution in the metal. In general, different excitation mechanisms will lead to different energy transfer pathways. In plasmon-mediated reactions, the indirect hot electron transfer mechanism is used to explain most cases. However, there is no direct evidence. Thus, the plasmon-mediated reaction mechanism is still a subject worthy of further study.

4.2. Plasmon-Induced Photolysis Reactions

The plasmon-induced photolysis of the S–S bond in a single dimethyl disulfide [(CH₃S)₂] molecule adsorbed on Ag(111) and Cu(111) surfaces can be realized by direct intramolecular excitation, which is confirmed by the STM study. Specifically, after 532 nm p-polarized light is used to excite the localized surface plasmon between the metal substrate and the Ag tip (**Figure 10**a), the STM images of (CH₃S)₂ molecules near the Ag tip are preferentially transformed into two identical circular light spots (Figure 10b).^[111] However, the rotation of the (CH₃S)₂ molecule could be observed before the dissociation of the S–S bond during the



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Figure 9. Excitation mechanisms for plasmon-mediated reactions of molecules adsorbed on plasmonic nanostructures. a) Indirect hot-electron transfer mechanism. b) Charge transfer mechanism. c) Direct intramolecular excitation mechanism. Reproduced with permission.^[111] Copyright 2018, AAAS.



Figure 10. Plasmon-mediated single-molecule reactions. a) Schematic illustration of the experiment for the plasmon-induced photodissociation reaction of dimethyl disulfide. b) The STM images of $(CH_3S)_2$ molecules before and after excitation with 532 nm p-polarized light. Reproduced with permission.^[111] Copyright 2018, AAAS. c) Schematic illustration of the experiment for the plasmon-induced photodissociation reaction of oxygen on the Ag(110) surface with Au tip. Reproduced with permission.^[114] Copyright 2020, Wiley-VCH GmbH. d) Porphycene tautomerization cross-section of the optical near-field excitation and far-field excitation. Reproduced with permission.^[117] Copyright 2017, American Chemical Society.

inelastic electron tunneling process by injecting tunneling electrons from the Ag tip, which indicates that the transient anion state of the absorbing molecule caused by electron injection is dissipated into a vibrationally excited state. Therefore, it can be inferred that the two CH_3S molecules are formed due to the dissociation of the S–S bond caused by the direct intramolecular excitation of high-energy electrons from the HOMO to the unoccupied orbital of the $(CH_3S)_2$ molecule. To be precise, the high-energy electron jumps from the nonbonding lone pair orbital of the S atom to the antibonding orbital of the S–S bond.

For a long time, the study on the dissociation reaction of O₂ molecules chemically adsorbed on metal surfaces has aroused great research interest, which is very important in the plasmon-catalysis reactions.^[112,113] Interestingly, the indirect hot-electron transfer mechanism for the dissociation of a single O₂ molecule

in a plasmon-catalysis reaction is generally considered to be a controversial issue. To clarify the excitation mechanism of the strong chemisorption molecular system, a single-molecule experiment of the plasmon-induced dissociation reaction of O₂ molecules with two adsorption orientations on the Ag surface has been carried out under low-temperature STM (Figure 10c).^[114] By further combining the STM action spectroscopy with density functional theory calculations, it is found that O₂ [001] and O₂ [110] molecules adsorbed on Ag(110) are negatively charged, which is due to the transfer of hot electrons from the metal states to the antibonding (π^*) orbitals of O₂ molecules. Since energy dissipation occurs within tens of picoseconds, the formed transitional negative ion O₂⁻ can continuously activate the O₂ molecule along the vibrational coordinate. When the vibration energy accumulates to a certain extent, it will eventually cause the dissociation of the O_2 molecule. Moreover, not only hot electrons but also hot holes can cause the dissociation of single O_2 molecules. The degree of hybridization between molecular orbitals and metal states contributes to the mechanism of molecular excitation and the yield of the plasmon-induced dissociation reactions, which inspires the design and control of plasmon-induced reactions.

4.3. Plasmon-Induced Tautomerization

Intramolecular H atom transfer-induced tautomerization can be catalyzed by plasmon as well. The study of porphyrin molecules based on STM provides a unique model for understanding the mechanism of tautomerization at the single-molecule level.^[115] For instance, by low-temperature STM and laser excitation from the near-infrared regime to the ultraviolet regime, the photoinduced tautomerization of a single porphycene molecule adsorbed on the Cu(111) surface from the unidirectional trans configuration to *cis* configuration has been observed.^[116] The results show that the tautomerization process occurs through the excitation of molecular vibrations after photoexcitation. In addition to the above-mentioned excitation process in photochemistry on the metal surface, the optical near-field excitation of metallic nanostructures induced by plasmon can also effectively promote the tautomerization of a single porphycene molecule in the nanoscale gap. In comparison with the excitation process in photochemistry, plasmon can significantly enhance the reaction cross-section, which is attributed to the near-field attenuation of excitation leading to an increase in the rate of carrier formation. For instance, porphyrin molecules adsorbed on the Cu(111) surface are in the thermodynamically stable trans or metastable cis configuration. When the incident photon is absorbed by the substrate, the excited hot carriers will be transferred to the porphyrin molecule, resulting in the transition of the porphyrin molecule from the ground state to the transition ionic state. Subsequently, the process of intramolecular H atom transfer is promoted by reducing the activation barrier. In addition, the tip enhancement effect can be demonstrated by comparing the tautomerization cross-section in the presence and absence of the metal tip. In the far-field excitation experiment, the metal tip is kept away from the Cu(111) surface during the illumination to exclude any influence from the STM tip to the reaction. It is proved that the tip enhancement effect is mainly attributed to the increase of hot carrier generation rate caused by the plasmon in the STM junction. Meanwhile, the wavelength-dependent tautomerization cross-section reveals the plasmon-induced near-field spectral response of a single porphyrin molecule (Figure 10d).^[117] The near-field spectral response characteristics of plasmon-induced STM junctions provide a reasonable idea for the design of single-molecule nearfield sensors, which will help to study the characteristics of an extremely confined light.[115]

5. Conclusion

Photochemical reaction is an important type of chemical reaction. The investigation of the photochemical reaction process and mechanism has drawn constant attention. The rapid development of single-molecule techniques provides opportunities for monitoring and controlling chemical reactions, which provide detailed information on reactions that are different from the ensemble events. Here, the latest developments in single-molecule electrical platforms and typical single-molecule photochemical reactions are discussed. Specifically, three typical single-molecule electrical platforms for studying photochemical reactions are introduced from the construction and measurement principles, including STM imaging, single-molecule metal break junctions and single-molecule junctions based on carbon electrodes. STM imaging can provide direct visualization of photochemical reactions, and single-molecule junctions can reveal the intrinsic pathways of reactions by monitoring single-molecule conductance. After that, two different types of single-molecule photochemical reactions are introduced, including photo-induced reactions and plasmon-mediated reactions. In detail, according to whether the formation or breaking of chemical bonds is involved, photo-induced single-molecule reactions can be divided into reversible cyclization reactions, conformation isomerization reactions and other photo-mediated reactions. For plasmon-mediated single molecule reactions, mechanisms such as indirect hotelectron transfer, charge transfer, and direct intramolecular excitation determine the photochemical reaction paths. Plasmoninduced of S-S bond and O-O bond photolysis and plasmoninduced porphycene tautomerization have been studied at the single-molecule level by STM.

Despite these advances, new strategies still need to be developed to solve the problems and challenges faced in the study of single-molecule photochemical reactions. Specifically, in order to monitor the intrinsic processes of single-molecule photochemical reactions, further molecular engineering and device design are required to reduce interface coupling and suppress the quenching effect of the electrode on the excited state. For instance, in the STM characterization process, the contact between the molecule and the metal surface is recognized to affect the photoisomerization properties, which is expected to be resolved using spacer groups for functionalization. Since excited intermediates are rarely captured in the inherent photochemical process, it is still a long-term challenge to reveal the mechanisms and pathways of photochemical reactions through realtime electrical measurements. It is necessary to further develop single-molecule electrical platforms with high resolution and efficiency to detect excited states and monitor the reaction processes. In addition, combining the femtosecond laser, Raman, infrared, and terahertz technologies with single-molecule electrical platforms may help obtain multimodal information and reveal the mechanism of single-molecule photochemical reactions. In addition to developing reliable single-molecule platforms, attention should be paid to photochemical reactions based on other classes of photochromic molecules, such as dihydroindolizines,^[118] chromenes,^[119] napthopyrans,^[120] and some important photophysical properties such as photoselection. These in-depth and systematic studies on photochemical reactions at the single-molecule level will promote the basic understanding and practical application of photochemical reactions.

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Conflict of Interest

The authors declare no conflict of interest.

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