



Physical properties of transition metal complexes in single-molecule junctions

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Abstract Transition metal possesses a unique d-orbital electronic structure, which imparts a diverse range of physical and chemical properties. These properties render them significant in fields such as chemistry and materials science. The distinctive optical, electrical, and magnetic properties of these complexes can be attributed to the variations in the quantity of d-orbital electrons, thereby influencing their spin and orbital characteristics. The d-orbitals facilitate the formation of stable multidirectional bonds with ligands, resulting in a variety of geometric structures and rich coordination chemistry. These interactions result in variations in energy levels, thereby producing diverse electrical properties, including low attenuation coefficients, high rectification ratios, and unique multi-channel transmission. Moreover, the unpaired electrons in

the d-orbitals can give rise to diverse magnetic behaviors, leading to magnetic effects such as spin-related interfaces, switches, and magnetoresistance. This paves the way for extensive possibilities in the design and application of single-molecule devices. This review elaborates on single-molecule physical properties of transition metal complexes, including length attenuation, rectification, multi-channel transmission, thermoelectric effect, and spin regulation, which are vital for the functionalization and regulation of molecular electronics. In addition, this review also explores the correlation between these physical properties and the electronic structure of transition metals, discussing the broad prospects of transition metal complexes in the fields of nanoelectronics, optoelectronics, and quantum technology.

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1 Introduction

Main-group elements hold a significant position within the periodic table and are distinctly classified into s-block and p-block elements [1]. The s-block elements include elements whose outermost electrons occupy s-orbitals, such as lithium (Li), sodium (Na), potassium (K), and magnesium (Mg). Conversely, p-block elements possess outer electrons predominantly arranged in p-orbitals, such as boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl). Additionally, elements situated between these two blocks, distinguished by their distinct electron configurations and properties, are referred to as transition metals,



including iron (Fe), copper (Cu), nickel (Ni), cobalt (Co), and manganese (Mn) [2].

Due to the diversity of their d-orbital electrons, transition metals can participate in the formation of variable complexes [3, 4]. The characteristics of the d-orbitals in transition metal complexes play a crucial role in determining their magnetic [6], spectroscopic [7], redox [8], and catalytic properties [9–12] by influencing electron distribution, energy-level splitting, and orbital mixing. Firstly, the interactions between the d-orbitals of the transition metals and the ligand fields are crucial to reveal the properties of these complexes [14, 15]. The magnitude of d-orbital splitting is subject to variation due to the strength of the ligand field, which consequently influences the distribution of electrons within these orbitals. In the instance of strong-field ligands, a more pronounced splitting energy is typically observed, prompting d-electrons to gravitate toward the orbitals of lower energy and thus triggering a state of low spin [16]. This particular behavior affects not only the magnetic properties inherent to the complex, but also significantly influences its spectroscopic characteristics, reactivity, and redox potential. Furthermore, the relationship between the d-orbitals and the geometric configuration of the complex is integral to its properties [17]. The spatial positioning of ligands has the potential to modify the energy levels and symmetry of the d-orbitals. For example, in octahedral and tetrahedral coordination structures, the energy splitting patterns of the d-orbitals vary, thereby directly influencing the color, stability, and reactivity of these complexes. Additionally, the electronic properties of the ligands, such as their capabilities for donating or withdrawing electrons, are crucial determinants of the electron density within the d-orbitals [18]. Ligands with a strong electron-withdrawing ability can reduce the electron density in the d-orbitals, thereby elevating the oxidation state of the complex, which consequently influences its redox properties and catalytic activity [19, 20]. When compounds serve as ligands to bind with transition metal atoms or ions, the transition metal complexes are formed through coordination bonds [22, 23]. These complexes integrate the distinct characteristics of transition metals, including catalysis [24, 25] and magnetism [26–28], while preserving the compounds' solubility and the design flexibility in molecular structure. Consequently, transition metal complexes demonstrate extensive potential applications in diverse fields such as materials science [30–32], chemical engineering [34], and biomedicine [35, 36]. Additionally, in comparison with the pure organic molecules, transition metal complexes exhibit higher conductance and lower resistivity, rendering them particularly valuable in areas such as electronic and optoelectronic devices [37, 38].

Transition metals exhibit attractive electrical, optical, and magnetic properties due to their distinctive d-orbital

electronic structures. They have rich geometric structures and properties by forming stable multidirectional bonds with ligands. Moreover, unpaired electrons in d-orbitals can also cause a variety of spin effects. The strategy of building single-molecule junctions with transition metal complexes in nanogap electrodes makes it possible to study the physical properties of the complexes at single-molecule level. Investigating these single-molecule physical effects is not only a frontier direction in molecular electronics, but also a crucial aspect for realizing the function of molecular devices. This paper focuses on the five key physical properties exhibited by transition metal complexes in single-molecule junctions: length attenuation effect [40, 41], rectification effect [43, 44], multi-channel effect [46, 47], thermoelectric effect [48, 49], and spin effect [50, 51]. In addition, this review also explores the correlation between these physical properties and electronic structure of transition metals, providing valuable information for their applications in switches, sensors, memory devices, and other fields. Finally, we discuss the broad prospects of transition metal complexes in the fields of nanoelectronics, optoelectronics, and quantum technology.

2 Foundation of research

2.1 Structural basis of transition metal complexes

For transition metal elements, it can be observed that the energy levels of the d-orbitals are lower than those of the s-orbitals, which indicate the electron configuration of the d-orbitals in transition metal elements critically influences their chemical properties. As shown in Fig. 1a, there are five different types of d-orbitals: d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, and d_{z^2} . The spatial arrangement and directionality of these orbitals enable them to bond with ligands in multiple directions, generating various, intricate, and stable complexes [53]. The diversity in d-orbitals refers to the phenomenon that when forming a complex with ligands, the originally degenerate five d-orbitals (d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, and d_{z^2}) of a transition metal ion undergo an energy-level splitting, resulting in the formation of sub-orbitals with unequal energies. This diversity in d-orbitals offers significant variability in the structures and properties of transition metal complexes. This diversity in d-orbitals results in significant variability in the structure and properties of transition metal complexes [9]. For example, specific catalytic activity for chemical reactions can be achieved by tuning ligands and transition metals in the complexes. Alternatively, precise control over the magnetic, optical, and other properties can be achieved by adjusting the structure of the complexes [54, 55].

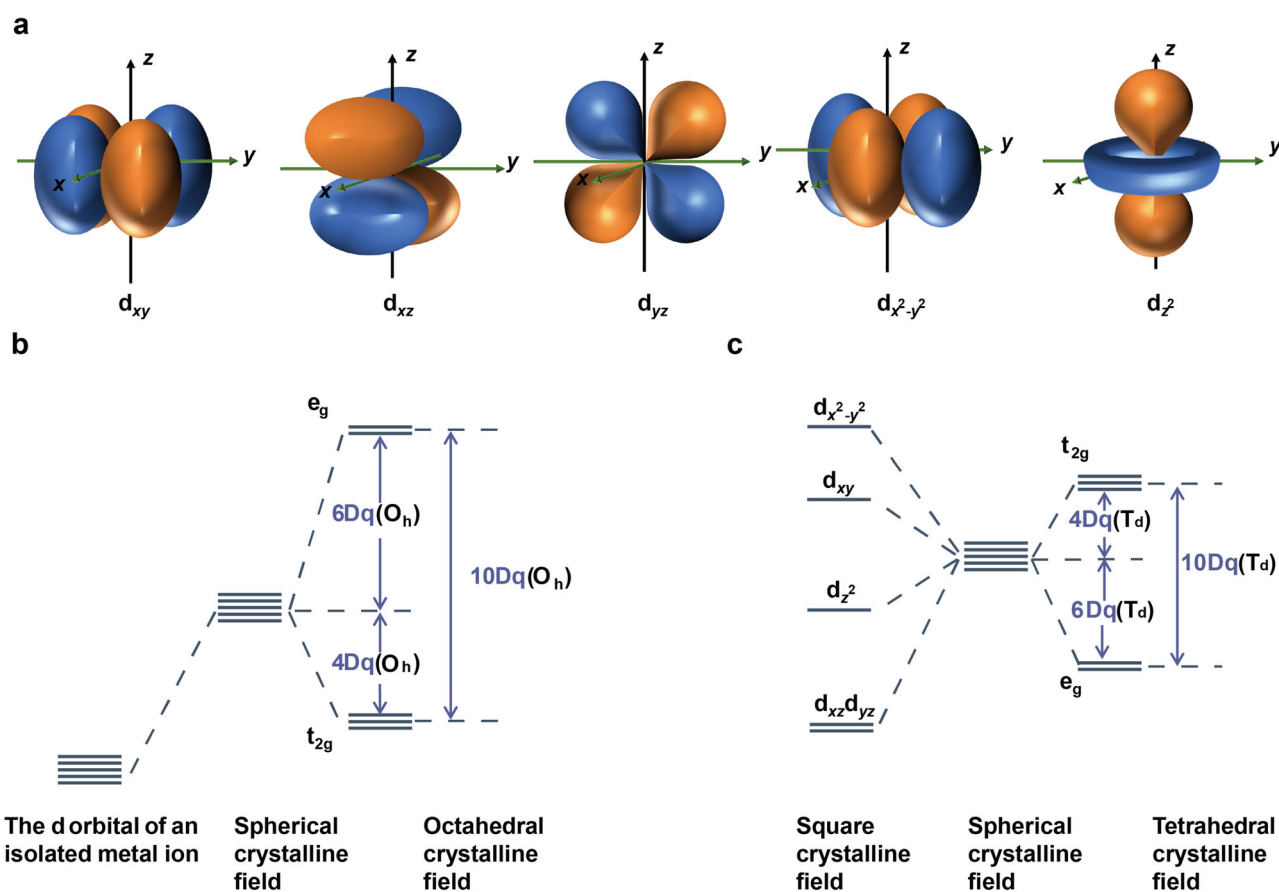


Fig. 1 a d-orbital splitting of the transition metal. Reproduced with permission from Ref. [53]. Copyright 2021, Chinese Chemical Society. d-orbital splitting of octahedral **b** and tetrahedral **c** structures under crystal field theory. Reproduced with permission from Ref. [9]. Copyright 2023, Elsevier

Therefore, the research of transition metal complexes is not only crucial for comprehending the fundamental principles of metal–ligand interactions, but also a powerful tool for developing novel functional materials.

Upon examining the coordination structures of transition metal complexes, researchers encounter an impressive level of complexity and diversity. Common coordination structures encompass tetrahedral, square planar, and octahedral geometries. These structures not only determine the geometric shape of the complexes, but also have profound effects on the d-orbital energy states of the transition metal ions. The d-orbital splitting in transition metal complexes with different coordination structures is demonstrated in Fig. 1b, c. In isolated d-orbitals, the electron distribution is uniform, and the energy states are consistent. However, when metal ions bind with ligands to form complexes, the electrons provided by the ligands interact with the d-orbital electrons of the metal ions, resulting in changes in the energy states of the d-orbitals, known as d-orbital splitting. For transition metal complexes with different coordination structures, their d-orbital splitting varies. When a metal ion

is surrounded by six unidentate ligands, forming an approximate octahedral configuration, the splitting of the d-orbitals is more pronounced due to the stronger electron repulsion between the negative charge of the ligands and the d-orbital electrons, such as $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{NH}_3)_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$. In contrast, in a square planar coordination structure, where the metal ion is surrounded by four unidentate ligands in a planar square arrangement, the splitting of the d-orbitals is relatively lower because the electron repulsion between the negative charge of the ligands and the d-orbital electrons is weaker [57], such as $[\text{PtCl}_2(\text{NH}_3)_2]$, $[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, and $\text{Rh}(\text{C}_5\text{H}_7\text{O}_2)(\text{CO})_2$. In addition to the influence of coordination structures, other factors of the complexes, such as the type of ligands, the coordination number [58], and the charge state of the metal ions, can also affect d-orbital splitting [59, 60]. Variations in these factors can lead to changes in the electrical, optical, and magnetic properties of the complexes. When comparing the splitting of d-orbitals under different structures, these influences become even more significant, enabling a deeper

understanding of the electronic structures and properties of complexes. This comprehension not only enhances our knowledge of the microscopic world but also provides valuable insights for further research and practical applications.

2.2 Single-molecule junction technology

Recent advancements in molecular electronics have made the integration of transition metal complexes into molecular circuits an ideal method for exploring their inherent molecular characteristics [61, 62]. The single-molecule junction (electrode–single molecule–electrode) as the fundamental molecular electronic device is an essential prerequisite for exploring electrical transport properties. Since 1996, when Weiss and his colleagues first connected a single molecule between two metal electrodes using an electron microscope, the direct exploration of the intrinsic properties of molecules and the realization of molecular electronic devices at the single-molecule level have invigorated scientific enthusiasm [63]. Due to d-orbital splitting and crystal field modulation, transition metal complexes exhibit distinct charge transfer patterns and quantum effects in molecular electronics.

In molecular electronics, the dynamic break junction technology (Fig. 2a–c) and the static junction technology (Fig. 2d–f) are two typical measurement technologies. The dynamic break junction technology achieves repetitive

connection and detachment with the molecules in solution by repeatedly breaking and reconnecting electrode pairs, thereby obtaining thousands of current signal data in a short period. Depending on the equipment used, the dynamic break junction technology can be categorized into mechanically controlled break junction technology (MCBJ) (Fig. 2a) [64, 65], scanning tunneling microscope break junction technology (STM-BJ) (Fig. 2b) [66, 67], and atomic force microscope break junction technology (AFM-BJ) (Fig. 2c) [69, 70]. Each of these technology offers distinct advantages: MCBJ provides excellent anti-interference ability and mechanical stability; STM-BJ enables testing of the charge transport properties of molecules and obtaining their surface topography; AFM-BJ realizes the electrical properties of molecular junctions and the mechanical properties of contact sites [71]. Static junction technology involves molecular capture and assembly on fixed nanogap electrode pairs. Although static junction technology cannot obtain statistical patterns from a large amount of experimental data like dynamic junction methods, it better aligns with the integrated circuit technologies. Depending on the nanoelectrode materials, they can be divided into gold electromigration electrode technology (Fig. 2d) [72, 73], graphene point electrode technology (Fig. 2e) [75–77], and eutectic gallium–indium alloy technology (Fig. 2f) [74, 79, 80]. The nanoelectrodes prepared by the first two technologies can connect and measure a single organic molecule, while the latter is used to

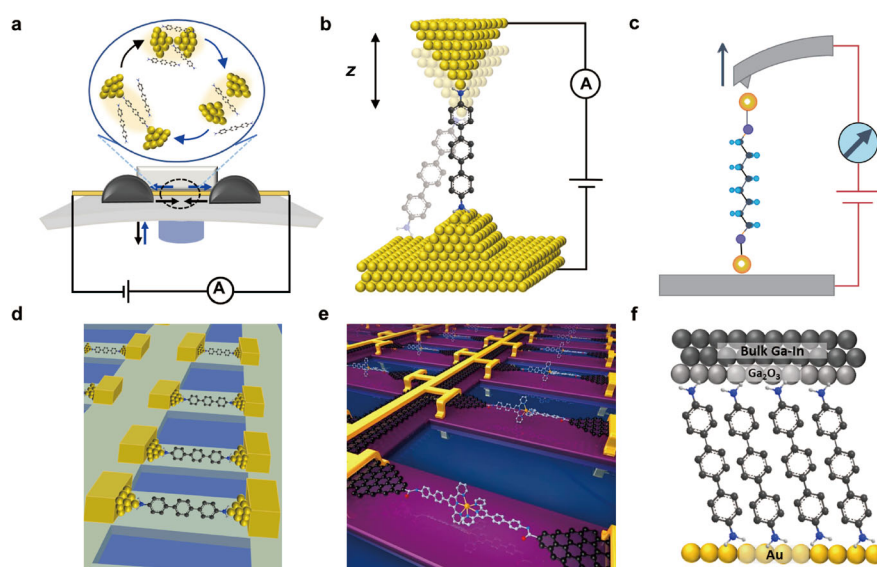


Fig. 2 **a** Mechanically controlled break junction. Reproduced with permission from Ref. [65]. Copyright 2013, Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim. **b** Scanning tunneling microscope break junction. Reproduced with permission from Ref. [68]. Copyright 2003, American Association for the Advancement of Science. **c** Atomic force microscope break junction. Reproduced with permission from Ref. [70]. Copyright 2000, American Chemical Society. **d** Electromigration technology of gold electrode. Reproduced with permission from Ref. [73]. Copyright 2016, American Chemical Society. **e** Graphene point electrodes technology. Reproduced with permission from Ref. [78]. Copyright 2014, Chinese Chemical Society. **f** Eutectic of Ga–In technology. Reproduced with permission from Ref. [79]. Copyright 2018, Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim

characterize the electrical properties of larger molecules or self-assembled monolayers.

In the field of molecular electronics, a thorough investigation of the energy-level relationship between the electrodes and the molecules is essential in comprehending the working principles of single-molecule electronic devices. Typically, the Fermi level of the electrodes is situated between the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule, rather than aligning directly with either [82, 83]. This mismatch in energy levels is a typical phenomenon in molecular electronics and is the primary reason for the formation of contact barriers, which significantly influence the charge transfer characteristics of the molecular junction. The height, width, and possible defects of the barrier are key factors in determining charge transport. Given that the part of the barrier originates from the molecular junction itself, the microscopic quantum effects within the molecular junction have become a hot topic of research. These quantum effects not only reflect the interaction between the molecule and the electrodes but also determine the performance and functionality of the molecular device [84]. Due to their distinct d-orbital splitting characteristics, transition metal complexes serve as ideal candidates for studying the correlation between barrier variations and quantum effects.

3 Charge transport characteristics

3.1 Length attenuation effect

In molecular circuits, analogous to macroscopic ones, resistance increases and molecular conductance decreases with the extension of the molecular wire's transmission distance. The tunneling attenuation constant (β), as a key indicator for characterizing the intramolecular charge transport efficiency, reflects the correlation between single-molecule conductance and charge transport distance. A lower β value indicates a higher efficiency of long-range charge transfer within the molecule, which is crucial for achieving efficient molecular electronic devices [61].

Charge transfer mechanisms at the single-molecule level can typically be divided into two categories: coherent tunneling and incoherent hopping. These two mechanisms exhibit a certain overlap in their length-dependent relationship. Under the coherent tunneling mechanism, the relationship between conductance and molecular length follows $G_m \propto e^{-\beta L}$, where G_m represents the single-molecule conductance and L signifies the molecular length. This equation suggests that conductance decreases exponentially with an increase in molecular length, with the rate of decrease modulated by the β value.

However, under the incoherent hopping mechanism, the relationship between conductance and molecular length follows $G_m \propto \beta L$. This means that during the incoherent hopping process, the conductance changes linearly with the increase in molecular length, but this change is also influenced by the β value [62]. Designing and achieving long-distance charge transfer at single-molecule scale is a paramount research objective in molecular electronics. To meet this goal, researchers have been exploring various approaches to minimize the tunneling attenuation constant (β). An effective strategy among these is the formation of metal complexes through the integration of metal centers. The incorporation of transition metal centers instigates the π -d- π interaction between the metal and ligand along the molecular skeleton, significantly raising the energy level of the HOMO orbital and thereby reducing the energy gap between HOMO and LUMO. Additionally, it establishes a new electron transport pathway within the molecular skeleton. These two effects synergistically lead to a lower length decay factor of the metal complexes, thus optimizing their properties in comparison with structurally similar organic compounds. Consequently, metal complexes display an enhanced efficiency and a mild decay during charge transport.

Since 2003, ruthenium (Ru) complexes have attracted significant attention due to their stable structural properties and diverse photophysical characteristics. In the realm of single-molecule science, the introduction of Ru centers has not only strengthened the stability of molecular junctions but also notably enhanced their conductivity. This development represents a crucial milestone in the advancement of molecular electronics [85, 86]. In 2018, Tanaka et al. systematically explored the length decay effect of Ru metal complexes with $\text{Ru}(\text{dppe})_2$ as the core and alkyne as the skeleton, by employing the STM-BJ technology [87]. The distinct doping effect of the $\text{Ru}(\text{dppe})_2$ fragment is described, resulting in high conductance and low attenuation factor of polyacetylene molecules with Ru centers. Specifically, the attenuation constant (β) value is $0.25 \text{ \AA}^{-1}$, slightly less than pyridyne ($0.29 \text{ \AA}^{-1}$) and phenylacetylene ($0.35 \text{ \AA}^{-1}$), suggesting superior charge transfer ability of the former.

Based on Tanaka's work, Zhang et al. narrowed the structural differences between metal complexes and organics, further verifying the high charge transport capacity of Ru complexes [62]. For structural stability and rigidity, they opted for oligophenylene as the skeleton and compared the decay constant between Ru complex and oligophenylene compounds with varying numbers of alkynes. They found that the introduction of Ru metal centers significantly enhanced molecular charge transport, aligning with Tanaka's findings and further affirming the substantial potential of Ru complexes in molecular

electronics. Furthermore, as illustrated in Fig. 3a, b, as the number of alkynes increased, the molecules' charge transport distance gradually increased while the conductance of Ru alkyne complexes progressively decreased. The decay constant of Ru complexes is approximately 2.60 nm^{-1} , compared to 4.60 nm^{-1} for pure organic compounds. This indicates that the conductivity of the Ru complex decays more slowly than that of the pure organic alkyne compound, suggesting that Ru complexes can maintain high-conductance properties even over longer molecular chains, opening up possibilities for the development of long-distance molecular wires. To further explain this phenomenon, Zhang et al. conducted comprehensive theoretical calculation. According to these

calculations, the high conductance of metal complexes can be attributed to elevation of the HOMO energy level, bringing it closer to the Fermi level. The decrease in conductance attenuation is due to the reduction in effective carrier mass after Ru's participation in electron delocalization. This discovery provides a new perspective on the charge transport mechanism of Ru complexes and also provides theoretical support for the future design of molecules with high-conductance transport properties. It is worth mentioning that Ru and platinum (Pt) both belong to the ruthenium group of metals, resulting in numerous similarities in properties for the metal complexes containing these two metals [88, 89]. Although the introduction of Pt metal centers may inhibit the charge transport capacity

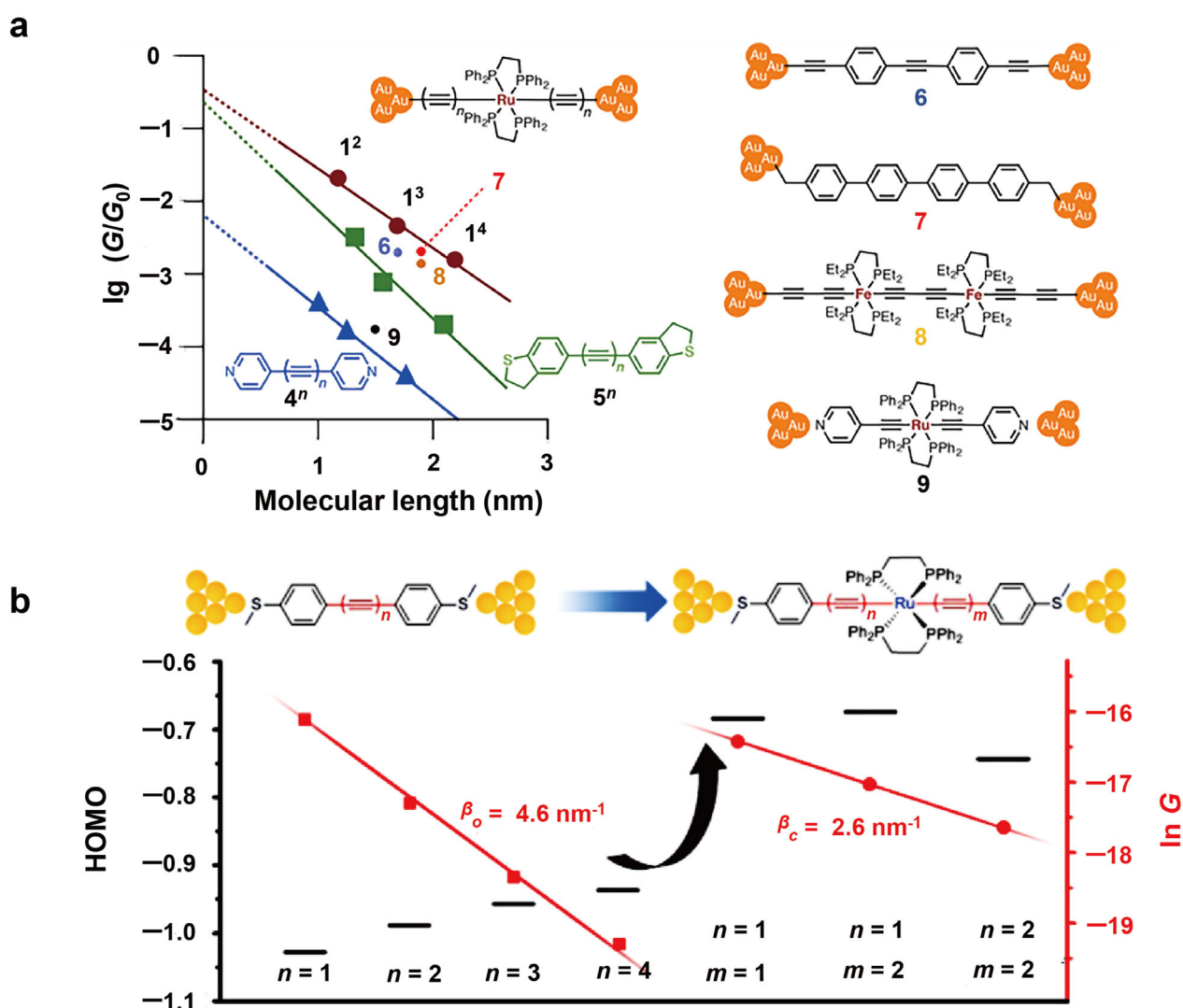


Fig. 3 **a** Single-molecule conductance and molecular lengths of the Ru complex, Fe complex, and the corresponding organic molecule. Reproduced with permission from Ref. [87]. Copyright 2018, American Chemical Society. **b** Comparisons of HOMO energies and conductance between Ru complex and oligophenylene. Reproduced with permission from Ref. [62]. Copyright 2019, American Chemical Society

of molecular junctions in some cases, it can also reduce the length decay effect of molecular junctions to a certain extent. This finding presents a new idea for designing molecular wires, namely optimizing the conductance of molecules by rationally selecting metal centers. In general, Ru complexes have shown great potential and application value in the field of molecular electronics. As researchers continue to deepen their understanding of their conductive mechanisms and innovate molecular design, it is reasonable to expect the emergence of more high-performance molecular electronic devices based on Ru complexes in the future.

Apart from Pt and Ru, Co, Fe, and Zn complexes manifest lower length decay coefficients compared to organic compounds at the same length. Interestingly, certain complexes exhibit even lower length decay coefficients than those of Ru. In 2020, Yao et al. synthesized Co/Ru polypyridyl oligomers on gold via the electrochemical reduction in diazonium salts, utilizing STM to construct single-molecule junctions, as shown in Fig. 4a [90]. Based on the experimental results illustrated in Fig. 4b, the charge transfer capacity of $\text{Au}[\text{Co}(\text{tpy})_2]_n\text{-Au}$ ($n = 1\text{--}4$) was found to be insensitive to the molecular length and displayed a minimal length decay constant ($\beta \sim 0.19 \text{ nm}^{-1}$). This suggests that an increase in molecular length does not significantly diminish its charge transport

capability. This efficient charge transport capability is attributed to its dominant resonant transport mechanism. In 2012, Lu et al. successfully amplified the molecular conductance of oligo(phenylene ethynylene) (OPE) under both tunneling and hopping mechanisms by incorporating ferrocene into the molecular backbone as shown in Fig. 4c [91]. In addition, they also analyzed the influence of ferrocene on the attenuation constant under various transmission mechanisms. Under the tunneling mechanism, ferrocene and OPE exhibit almost identical attenuation constants, but under the hopping mechanism, ferrocene demonstrates a milder attenuation effect. Furthermore, Yao et al. conducted the first comparison between the attenuation coefficient of porphyrin Co and pure porphyrin [92], revealing that the former's attenuation coefficient is 0.28 nm^{-1} , significantly lower than the 0.67 nm^{-1} of pure porphyrin oligomers. This finding not only underscores the distinct advantage of porphyrin Co oligomers in electron transport but also serves as a valuable reference for future research. Besides porphyrin Co, porphyrin Zn also displays a lower length decay coefficient than pure porphyrins, as demonstrated in Fig. 4d–f [93].

The charge transport behavior of molecules strictly adheres to established physical laws, with the tunneling decay constant (β) serving as a core metric that significantly impacts charge transport efficiency. To facilitate the

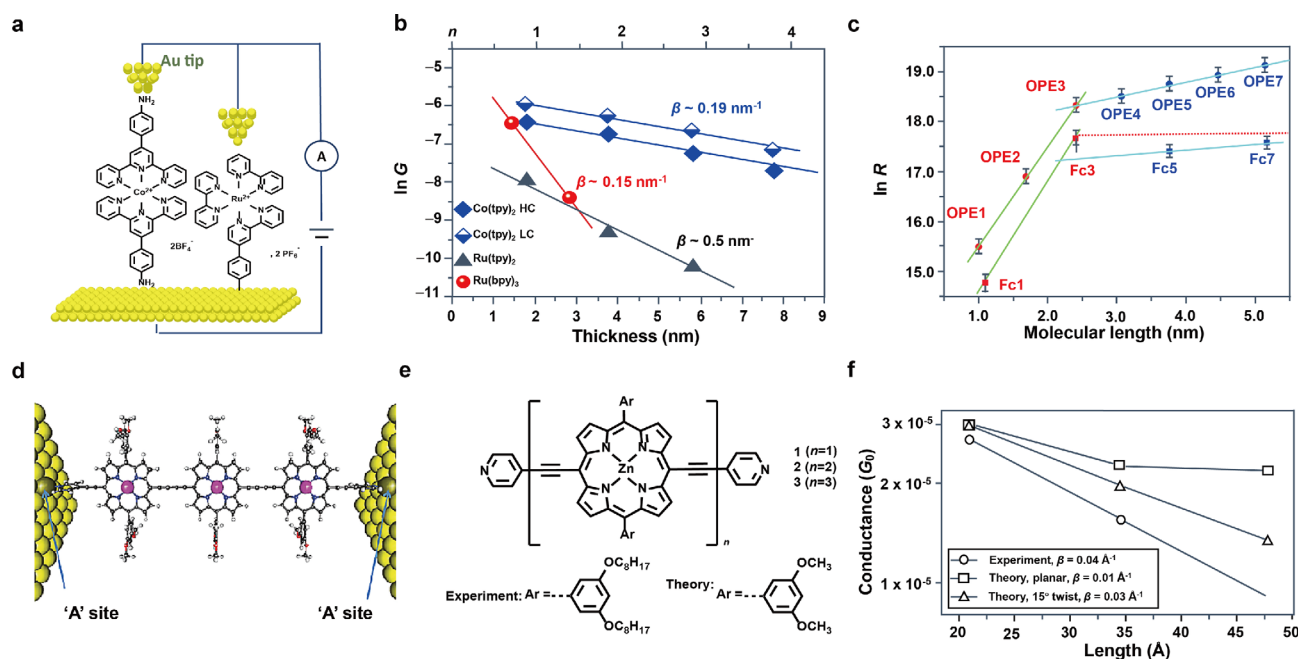


Fig. 4 **a** Schematic illustration of $\text{M}(\text{tpy})_2$ and $\text{M}(\text{bpy})_3$. **b** Attenuation factor (β) versus thickness dependence for $\text{Co}(\text{tpy})_2$, $\text{Ru}(\text{tpy})_2$, and $\text{Ru}(\text{bpy})_3$ SMJs (tpy = terpyridine, bpy = bipyridine). Reproduced with permission from Ref. [90]. Copyright 2020, American Chemical Society. **c** Plot of single-molecule resistance versus molecular length for oligo(phenylene ethynylene) (OPE) and ferrocene (Fc) junctions. Reproduced with permission from Ref. [91]. Copyright 2012, American Chemical Society. **d** Schematic representation of the butadiyne-linked trimer between Au electrodes. **e** Structure of the oligo-porphyrins. **f** Length dependence of conductance for oligo-porphyrins. Reproduced with permission from Ref. [93]. Copyright 2011, Springer Nature Limited

development of highly efficient molecular electronic devices, scientists have consistently strived to minimize β values. One effective strategy involves introducing metal centers, such as Ru, to construct metal complexes. This approach not only substantially augments conductivity but also ingeniously optimizes length decay characteristics, resulting in a more efficient and stable charge transport. Furthermore, it is important to acknowledge that the complexes with other transition metals, including Pt, Co, Fe, and Zn, also exhibit considerable potential in reducing length decay coefficients, thereby broadening the scope for innovative design in the field of molecular electronics and presenting a diverse range of possibilities. These researches will significantly accelerate progress in molecular electronics technology, guiding us toward an intelligent and efficient era of electronics.

3.2 Rectifying effect

The rectification effect occurs when the conductivity of an electronic component is directional and dependent on the direction of the applied current. Electronic components exhibiting this effect are termed diodes. Diodes have extensive applications in electronic circuits, and their distinct rectification properties render them an essential component of the circuit. Through the coordination with other electronic components such as resistors, capacitors, and inductors, the diodes can construct circuits with various functions to accommodate various electronic application requirements, achieving functions such as power rectification, signal detection, amplitude limitation, modulation voltage clamping, and voltage stabilization. The rectification ratio of a diode serves as a crucial performance indicator, describing the difference in conductivity between the measurements under forward and reverse biases [94]. A higher rectification ratio facilitates one-way conductivity in the circuit, which is the key to the widespread use of diodes in many electronic applications.

In 1974, Aviram and Ratner first presented the concept of the single-molecule diode, discovering that some molecules exhibit a rectification effect similar to that of semiconductors, and they further proposed the possibility of replacing semiconductor components with molecules [95]. From 1974 to the present, the performance of molecular diodes has gradually improved, and the rectification ratio has increased from the original single-digit to nearly three orders of magnitude. By exploring a large number of molecular diodes with donor-bridge-accept structure, it has been found that the rectification ratio of organic molecular diodes based on a single energy level is difficult to exceed 1000, indicating the need to explore alternative charge transfer mechanisms to achieve larger values. With their distinct electronic structures, metal

complexes serve as excellent research subjects in this context.

In 2018, Huseyin et al. employed conductive-probe atomic force microscopy (CP-AFM) to assess the electrical properties of binuclear Ru complexes **2-Ru-N**, employing tetrapodal phosphonic acid as an anchoring group, as depicted in Fig. 5a [96]. They directly regulated humidity levels between low ($\sim 5\%$) and high ($\sim 60\%$) to examine the charge transfer characteristics of the **2-Ru-N** junction under both conditions. The experimental results revealed a significant impact of humidity on the I - V characteristics of the **2-Ru-N** junction. Under high humidity condition, the I - V curve of the junction exhibits diode characteristics, whereas it is nearly symmetrical under low humidity condition. To quantify and calculate the rectification ratio at each voltage, $RR(V) \equiv |I_{(+V)}/I_{(-V)}|$ was defined. It is noteworthy that this rectification effect occurs under chemically symmetric conditions. At low humidity, the RR value of the **2-Ru-N** junction approaches 1 throughout the entire voltage range, whereas it reached ~ 1000 at high humidity, when $V > 0.7$ V (Fig. 5b). It is noteworthy that the **2-Ru-N** junction exhibits a rectification effect with a rectification ratio exceeding 1000 under chemically symmetric conditions. For a deeper understanding of this novel phenomenon, researchers analyzed the **2-Ru-N** junction through theoretical calculations, discovering that the HOMO and HOMO-1 of the **2-Ru-N** molecule have symmetric and antisymmetric structures, respectively. The interaction of these two orbitals could generate two nearly degenerate localized molecular orbitals (LMOs): one distributed on the Ru segment near the tip, and the other distributed on the Ru segment near the substrate. When a bias is applied to this junction, these two degenerate orbitals are separated, inhibiting charge transport in the molecular junction. In dry environments, positive bias (from tip to substrate) and negative bias (from substrate to tip) occur symmetrically, resulting in no rectification in the I - V curve. However, in humid environments, the needle tip attracts more H_2O molecules than the substrate surface due to the higher hydrophilicity and capillary effect of pure ITO compared to **2-Ru-N** modified ITO. When a positive bias is applied to both ends of the molecular junction in humid environment, the counterion moves away from the tip and closer to the molecule, thus increasing the energy of the LMOs at the tip, reducing the energy difference with other LMOs, and ultimately increasing the transport capacity of the molecular junction. Conversely, when a negative bias is applied, the LMOs from the tip will gradually move away from other LMOs, further inhibiting the charge transfer in the molecular junction (Fig. 5c).

In humid environment, the directions of applying biases affect the movement directions of the counter ions and induce a change in gap difference between the tip LMOs

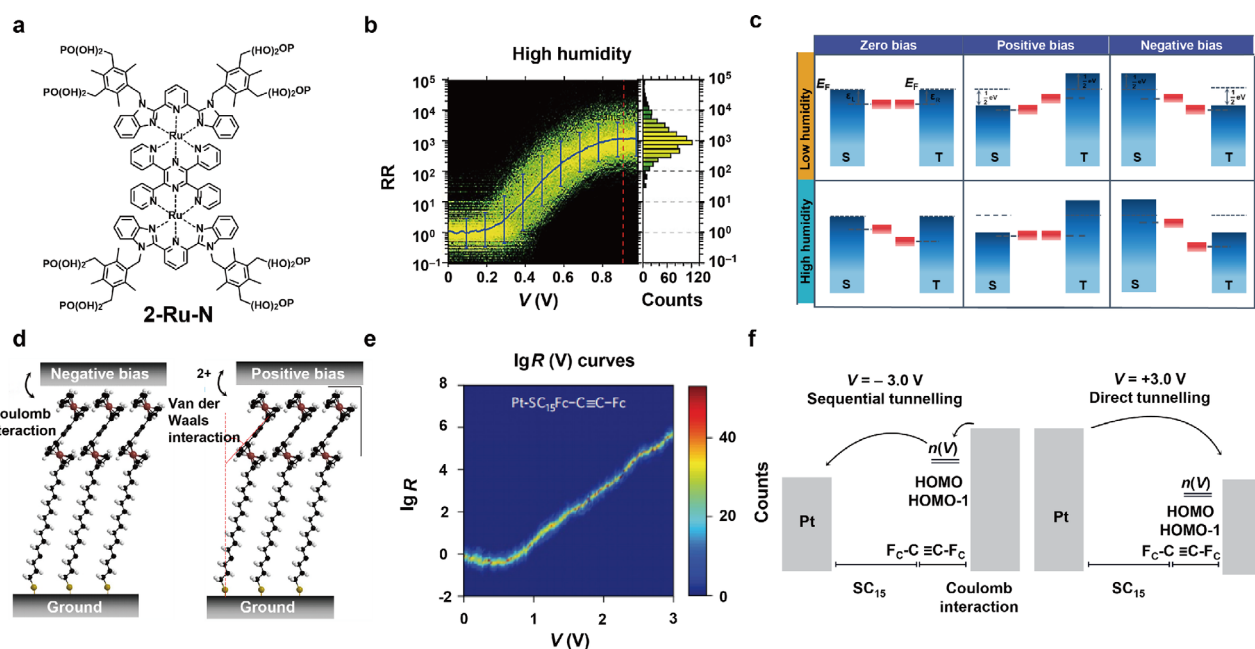


Fig. 5 **a** Molecular structures of **2-Ru-N**. **b** 2D histogram of logarithmically binned RR for the humid case. **c** Illustration of a two-site system between substrate (S) and tip (T) electrodes in dry and humid conditions: the two LMOs are aligned at zero, positive and negative biases. Reproduced with permission from Ref. [96]. Copyright 2018, Springer Nature Limited. **d** Schematic illustration of the **Fc-C≡C-Fc** junction. **e** Heat maps of the **lg R(V)** curves for M-SC₁₅Fc-C≡C-Fc/Ga₂O₃/EGaIn. **f** Energy-level diagrams at negative and positive biases. Reproduced with permission from Ref. [97]. Copyright 2017, Springer Nature Limited

and other orbital energy, ultimately yielding a molecular diode with a rectification ratio of up to 1000. Despite achieving a rectification ratio of 10^3 through the regulation of environmental humidity, molecular junctions still cannot match the performance of traditional diodes, which typically exhibit a rectification ratio (R) of at least 10^5 . In order to further improve the efficiency of molecular diodes, another rectification mechanism has been adopted. In 2017, Chen et al. designed a self-assembled single-ended monolayer as shown in Fig. 5d [97]. They employed ferrocene–diacetylene–ferrocene (**Fc-C≡C-Fc**) unit as an anchoring group to form van der Waals contact with the top EGaIn electrode and use a pentadecanyl (**C15**) chain as isolating group to separate the monolayer from the bottom electrode. Pt electrodes were incorporated to increase the breakdown voltage of the device to ± 3 V. Surprisingly, under a voltage range of ± 3 V, the diode device exhibited a rectification ratio as high as 6.3×10^5 . To reveal the origin of this high rectification ratio, the researchers investigated device's optical excitation properties. Their finding suggests that the quantity of luminescent spots is directly related to the number of molecules responsible for conduction within the molecular junction, which may account for the observed rectification ratio (Fig. 5e). Theoretical calculations indicate that under the influence of an electric field, the ferrocene group undergoes ionization from a neutral state to a positive one. The

strength of the electric field is proportional to the number of the ferrocene units ions. When a negative bias is applied to the top EGaIn electrode, an electrostatic interaction occurs between the top electrode and the positive ferrocene ions (Fc^+), resulting in an increased number of conductive molecules. The HOMO and HOMO-1 of these conductive molecules are located between the Fermi energy level of the Pt electrode and the EGaIn electrode, leading to a continuous tunneling mechanism and a consequent increase in conductance. Conversely, when the bias is applied in the opposite direction, the top electrode and Fc^+ merely interact through van der Waals forces, leaving number of conductive molecules unchanged. In this case, the HOMO and HOMO-1 of conductive molecules are lower than the Fermi energy level of the EGaIn electrode and do not participate in charge transfer (Fig. 5f). At this time, the transmission mechanism is direct tunneling, resulting in a lower transmission current. The electrostatic interaction between the top electrode and the ferrocene group is the primary factor contributing to the ultra-high rectification ratio.

The rectification effect observed in transition metal complex systems is fundamentally rooted in the intricate interplay between the electrodes and the complexes. This interactive dynamic is significantly shaped by the prevailing environmental conditions, underscoring the critical role of external factors in dictating the behavior of these

systems. These combined effects create an asymmetric charge transport pathway, resulting in the rectification property. Specifically, these effects can be summarized as follows: Firstly, the difference in interactions between the electrodes and the anchoring points determines the direction of current flow. The metal functional center, acting as an anchoring point, exhibits significant variations in its structure, electronic configuration, energy-level distribution, and interactions with the electrode materials on either side, depending on the current flow direction. When the direction of the applied voltage changes, the stable electronic structure of the metal center leads to disparities in the facilitation of electron and hole transport from the interface to the metal, thereby inducing a rectification effect. Secondly, the asymmetry in the electrode–molecule–electrode structure is caused by environmental factors. When an external electric field is applied, water molecules or solvent molecules in the environment may accumulate at one end of the electrode, altering the charge state of the molecule and the electrode surface, which results in an asymmetry in the molecular junction, thereby the rectification effect. To meet the needs of application fields, it is possible to optimize rectification performance by regulating these asymmetric factors, such as increasing the rectification ratio and lowering the turn-on voltage.

3.3 Multi-channel transmission effect

Engineers have spent a century exploring the complexities of Kirchhoff's superposition law in their pursuit to construct intricate electronic devices capable of advanced data processing and recording. However, the ongoing trend toward circuit miniaturization, with its focus on enhancing speed, reducing energy consumption, and achieving the ultimate compression of device dimensions, is leading us toward the thresholds of molecular and even atomic scales. As computer architectures evolve to be constructed from atoms or molecules with specific functional groups at microscopic scale, the traditional principles of Kirchhoff's superposition law may face applicability challenges, stemming from the fact that electron tunneling within molecules adheres to the distinctive laws of quantum physics, as opposed to the ones of statistical physics that govern larger scales [47]. Investigating the fundamental principles that govern parallel and superposition phenomena at the molecular level not only illuminates the complex mechanisms of electron movement in the microscopic world but also provides invaluable experimental foundations and theoretical insights for advancing electronic devices toward smaller, faster, and more efficient designs. This exploration transcends technological boundaries. It embodies a profound understanding of how the

fundamental laws of nature operate at nanoscale and delves into even smaller microscopic domains.

According to Kirchhoff's law, the conductivity at a node in a macroscopic circuit is the sum of the conductivities of each branch, which, however, differs from the microscopic world [46, 98]. Taking aromatic compounds as an example, extensive experimental results and precise transport calculations have demonstrated that the conductance of dual-channel compounds significantly surpasses that of single-channel compounds, often more than twice [47]. This substantial improvement suggests that the dual-channel structure provides a more efficient path for electron transport at the microscopic level. Conversely, this phenomenon exhibits an opposite trend in saturated alkane molecules. Regardless of whether it is a carbon chain or a silicon chain, the conductance of the dual-channel structure of saturated alkane molecules is lower than that of single-channel structure, further illustrating the non-additive nature of conductivity in the microscopic world. Comprehensive explanations have been provided [46, 99]. The multi-channel effect observed in aromatic compounds is not coincidental but originates from their distinct dual aromatic structure, which can induce constructive quantum interference and enhance conductance. In contrast, the multi-channel effect of saturated alkane molecules results from σ -destructive quantum interference, leading to a decrease in conductance. It is more intricate for metal complexes. Due to their distinct electronic structure and orbital distribution, metal complexes may deviate substantially from the predictions of Kirchhoff's law. This implies that when designing and investigating multi-channel molecular devices with metal complexes as the functional center, it is crucial to consider the properties of various metal-centered molecular systems. By adopting sophisticated and intricate theories and methods, we can gain a deeper understanding and a proper control of the conductance characteristics of these devices, ultimately aiding in the development of efficient and stable electronic devices.

In 2021, Duan et al. conducted a systematic study of the multi-channel effect in metal complexes for the first time [37]. To ensure structural similarity, single-channel compound **1**, dual-channel complex **3**, and tri-channel complex **4** were designed and synthesized using oligophenylacetylene as the high-conductance channel (HCC) module, and the *cis*-platinum-bis(acetylide) connected to the meta site of the phenylsulfane with destructive quantum interference served as the low-conductance channel (LCC), as shown in Fig. 6a. According to the STM-BJ test results, the conductance of the junction decreases as the number of LCC channels increases from 0 to 2. More significantly, for complexes **3** and **4**, the impact of LCC is particularly significant (Fig. 6b). Theoretical calculations reveal that

single-channel compound **1** has the highest transmission probability (Fig. 6c). In contrast, dual-channel complex **3** shows a lower transmission probability than **1**, and the transmission probability of triple-channel complex **4** shows a more than one order decrease in transmission coefficient compared with complex **3**. In addition to transmission spectra, the orbital distribution and transmission pathways in the conductive backbones also contribute to understanding multi-channel transport effects of metal complexes. HOMO and LUMO are mainly distributed on HCC in complex **3**. The HCC contributes more to both HOMO and LUMO than LCC. However, for complex **4**, the LCC not only makes higher contributions to HOMO but also dominates LUMO. Although the contribution of LCC to LUMO is still smaller than that of HCC, the contribution of LCC to HOMO sharply increases, surpassing that of HCC. The results of molecular projected self-consistent Hamiltonian (MPSH), and transmission pathways (Fig. 6d), demonstrate that the electrons can be transported simultaneously along HCC and LCC, while the possibility of

electron transfer along the LCC bridge in complex **4** is higher than that in complex **3**. Therefore, for multi-channel metal complexes, the multi-channel law is different from Kirchhoff's law. Electrons can be transmitted simultaneously in paths with varying transmission capabilities. Furthermore, the more channels with lower transmission capabilities, the lower the contribution of high-conductance channels to the conductive orbit, which leads to moderate suppression of conductance.

In comparison with traditional organic compounds, metal complexes exhibit a distinct phenomenon of conductivity superposition in their electrical properties, profoundly revealing the complexity and diversity of their internal electron transport mechanisms. This superposition is neither a simple sum of the conductivities of multiple independent channels nor based on distinct quantum effects between channels. Instead, it represents a novel mode of charge transport. In metal complexes, charges can traverse simultaneously along multiple paths, each possessing different transmission capacities and varying transmission

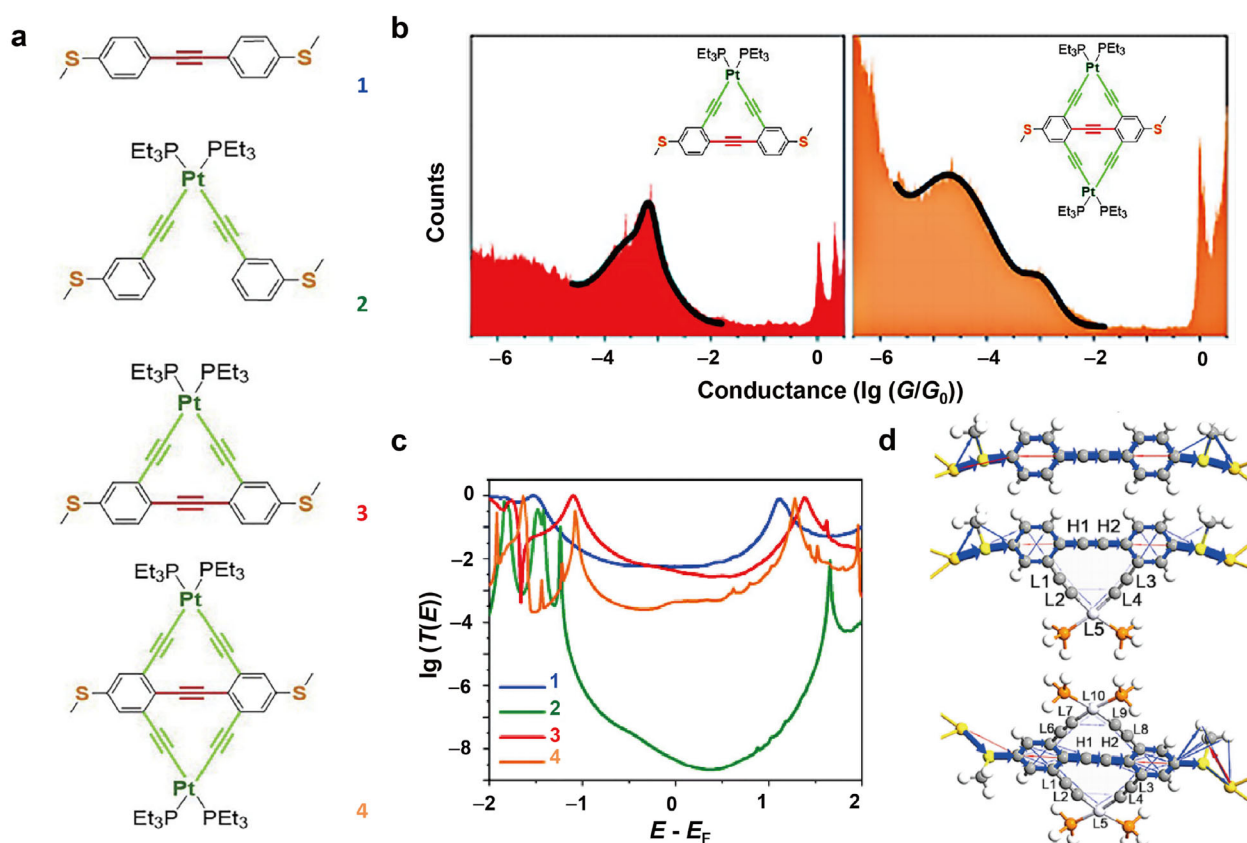


Fig. 6 a Molecular structures of HCC compound **1**, LCC compound **2**, and the multichannel complex **3** and **4** with a combination of the HCC and LCC. b Conductance histograms for complex **3**, **4** with the black lines representing the peak simulation. c Transmission spectra for Compounds **1**–**4**. d Transmission pathways plotted at $E - E_F = 0$ eV for Compounds **1**, **3**, and **4**. Reproduced with permission from Ref. [37]. Copyright 2021, Elsevier

efficiencies. This collectively forms a complex charge transport mechanism. Within this mechanism, channels with lower transmission efficiency inevitably siphon off some current during parallel transmission, consequently reducing the current share originally carried by the high-conductivity channels. This diversion effect not only changes the distribution pattern of current within the metal complexes, but also directly leads to a reduction in the contribution of high-conductivity channels to the overall conductive performance. Therefore, the phenomenon of conductivity superposition in metal complexes is an intuitive manifestation of the complexity and dynamic balance of their internal charge transport mechanisms and is a significant source of their distinct physical properties. Additionally, it is worth noting that this characteristic of conductivity superposition in metal complexes also provides vast potential for their applications in electronic devices, sensors, and energy conversion.

4 Spin effect

Spin, an intrinsic property of electrons, significantly impacts the optical [100, 101], electrical [103, 104], and magnetic characteristics of materials [106–108], and plays a crucial role in the emerging field of spintronics. Building on the foundation of conventional microelectronics, spintronics explores new research avenues centered on accurately measuring and manipulating electron spin. The goal is to utilize the electron spin state, rather than the traditional charge state for information transmission and storage, thereby revolutionizing electronic device design and offering unprecedented flexibility and efficiency. Molecular spintronics, a fusion of spintronics and molecular electronics, pushes the scale boundaries of electronic devices, striving for precise molecule-level control. It employs single organic molecules, meticulously designed supramolecular structures, or molecular clusters as core functional units or conductive channel materials to construct a molecular-scale electronics platform. This platform investigates the efficient injection, precise control, and accurate measurement of spin carriers within molecular structures, aiming to enhance our understanding of spin transport mechanisms at the molecular scale. Single-molecule spintronics integrates the features of both spintronics and molecular electronics, offering benefits such as small size, high integration, low cost, strong modifiability, low energy consumption, and large information storage capacity [103]. The primary objective of single-molecule spintronics is to investigate functional single-molecule spin devices, which necessitates the introduction of spin through the incorporation of magnetic components. From the perspective of device

composition, single-molecule spin devices can be categorized into three types: (1) those composing magnetic electrodes and non-magnetic molecules; (2) those consisting of magnetic molecules and magnetic electrodes; (3) those featuring magnetic molecules and non-magnetic electrodes. Different combinations of device structures and functional molecules yield multifunctional single-molecule spin devices. For pure organic functional molecules, spintronics research has focused on free radical systems. However, limitations such as structural instability, synthesis complexity, and uncertainty in radical positions have hindered in-depth exploration of these systems for single-molecule spin device applications. In contrast, metal complexes, characterized by their high stability, well-defined and tunable spin states of metal ions, are considered ideal candidates for single-molecule spintronics research.

The spin effects can be categorized into spin switching effect [105], spin interface effect [110], giant magnetoresistance effect [111], and others. The basic working mechanism of spintronic devices is to generate specific spin effects by altering the spin state of certain components within the device. This enables the development of applications such as spin valves, spin switches, spin memories, spin filters, and spin thermo-electrics [112].

4.1 Spin switching effect

The spin switching effect refers to a phenomenon in spin devices where external stimuli, such as gate voltage [113–115], electric fields [117, 118], mechanical forces [120, 121], or solution environments [122], induces changes in the spin states of functional molecules, which leads to a controlled, steady-state switching of molecular conductance. The spin switching effect stems from the spin crossover phenomenon exhibited by spin crossover complexes.

In 2009, Osorio et al. demonstrated the direct electrical control of the spin ground state of individual metal complexes by pairing asymmetric molecules ($[\text{Mn}(\text{terpy-O}(\text{CH}_2)_6\text{-SAc})_2]$) with two gold electrodes in a three-terminal device, as shown in Fig. 7a [123]. They manipulated the “high-spin” ($S = 5/2$) and “low-spin” ($S = 1/2$) states of individual manganese–pyridine derivatives through gate electrode control at low temperatures, thus showcasing the capacity to adjust the spin states of individual metal complexes. The researchers fabricated these devices by using electromigration of a gold wire in the molecular solutions. As the transport measurements shown in Fig. 7b, sharp inelastic cotunneling lines revealed a significant gate dependence of the spin-excitations on the Mn complex. This research illustrated the direct modulation of the spin state of a single metal complex by electrical means. To

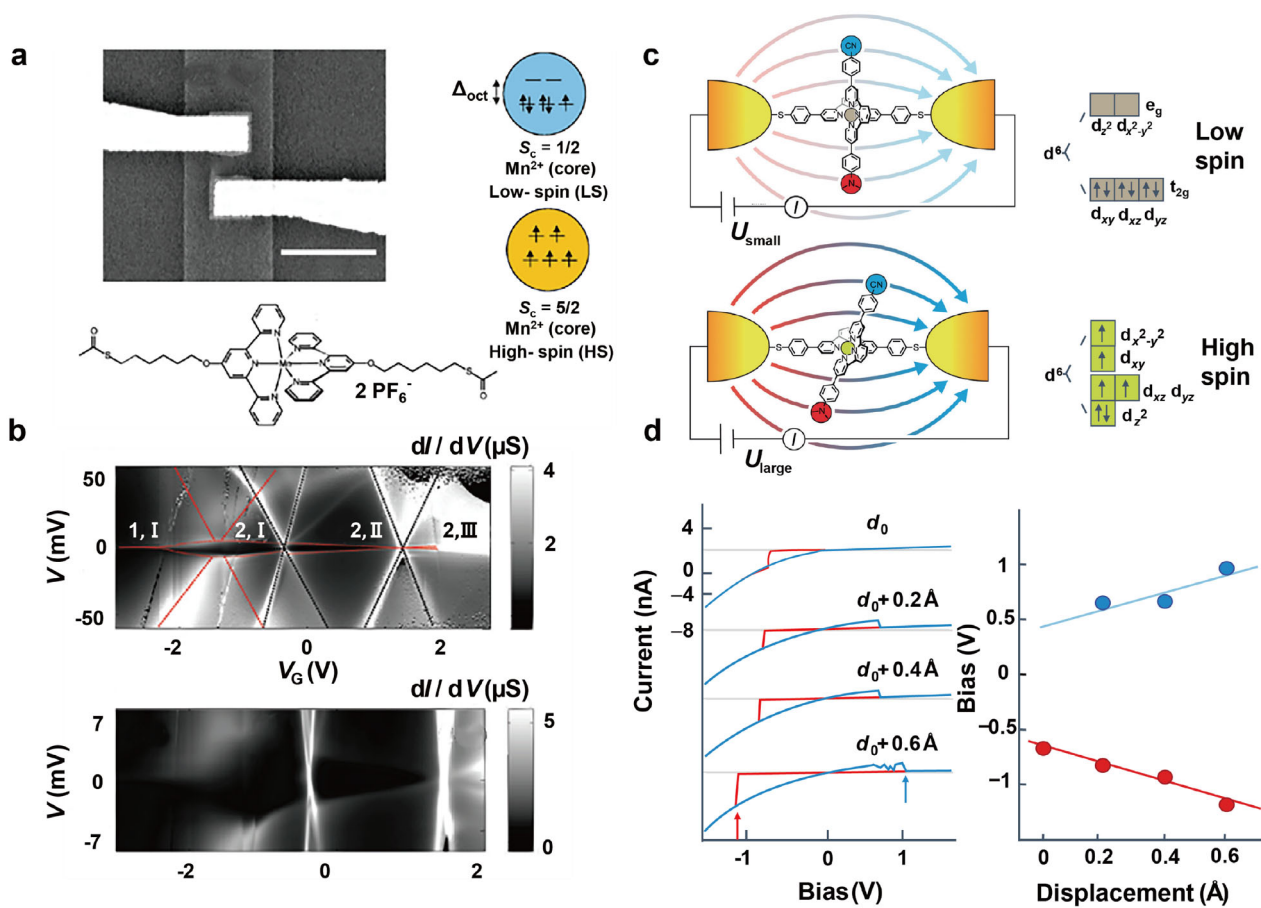


Fig. 7 **a** Schematic device layout and structure of $[\text{Mn}(\text{terpy-O}-(\text{CH}_2)_6\text{-SAC})_2]^{2+}$. **b** Density plot of the differential conductance, dI/dV , versus V and V_G at $T = 1.7$ K. Reproduced with permission from Ref. [123]. Copyright 2009, American Chemical Society. **c** Idealized sketch of the voltage-triggered spin crossover switch between low-spin Fe^{2+} and high-spin Fe^{2+} . **d** Current-voltage characteristics for increasing electrode separation and switching bias voltage as a function of electrode separation for the I - V data. Reproduced with permission from Ref. [124]. Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

investigate the spin configuration of the two charge states of the Mn complex, bulk superconducting quantum interference device (SQUID) susceptibility measurements were conducted. As Fig. 7a shows, the crystalline form of the metal complex possessed a high-spin (HS) ground state with $S = 5/2$, aligning with the expectations of ligand field theory. Bias spectroscopy experiments dependent on magnetic fields validated the singlet ground state's presence in Region (2). This confirmed that in this state, the Mn center adopted a low-spin configuration (LS) ($N = 6$, $S = 0$). This low-spin state could pair with the additional electron of spin 1/2 of an added electron to produce the observed singlet. However, the formed low-spin state was inherently unstable and required external assistance. Owing to the increase in ligand field strength upon ligand reduction in the terpyridine ligand system and the known reduction in the terpyridine ligand upon coordination with divalent metal centers, increasing the gate voltage to

charge the ligand could facilitate the transition from HS to LS in the Mn center.

In 2015, Harzmann et al. utilized on the sensitivity of the $[\text{Fe}^{2+}(\text{tpy})_2]$ complex spin states to the spatial arrangement of ligands, achieving the conversion between HS and LS states by modulating the strength of the electric field [124]. With STM at low temperatures, they realized a single-molecule switching mechanism. The study commenced with an examination of the formation of high-spin and low-spin states in the research system. In the $[\text{Fe}^{2+}(\text{tpy})_2]$ complex, the octahedrally coordinated Fe^{2+} ion led to five spin-degenerate levels, resulting in a LS ground state with zero net spin ($S = 0$). As Fig. 7c illustrates, mechanically deforming the coordination sphere to increase the metal-ligand distance reduced the crystal field interaction. This reduction decreased the crystal field splitting parameter Δ_{oct} and brought the e_g states closer together. Filling the levels according to Hund's rule

maximized the total net spin ($S = 2$), leading to the formation of a HS state. The HS state is theorized to possess superior conductance, as suggested by theoretical predictions and low-temperature STM experiments. Based on these findings, the authors proposed a theoretical single-molecule structure with an electric field-dependent spin crossover (SCO) phenomenon. They synthesized a series of metal complexes with varying dipole moments and observed bistability characteristics in single-molecule junctions. Comparisons with similar organic rigid rod molecules with the same terminal anchor groups confirmed that the observed bistability originated from the SCO complex hypothesis. To further investigate the switching mechanism, the authors analyzed the I - V characteristics of all bistable states with the Fe^{2+} complex (Fig. 7d). Two distinct maxima were observed, one at negative and one at positive bias, representing typical switch voltages between 0.25 and 1.5 V. Lastly, utilizing the distinctive features of bridged complex, the switching mechanism was investigated on single-molecule junctions. Varying the electrode distance by MCBJ, they discovered a linear relationship between the electrode distance and the required voltage for triggering bistability. This relationship confirmed a constant threshold for the electric field required for the switch event in the given structure, further substantiating the hypothesized switching mechanism.

In 2016, Frisenda et al. conducted an experimental study where they used MCBJ to construct a molecular junction composed of gold electrodes, a tris(terpyridine) iron metal complex, and gold electrodes, as shown in Fig. 8a [125]. By applying mechanical stretching, they manipulated the spin state of the iron elements, resulting in a two-order-of-magnitude increase in the device's conductance (Fig. 8b). Theoretical calculations suggested that the interaction between the iron atom and the ligands weakened during the stretching process. Consequently, the central molecule transitioned from a LS state to a HS state, leading to the appearance of additional spin-dependent transmission peaks above the Fermi energy (E_F). These additional peaks were responsible for the enhancement of the device's conductance.

It is worth noting that the metal complex models extensively investigated in the aforementioned studies often necessitate stringent experimental conditions, such as vacuum environments and liquid nitrogen cooling, to minimize interference from external factors in regulating their spin states and switching characteristics. However, the successful development of spin manipulation technology at room temperature has overcome the constraints of low-temperature environments. This breakthrough significantly enhances the experimental practicability, thereby paving the way for technological advancements and application expansions in the field of spintronics. This

accomplishment not only streamlines experimental procedures but also accelerates the transition of spintronics technologies from laboratories to practical applications.

In 2022, Li et al. achieved a remarkable breakthrough in the field of room-temperature spin switching [126]. They ingeniously designed and synthesized a planar four-coordinate Ni^{2+} porphyrin derivative (**NiTPPF**) and utilized STM-BJ technology to achieve precise and flexible regulation of the molecular spin state under room temperature and mild solution conditions. As illustrated in the one-dimensional conductance histogram in Fig. 8c, a prominent low-conductance peak and an inconspicuous high-conductance peak were observed. As the concentration of 3,5-dimethylpyridine increased, the conductance gradually decreased from **NiTPPF** to **NiTPPF-2**. Based on length statistics, the low-conductance lengths of **NiTPPF**, **NiTPPF-1**, and **NiTPPF-2** were almost identical, indicating that the decreasing trend in conductance resulted from the spin state transition after coordination. Furthermore, thanks to the stability of **NiTPPF** in trifluoroacetic acid solution, five-coordinate or six-coordinate **NiTPPF** could be decomplexed to pure **NiTPPF** by adding an excess of trifluoroacetic acid to fully protonate the 3,5-dimethylpyridine. This process allowed for switching from a high-spin state ($S = 1$) back to a low-spin state ($S = 0$), as shown in Fig. 8d. Consequently, reversible conductance switching was observed by adding trifluoroacetic acid or 3,5-dimethylpyridine to the sample, as shown in Fig. 8e, f. The antimagnetic **ZnTPPF** system showed only about a 22.8% slight decrease under the same test conditions. In comparison, the 169% conductance change observed in the **NiTPPF** system confirmed that the conductance change resulted from the spin state change after coordination. The researchers successfully manipulated the complexation-decomplexation cycle between pyridine derivative molecules and the specific planar four-coordinate Ni^{2+} porphyrin, achieving seamless switching of the molecular spin state between the singlet state ($S = 0$) and the doublet state ($S = 1$). Theoretical simulations indicated that free **NiTPPF** exists in the low-spin ground state ($S = 0$) with an empty $\text{d}_{x^2-y^2}$ orbital. Upon coordination with at least one 3,5-dimethylpyridine molecule, one electron transfers from the d_{z^2} orbital to the $\text{d}_{x^2-y^2}$ orbital, consistent with macroscopic NMR spectra. Additionally, the transmission coefficients near the Fermi level, $T(\text{NiTPPF}) > T(\text{NiTPPF-1}) > T(\text{NiTPPF-2})$, align with the experimental results.

The spin switch effect is pivotal to research in spintronics. Its principle involves the regulation of the spin states of functional molecules by external stimuli, thereby achieving conductivity switching. Although early studies heavily relied on stringent conditions such as low temperatures and vacuum environments, recent breakthroughs, including the realization of room-temperature spin

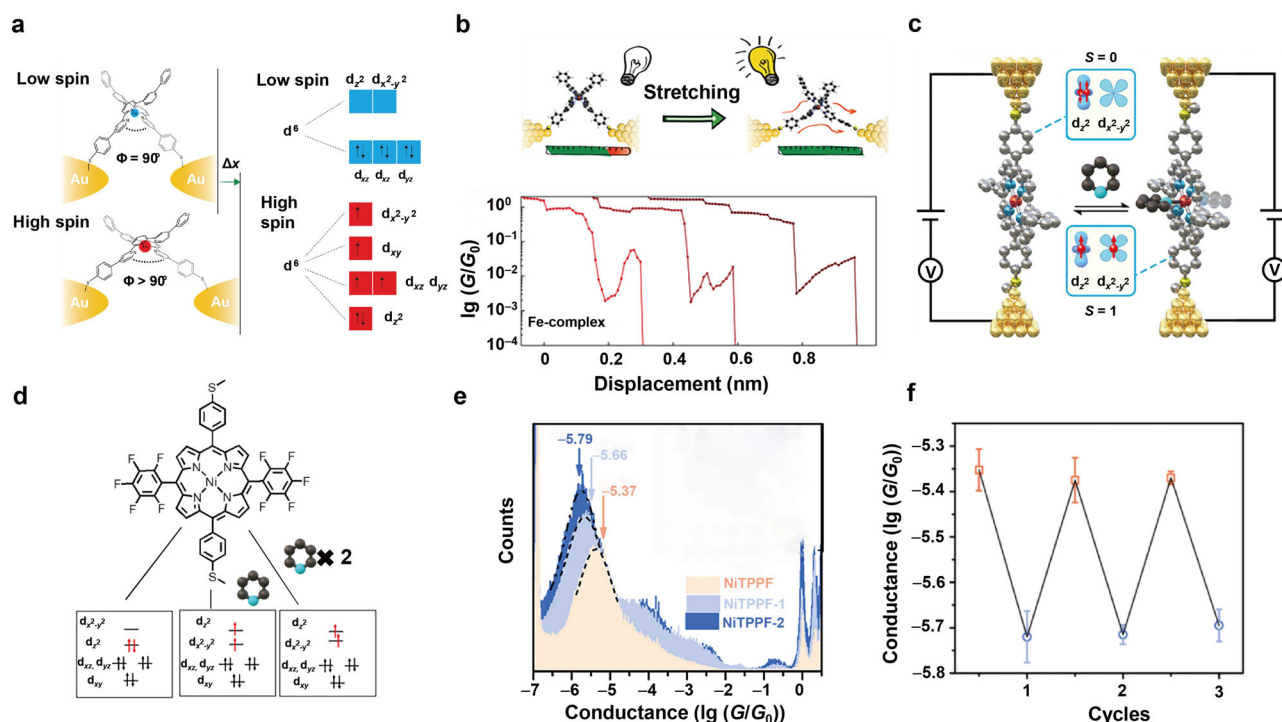


Fig. 8 **a** Sketch of the Fe^{2+} -SCO junction in the ideal arrangement to trigger the LS to HS switch by separating the electrodes by Δx . **b** Conductance measurements of the Fe^{2+} complex during the stretching. Reproduced with permission from Ref. [125]. Copyright 2016, American Chemical Society. **c** Reversible coordination reaction between **NiTPPF** and 3,5-lutidine, and the related spin switch. **d** Contact geometries for the **NiTPPF** series of molecules. **e** Logarithmically binned conductance histograms of **NiTPPF**, **NiTPPF-1**, and **NiTPPF-2**. **f** Reversible ON/OFF conductance switches of the **NiTPPF** system by adding 3,5-lutidine and CF_3COOH . Reproduced with permission from Ref. [126]. Copyright 2021, Chinese Chemical Society

switches, have significantly enhanced their practicality. These advancements have not only expanded the application scope of spintronics but also established a solid foundation for the development of future nanoscale electronic devices. Through innovative designs and upgraded technologies, researchers have successfully demonstrated the controllability of spin states at the molecular level, thereby injecting new vitality into the rapid progression of this field.

4.2 Spin interface effect

In the organic electronic devices, exploring the interface coupling between metal interfaces and organic materials is of great significance for the devices' construction and performance regulation [127, 128]. Adjusting and optimizing this interface coupling can deepen our understanding of device performance, thereby promoting the dual enhancement of device efficiency and reliability [130, 131]. For device structures involving metal complexes, the interface effects are closely related to the complexity of the electronic structure of the metal complexes [132, 133]. When these molecules interact with metal electrodes, a series of distinct electronic phenomena,

such as spin-polarized transport [134] and spin blockade effects [135], are triggered. These effects arise from the fine coupling between the spin degrees of freedom in the material interfaces or heterojunctions [136, 137]. These phenomena not only reveal the underlying mechanisms of electron behavior at the molecular interface but also show considerable research value and application potential in frontier technology fields such as nanoelectronics, spintronics, and magnetic storage [138]. The magnetoresistive response of molecular spintronic devices depends on the interface between the magnetic surface and the molecular layer. Research on interface engineering is essential for achieving precise control and comprehensive understanding of the interaction properties between magnetic molecular layers and ferromagnetic surfaces [139]. Specific metal complex, when in contact with materials, such as magnetic metal electrodes, can exhibit spin-polarized transport characteristics [140]. These characteristics result from spin-coupling effects between metal ions and ligands within the metal complex molecule, as well as interactions with the spin-polarized electrodes.

In 2016, Talal Mallah et al. designed and synthesized metal-containing (Ni^{2+} and Co^{2+}) magnetic complexes [141], demonstrating a strong correlation between the

properties of magnetic ions within the metal complexes and the exchange coupling with the magnetic substrate, as shown in Fig. 9a, c. In this research, the authors constructed Fe–O–P bonds to establish a robust interaction through chemical bonding between the metal complex and α -Fe₃O₄ (111) magnetic substrate. This interaction defined the interface between the molecule and the electrode, forming a stable molecular device. The interface serves as the foundation for analyzing the exchange coupling interaction of the magnetoresistance response. To obtain deeper insight into the nature of interactions between Co(Pyipa)₂ and Ni(Pyipa)₂ and the α -Fe₃O₄ substrate, the devices were characterized by X-ray magnetic circular dichroism (XMCD) spectroscopy. Circularly polarized X-rays were irradiated at two incident angles ($\theta = 0^\circ$ and 45°) between the sample normal and the propagation vector, and the changes in XMCD intensity as a function of magnetic field were studied, as shown in Fig. 9b, d. Notably, an opening in the magnetic hysteresis loop of Co(Pyipa)₂ was observed at $\theta = 45^\circ$, which disappeared when the magnetic field was perpendicular to the substrate. These results suggest a certain coupling between Co complexes and the α -Fe₃O₄ (111) surface, and a magnetic orientation of the molecules; otherwise, the angular dependence of magnetization intensity would not be observed. When the substrate was replaced with Al₂O₃, which has a similar reactivity but lacks a fixed shape, no open magnetic hysteresis loop was observed. This indicates that the magnetic hysteresis in the Co/Fe₃O₄ system arises from magnetic coupling between the molecules and iron oxide. As the presence of antiferromagnetic Al₂O₃ eliminates magnetic coupling, no

hysteresis loop was observed. The distinction in coupling behavior between Ni(Pyipa)₂ (without hysteresis) and Co(Pyipa)₂ (with hysteresis) rules out dipole–dipole interaction between Co(Pyipa)₂ and the substrate, as this interaction would lead to identical behavior for both molecules. Consequently, the magnetic coupling between Co(Pyipa)₂ and Fe₃O₄ arises from exchange coupling. Theoretical simulations revealed that the chemical anchoring responsible for exchange coupling altered the easy-magnetization plane direction of the Co²⁺ complex, or changed its magnetic anisotropy from a simple plane to a single-axis magnetization, thus modifying the magnetization properties of the device. Co²⁺ complexes exhibit strong ferromagnetic coupling with the Fe₃O₄ magnetic substrate, while Ni²⁺ complexes exhibit weaker exchange coupling, indicating its antiferromagnetism. These results suggest that their electronic structure of metal ions is critical to the coupling properties.

However, certain metal complex molecules at specific electrode complex interfaces may experience a spin blockade effect, leading to the hindrance of electron spin in certain directions within the molecular structure, thus affecting electron transmission.

In 2017, Ruiz et al. designed and synthesized metal complexes [M(tzpy)₂(NCSe)₂] (M = Mn, Co, and Ni) with NCSe as anchor groups and tested their spin-dependent single-molecule transport properties, as shown in Fig. 10a [142]. Stable molecular junctions were constructed by capturing the metal complexes between gold electrodes and magnetized Ni electrodes. According to experimental results, the authors observed that as the magnetization

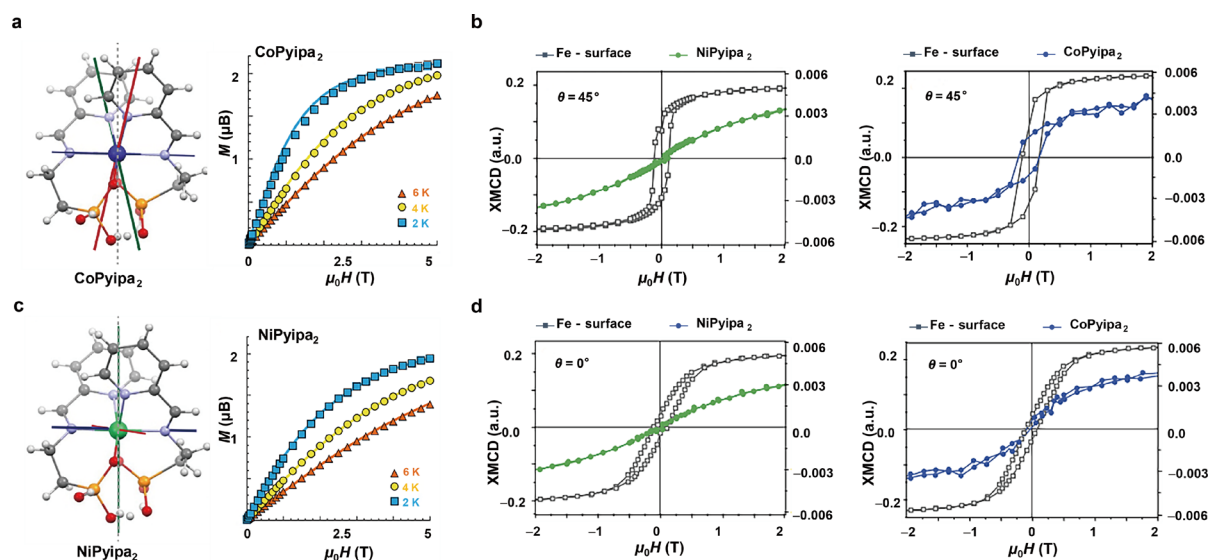


Fig. 9 X-ray crystal structure and the magnetization as a function of field plots for complex **a** Co(Pyipa)₂ and **c** Ni(Pyipa)₂ (Pyipa = (Pyridin-2-ylmethylene)amino ethyl phosphonic acid). Element-specific field dependence of the magnetization of the complexes and surface (Fe) at $\theta =$ **b** 45° and **d** 0° . Reproduced with permission from Ref. [141]. Copyright 2016, Springer Nature Limited

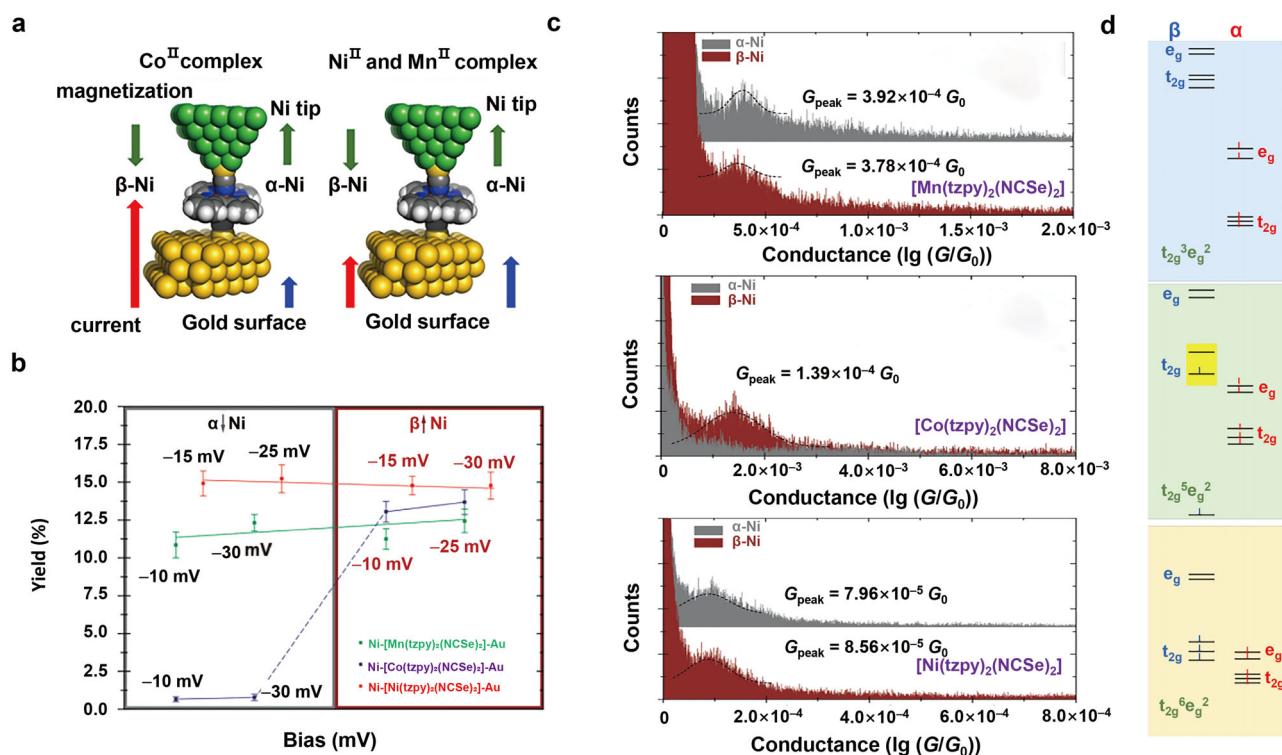
direction of the Ni electrode changed from downward to upward, causing a spin flip in injected electrons, the single-molecule conductance of the Co complex increased by more than a 100-fold. However, no such phenomenon was observed for Ni and Mn complexes. Since Co, Ni, and Mn all have unpaired electrons, the reason for the conductance difference may lie in the electronic structure of the metal ions (Fig. 10b, c). Theoretical simulations demonstrated that for the Co complex, the $t_{2g}^5 e_g^2$ electron configuration provided an efficient spin-selective channel. Compared to the highest occupied αe_g orbital, the lowest unoccupied βt_{2g} orbital was closer to the Fermi level, and the broadening of energy levels between these two orbitals also indicated hybridization effects between the remaining metal electrode orbitals. Consequently, the measured conductance of the single-molecule junction through the β orbital channel was higher. In contrast, for the $S = 1$ Ni^{2+} complex with a $t_{2g}^6 e_g^2$ electron configuration, the delocalized orbitals were close to the Fermi level for both α and β electrons, showing a higher β contribution. In this case, the vacant β orbital of the e_g orbital was relatively close to the Fermi level. The corresponding transmission peak was narrow, indicating weak mixing of the axial SeCN — orbital's π character with the frontier σe_g orbital of Ni^{2+}

complexes interacting with the gold surface energy levels. This weaker hybridization also explained the lower conductance measured in the case of the Mn^{2+} complex with a $t_{2g}^3 e_g^2$ electron configuration, where both the highest occupied αe_g orbital and the lowest unoccupied βt_{2g} orbital were far from the Au Fermi level (Fig. 10d).

Therefore, the understanding of interface effects is pivotal to the advancement of molecular spintronics. The research on metal complexes in the interface effects of single-molecule devices can facilitate a more profound understanding of the regulation mechanism of spin states at the interface, thereby enabling more precise and reliable spin transport and manipulation. This understanding is notably critical for the development of novel devices such as spin valves, spin switches, and spin memories. These new devices not only exhibit superior performance and stability, but also enable the storage and transmission of spin information at a smaller scale, paving a new way for the future development of information technology.

4.3 Giant magnetoresistance effect

The giant magnetoresistance (GMR) effect refers to the phenomenon where the electrical resistance of magnetic



materials changes an external magnetic field [143]. Within the two magnetic electrodes, one functions as the reference electrode with a fixed magnetization direction, whereas the other, known as the free electrode, exhibits two stable orientations for magnetization, either parallel or antiparallel to the reference layer. As shown in Fig. 11a, when the magnetization directions of the two magnetic electrodes align and the spin electron states in each electrode are uniformly distributed, spin carriers from the left electrode can be transferred to the right electrode, resulting in low resistance for the device [144]. Conversely, when the magnetization directions between the electrodes are opposite, the spin electron states in the two electrodes are antiparallel, thereby leading to high resistance in the devices.

The spin valve represents the significant structure for the GMR effect, playing a crucial role in the industrialization of GMR technology. In 2011, Urdampilleta et al. harnessed the GMR effect of spin devices to construct a supramolecular spin valve using terbium metal double-decker porphyrin clusters [145]. As depicted in Fig. 11b,

this device incorporated single-walled carbon nanotubes embedded in metal electrodes as the non-magnetic substrate. Multiple terbium metal double-decker porphyrin clusters, adsorbed onto the substrate through π - π interactions, served as the functional molecules to construct spin devices. The device's spin arrangement was manipulated by applying an external magnetic field at a 30-degree angle to the sample plane, enabling the smooth flow of spin carriers, when all magnetic moments were aligned in parallel (Fig. 11c, d). Conversely, when the magnetic moments were oriented antiparallel, the electronic flow of spin carriers was impeded. This configuration produced a supramolecular spin valve with a remarkable magnetoresistance of up to 300%.

Since the pioneering discovery of the GMR effect in magnetic multilayer films, molecular spin valves, an innovation based on this effect at the molecular level, have maintained at the forefront of scientific research. Specifically, transition metal complexes, with their distinct spin properties, play a vital role in advancing the GMR effect

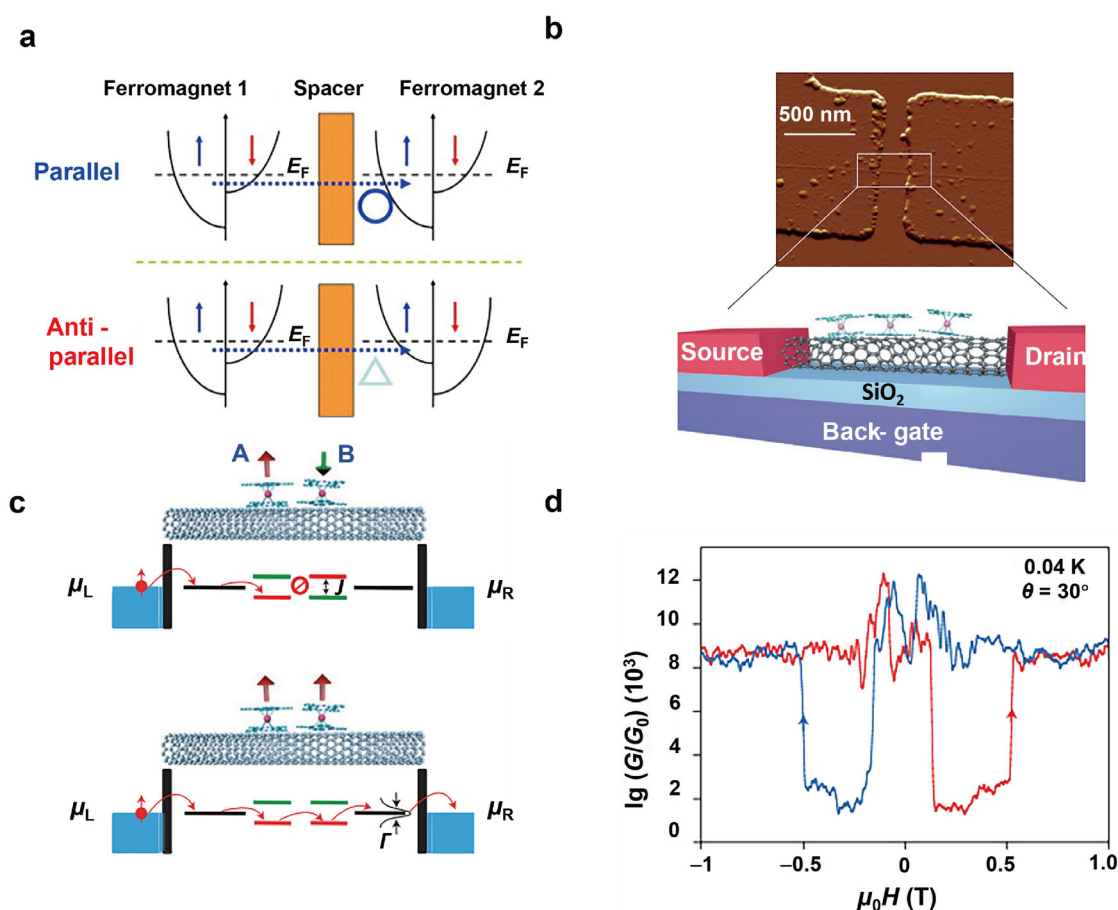


Fig. 11 **a** Schematic diagram of the giant magnetoresistance and spin-dependent transport. Reproduced with permission from Ref. [144]. Copyright 2011, Elsevier. **b** Scheme of the supramolecular spin valve architecture. **c** Schematic representation of the mechanism involving two TbPc₂ SMM molecules (A and B) grafted on an SWCNT. **d** Zero-bias conductance measured as a function of the magnetic field. Reproduced with permission from Ref. [145]. Copyright 2011, Springer Nature Limited

from theory to practical application. These complexes, with their rich electronic structures, exhibit diverse spin polarization characteristics, offering infinite possibilities for the precise manipulation of electron spin states and magnetism. By designing the structure of ligands and their coordination modes with metals, precise control over electron spin states and magnetism can be achieved, thereby establishing a solid foundation for optimizing the performance of molecular spin valves. Furthermore, the spin states of transition metal complexes exhibit responsiveness to external stimuli, significantly enhancing the device sensitivity and enabling reversible control of spin states. This progress paves the way for the development of high-performance spin switches. Molecular spin valves based on the GMR effect of transition metal complexes possess distinct advantages and are expected to have broad application potential in high-density data storage, low-power electronic components, advanced quantum computing platforms, and high-precision sensor technologies.

5 Thermoelectric effect

In macroscopic materials, the thermoelectric effect refers to the generation of electric potential due to temperature differences and the reversible thermal effect caused by electric current [49, 146, 147]. There are two mechanisms underlying the thermoelectric effect: (1) when a temperature gradient exists in the material's environment, the free movable carriers within the material will naturally flow from the higher temperature end to the lower temperature, generating a potential difference; (2) by applying an external electric field, a temperature gradient is generated across both ends of the material, allowing the direct conversion of electrical energy into thermal energy, or vice versa.

One specific aspect of the thermoelectric effect is the Seebeck effect, which refers to the electrical effect induced by temperature differences [149, 150]. By connecting both ends of Material A with another material, Material B, a closed loop forms with an external circuit. If a temperature difference exists between the two connecting nodes (T_1 and T_2 , where $T_1 > T_2$), a thermoelectric potential will be generated in the loop, resulting in an electric current. The magnitude of the generated potential can be represented as $V = S_{AB} (T_1 - T_2)$, where S_{AB} represents the relative Seebeck coefficient between the two materials A and B. If the generated electric current flows from the hot end to the cold end of materials A and then flows into materials B, the Seebeck coefficient, S_{AB} , is defined as positive; otherwise, it is considered negative. Therefore, the magnitude and sign of the Seebeck coefficient depend solely on the intrinsic properties of different materials, which determine

the dominant charge carriers responsible for electrical transport within the material and are independent of the magnitude and direction of the temperature gradient. The thermoelectric power factor represents the material's ability to extract energy from a temperature difference and is calculated as the square of the Seebeck coefficient. A larger thermoelectric power factor indicates a higher efficiency of the thermoelectric material in converting thermal energy into electrical energy.

Studying thermoelectric effects at the single-molecule scale can elucidate the fundamental physical mechanisms of electron and heat flow, thereby advancing the understanding of nanomaterials and molecular electronics [152]. In addition, research on single-molecule thermoelectric effects has fostered the development of new materials and devices, improved the efficiency of energy conversion and management, and provided insights for overcoming the limitations of traditional materials and technologies. Through comprehensive research and application of single-molecule thermoelectric effects, significant progress is expected in the fields of energy, electronics, sensing, temperature control, and beyond in the future. In comparison with bulk molecules, single molecules exhibit discrete electronic energy levels, with quantum effects playing a critical role in thermoelectric transport. Therefore, the single-molecule system offers a distinct scientific opportunity to conduct atomic-level investigations of the mechanisms governing energy conversion in thermoelectric materials. Delicate atomic imaging from bulk structures is challenging, yet it can offer valuable insights for the development and screening of innovative thermoelectric materials.

The thermoelectric effect of single-molecule junctions can also be characterized by the Seebeck coefficient and thermoelectric power factor. The sign of the Seebeck coefficient will determine the charge carrier transport mode in a single-molecule junction, while the sign of the thermoelectric potential depends on the relative position of the electrode Fermi level with respect to the molecular orbital energy levels. If the Fermi level is closer to the HOMO level, the thermoelectric potential is positive, and the hole-dominated transport occurs. Conversely, if the LUMO level is closer to the Fermi level, the thermoelectric potential is negative, and electron-dominated transport prevails. Moreover, the thermoelectric power factor of a single molecule can be utilized to evaluate the thermoelectric conversion efficiency of molecular-level thermoelectric materials [153].

The thermoelectric effect of transition metal elements is significantly influenced by the interaction between their d-orbitals and the ligand orbitals. This impact is due to the distinct orbital hybridization characteristics and the degree of electron delocalization. Studying the orbital

characteristics of metal complexes can enhance the thermoelectric conversion efficiency of thermoelectric materials, thereby improving energy conversion in practical applications. In 2021, Masnum et al. studied the thermoelectric properties of structurally similar metal Pt complexes, Ru complexes, and organic compounds, as shown in Fig. 12a, b [154]. This research extensively analyzed the correlation between the electrical conductance of metal complexes and their orbital energy levels, while comparing the thermoelectric power factors of different metals. These findings offer a clear and effective direction for the future design of superior thermoelectric materials. Paul et al. measured the single-molecule conductance and Seebeck coefficient by STM-BJ. The Seebeck coefficient indicates that the charge transfer orbitals are located closer to the HOMO energy level between the HOMO and LUMO, which is consistent with the theoretical calculations. With Pt^{2+} into the molecule's main chain, the charge transport ability of the device is suppressed, while it exhibits higher S and thermoelectric power factor. In contrast, the Ru^{2+} center exhibits superior charge transfer capability while also having high S and thermoelectric power factor (Fig. 12c). Introducing metal centers into frameworks with

similar structures significantly enhances the thermoelectric effect. More importantly, the ability to modulate the charge transport capability by altering the type of metal center without affecting the thermoelectric effect allows meeting diverse circuit requirements. These crucial experimental findings provide valuable insights for the development of single-molecule thermoelectric materials.

Investigating the thermoelectric properties of different metal complexes is beneficial for identifying metal elements with superior thermoelectric effect. Simultaneously, investigating complexes of the same type but with varying numbers of metal centers and distinct framework structures aims to explore the optimal complex structure with the highest thermoelectric efficiency. In 2022, Park et al. conducted research on the thermoelectric properties of mononuclear Ru complexes, dinuclear Ru complexes, and trinuclear Ru complexes with various substituents by using liquid metal technology, as shown in Fig. 12d [155]. The experimental results demonstrated the mononuclear complex Ru1 with an S of $27 \mu\text{V}\cdot\text{K}^{-1}$. The dinuclear complex Ru2 exhibited a significantly increased S value of $62 \mu\text{V}\cdot\text{K}^{-1}$, and as the phenyl substituent changed from CF_3 ($31 \mu\text{V}\cdot\text{K}^{-1}$) to CH_3 ($44 \mu\text{V}\cdot\text{K}^{-1}$), and finally to H

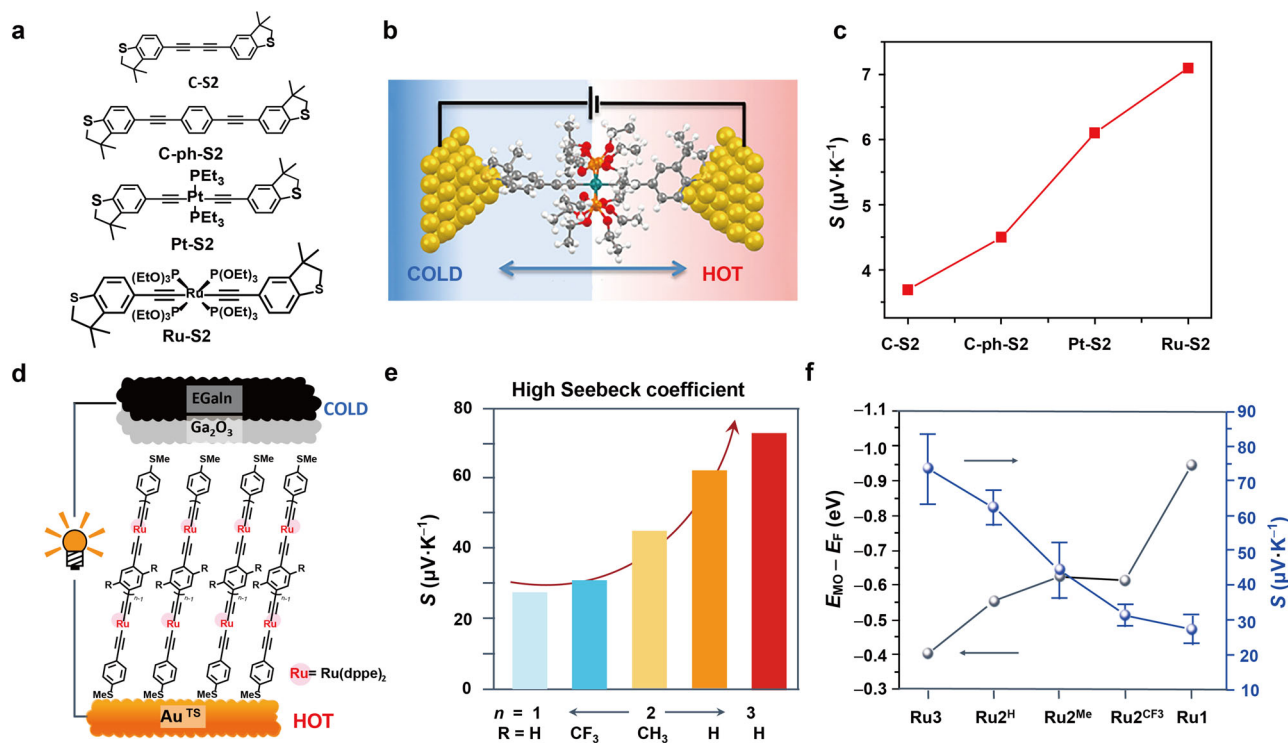


Fig. 12 a Structures of compounds C-S2, C-ph-S2, Pt-S2, Ru-S2. b Illustration of a molecule connected between the hot tip and the cold substrate. c Trend of experimentally determined S values. Reproduced with permission from Ref. [154]. Copyright 2021, American Chemical Society. d Schematic illustrating the structure of the Ru-complex junction. e Plot of Seebeck coefficient (S , $\mu\text{V}\cdot\text{K}^{-1}$) as a function of the molecular length and substituents. f Relationship between the trend of experimentally determined S values and the trend of energy offset (ΔE) between HOMO energy level (E_{MO}) and Fermi level (E_{F}), determined by ultraviolet photoelectron spectroscopy analysis. Reproduced with permission from Ref. [155]. Copyright 2022, American Chemical Society

($62 \mu\text{V}\cdot\text{K}^{-1}$), the thermoelectric effect gradually improved. In comparison, the performance of the trinuclear complex Ru₃ exhibited further enhancement, reaching $73 \mu\text{V}\cdot\text{K}^{-1}$ (Fig. 12e). Through experimental results and theoretical calculations, the study revealed that the high thermoelectric properties of these metal complexes originate from the relative position of the HOMO and the Fermi level (Fig. 12f). Their closer positions will offer a higher thermoelectric potential and thermoelectric power factor. This discovery provides a research foundation for the design of molecular devices with efficient temperature regulation and thermoelectric conversion. The research findings contribute to the exploration for metal complexes with excellent thermoelectric effect and offer beneficial design guidance for the development of efficient temperature-regulating and thermoelectric conversion devices.

Incorporating metal complexes into molecular frameworks via coordination bonds is beneficial for exploring the correlation between metal centers and thermoelectric properties. Moreover, the research on metal-encapsulated endohedral fullerenes with internal cavities provides a method for tuning thermoelectric properties. In 2015, Hirokazu et al. utilized the STM-BJ to investigate the thermoelectric properties of C₈₂ fullerene and two types of endohedral metallofullerene derivatives, as shown in Fig. 13a [156]. The thermoelectric potential of all three molecules was negative, indicating that the carriers in these molecular junctions are electrons, and the LUMO is closer to the Fermi level. Although the electrical conductance of all three molecules was similar, there was still a significant difference between the thermoelectric potentials of C₈₂ and the endohedral metallofullerene derivatives. The endohedral metallofullerene junctions not only exhibited a 50% higher thermoelectric potential than the C₈₂ junction, but also possessed almost twice the thermoelectric power factor ($\text{PC}_{\text{C}_{82}} = 8.0 \text{ fW}\cdot\text{K}^{-2}$, $\text{PGd@C}_{82} = 16.2 \text{ fW}\cdot\text{K}^{-2}$, and $\text{PCe@C}_{82} = 14.6 \text{ fW}\cdot\text{K}^{-2}$).

To explore the transport mechanism of endohedral metallofullerenes, Hirokazu et al. employed density functional theory (DFT) and the Landauer–Büttiker formalism for theoretical simulations. They examined three molecules and found that the transport predominantly occurs through LUMO situated on the C₈₂ cage. Notably, the encapsulated lanthanide elements do not directly contribute to the transport process, which is consistent with experimental conductance results (Fig. 13b). When compared to pure fullerene, the presence of encapsulated lanthanide metals significantly influences the thermoelectric properties of the molecules, despite not being directly involved in the transport process. This results in a substantial enhancement of the thermoelectric potential and power factor of the molecular junctions. These findings provide valuable insights for developing and screening the endohedral

metallofullerene thermoelectric materials. Endohedral metallofullerenes can also exhibit properties similar to those of regular metal complexes, as they can undergo a conversion between positive and negative thermoelectric potential under external stimuli, functioning as dual thermoelectric materials. In 2016, Rincón-García et al. conducted experiments on the Sc₃N@C₈₀ endohedral metallofullerene, as depicted in Fig. 13c [157]. By modulating the distance between the needle tip and the substrate, they controlled the pressure at both ends of the complex, successfully achieving a conversion between the positive and negative thermoelectric potentials. The charge transport and thermoelectric properties of gold-Sc₃N@C₈₀-gold single-molecule junctions were investigated by using an improved STM (Fig. 13d). For Sc₃N@C₈₀ complex, the distinct orientations of the three Sc metal planes within the fullerene can result in significant variations in the thermoelectric properties of the molecular junction. The angle defines the orientation of the Sc₃N molecule within the cage relative to the gold surface. As the STM needle tip undergoes reciprocal motion, the Sc₃N@C₈₀ molecule at $\theta = 57^\circ$ experiences compression forces, leading to cyclic variations in the thermoelectric potential from positive to negative (Fig. 13e). Theoretical simulations demonstrate that as the needle tip advances, the molecule undergoes external compression, leading to the broadening and shift of the LUMO resonance peak near the Fermi level toward lower energy. As a result, the relative position of the Fermi level to the HOMO and LUMO changes, ultimately leading to a transformation of the positive Seebeck coefficient into a negative value, which is in good agreement with experimental results (Fig. 13f). This research not only highlights the significant impact of the coupling between molecules and electrodes on the experimental variations in thermoelectric potential, but also introduces the concept of dual thermoelectric materials, achieving tunability of the sign and magnitude of thermoelectric potential in the field of molecular electronics. Furthermore, it provides experimental strategies and theoretical frameworks for future research on nanoscale thermoelectric materials.

The study of the thermoelectric effect in single-molecule metal complexes is significant for comprehending the fundamental mechanisms of thermoelectric conversion, optimizing new high-efficiency thermoelectric materials, advancing nanoscale thermoelectric devices, improving energy-utilization efficiency, and reducing environmental impact. Exploring the thermoelectric properties at the single-molecule level allows the discovery of new quantum effects and electron transport mechanisms, thereby providing a scientific foundation and fostering inventive concepts for the development of high-performance thermoelectric materials and devices in the future.

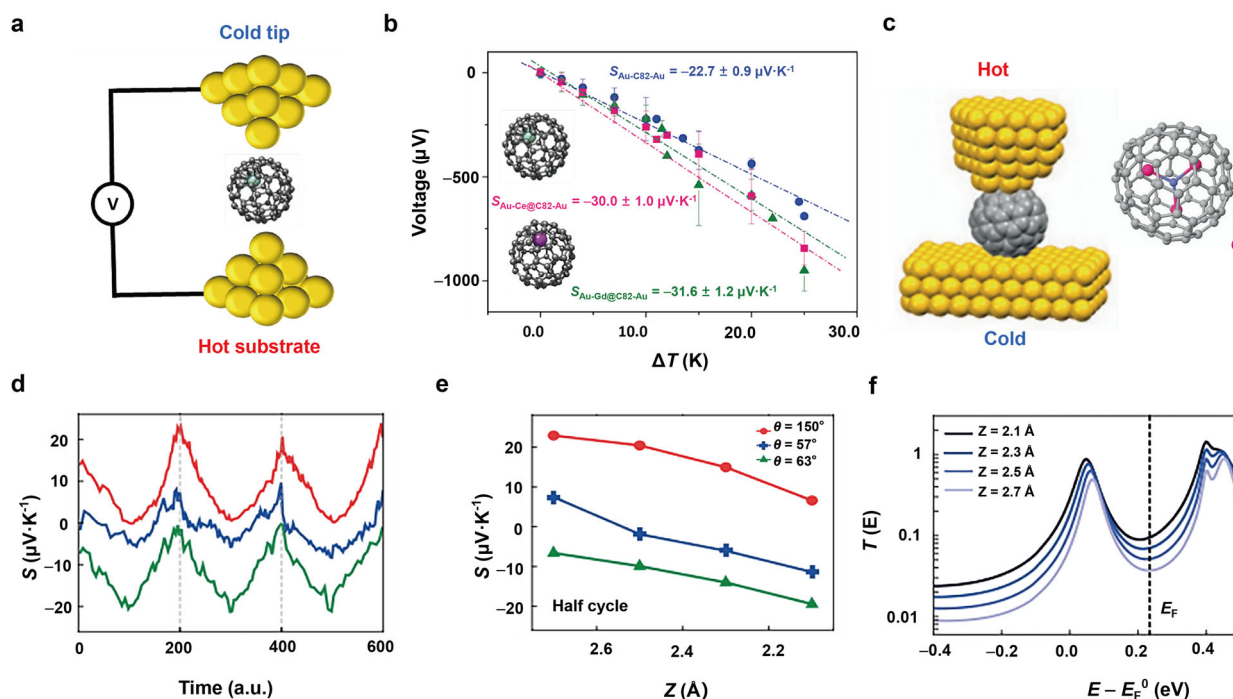


Fig. 13 **a** Schematic representation of the experimental setup of C_{82} , $Gd@C_{82}$, and $Ce@C_{82}$. **b** Thermoelectric voltage as a function of ΔT for C_{82} , $Gd@C_{82}$, and $Ce@C_{82}$ molecular junctions. Reproduced with permission from Ref. [156]. Copyright 2015, Royal Society of Chemistry. **c** Schematic representation of the experimental setup of individual $Sc_3N@C_{80}$ molecules. **d** Periodical variations of S , as the STM tip advances and retracts during three cycles. **e** Calculated S , for three different orientations (θ) as the tip–molecule separation z decreases from 2.7 to 2.1 Å, which corresponds to increasing pressure in the first half of experimental cycles. **f** $T(E)$, for the orientations ($\theta = 57^\circ$) and for different z values. Reproduced with permission from Ref. [157]. Copyright 2016, Springer Nature Limited

6 Conclusion

This review explores the role of transition metal complexes as active centers, leveraging their distinct electronic configurations to promote efficient electron exchange between molecules and electrode surfaces in single-molecule electronics. Consequently, it leads to a significant enhancement in the conductivity of molecular junctions. Furthermore, introducing metal centers can partially alleviate the pervasive length attenuation effect seen in traditional molecular wires, where conductivity sharply decreases with an increase in molecular length. This discovery provides a new path for designing molecular electronic devices with longer transmission distances and higher conductivity efficiencies. Beyond that, the precise manipulation of the composition, structure, and ligand environment of transition metal complexes enables fine-tuning of the electronic properties of molecular junctions, thereby achieving a lower length decay effect, unique multi-channel transport effect, thermoelectric effect, and rectification effect with an ultra-high rectification ratio. Furthermore, the spin crossover and spin selectivity properties of magnetic transition metals also render transition metal complexes crucial in the

research of spin switching effects, spin interface effects, and giant magnetoresistance effects. This high degree of tunability establishes transition metal complexes as an ideal platform for constructing molecular devices with specific functional characteristics, such as switches, sensors, and memories.

This review provides an in-depth analysis of the role of transition metal complexes in molecular electronics and emphasizes the importance of strategies for enhancing their electrical performance through structural optimization. Further works should focus on the following key areas: (1) the introduction of functional ligands or multinuclear metal structures to enhance the electron transport efficiency and stability of the complexes, expanding the study of their multifunctional properties; (2) the integration of advanced methods of computational chemistry to predict and design complexes with specific electrical behaviors; (3) the close combination of experimental and theoretical approaches to accelerate the development and practical application of novel molecular electronic devices. Exploration in these directions will not only advance the frontier of molecular electronics but may also trigger revolutionary breakthroughs in the fields of nanoelectronics and spintronics.

Looking ahead, single-molecule metal complexes not only hold great promise for constructing spin-electronic and spin-quantum devices, as well as electroluminescent applications, but also continuously expand the frontiers of the research by integrating ultra-low temperature and ultra-fast technologies. They lay a solid foundation for the diversified development of single-molecule devices, with their tunable electronic structure characteristics directly affecting the charge transport efficiency. They also present a new perspective for investigating the transport mechanisms under different conditions. A comprehensive understanding at molecule level not only deepens our knowledge of fundamental physical processes, such as exciton structure, charge transfer dynamics and electron-phonon coupling, but also provides precise theoretical guidance and experimental foundations for the tailored design of functional materials in fields like nanoelectronics, optoelectronics, and quantum technologies, which promise significant breakthroughs and opportunities for future development of technologies.

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Declarations

Conflict of interests The authors declare that they have no conflict of interest.

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