REVIEW ARTICLE

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Electrical and spin switches in single-molecule junctions

Guojun Ke^{1,2,3} | Chunhui Duan^{1,3} | Fei Huang¹ | Xuefeng Guo^{2,4}

¹Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, China

²Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing, China

³Beijing National Laboratory for Molecular Sciences, Beijing, China

⁴Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing, China

Correspondence

Fei Huang, Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China. Email: msfhuang@scut.edu.cn

Xuefeng Guo, Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. Email: guoxf@pku.edu.cn

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Abstract

Single-molecule electrical and spin switches have been one of the main research focuses in molecular electronics and spintronics because they may form the most important elements for the future information technology, thus attracting great attention in the scientific community and witnessing significant progresses benefiting from the combination of physics, chemistry, materials, and engineering. The key issue of constructing single-molecule switches is the development of stimulus-responsive systems that provide bistable or multiple states. In this review, we summarize the recent advances of this field in terms of the external stimulus that induces the switching. A variety of external stimuli, such as light, electric field, magnetic field, mechanical force, and chemical stimulus, have been successfully employed to activate the reversible switching in single-molecule junctions by manipulating molecular structures, conformations, electronic states, and spin states. As a burgeoning field, we finally put forward the challenges in molecular electronics and spintronics that need to be solved, which will initiate intense research.

KEYWORDS

electrical switch, single-molecule junction, spin switch, stimuli-responsive system

1 | INTRODUCTION

Microelectronics, optoelectronics, and integrated circuits have achieved unprecedented rapid developments over the past century, profoundly changing people's lives. This great progress is mainly attributed to the sophisticated, so-called "top-down" micro/nanofabrication technologies developed by experimental physicists and engineers, which make the size of semiconducting silicon-based electronic components (such as diode, transistor, and memory element) smaller and smaller. However, the currently employed complementary metal oxide semiconductor technology faces the challenge and physical theory limitation in the further miniaturization of electronic devices, and thus, Moore's law will collapse soon. From a contrary "bottom-up" pathway, molecular

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electronics utilize single molecule or several molecules to assemble molecular devices, which can be further integrated into functional circuits. It provides a completely new thought and strategy to solve the technological difficulty and theoretical limitation in the miniaturization process of conventional silicon-based electronic devices. In addition, the establishment of a single-molecule device platform allows the exploration of the intrinsic properties of functional molecules and reveal of novel physical phenomena.

The history of single-molecule electronics can be traced back to 1974, when Aviram and Ratner, for the first time, put forward the theoretical model of a molecular rectifier that a single molecule with an electrondonating group at one side and an electron-withdrawing group at opposite side could behave as a rectifier.¹ After many years of great efforts and developments, several methods for fabricating and studying molecular junctions have been established, including scanning tunneling microscopy break junction (STM-BJ), mechanically controllable break junction (MCBJ), conductive atomic force microscopy, electromigration, oxidative lithography, and other approaches. The initially ultimate goal of molecular electronics is to build integrated circuits for the next generation of super-fast computer and ultrahigh density information storage. Currently, many functional singlemolecule electronic components, including molecular wires,²⁻⁵ molecular switches,⁶⁻¹⁰ molecular rectifiers,¹¹⁻¹⁶ molecular transistors,¹⁷⁻²⁰ and sensors,^{21,22} have been realized. In addition, many novel physical phenomena, interference,^{23,24} quantum such as Coulomb blockade,^{25,26} and Kondo effect,²⁶⁻³⁰ were discovered in the process of investigating charge transport within molecular junctions. Meanwhile, apart from its initial goal, the single-molecule device platform also offers unique opportunities for the exploration of singlemolecule dynamic and detection,³¹⁻³⁵ which might provide detailed information that the traditional methods are not accessible. This field will not be covered in this article, and people who feel interested are recommended to read several articles.³⁶⁻³⁸

In traditional silicon-based microelectronic devices, electronic switches constitute the foundation of highspeed information processing and high-density data storage. Single-molecule electrical and spin switches are also the most important electronic components in molecular electronics and spintronics, which have drawn great attention in the past decades. This kind of devices requires materials with bistable or multiple states that are reversibly switched under external stimuli, such as light, electronic field, magnetic field, and mechanic force. In this review, we focus the survey on the most important progresses of developing stimuli-responsive systems for both electrical switches and spin switches in singlemolecule junctions. It should be emphasized that the change of spin states can lead to the change of molecular conductance. At present, the electrical signal is one of the most commonly used ways to monitor the change of spin states in single-molecule junctions. Therefore, the spin switch can also be considered as one kind of special electrical switches. We first summarize electrical switches. excluding spin switches, in Section 2. Then, in Section 3, we specially discuss about spin switches based on bistable materials that can reversibly switch between two distinct magnetic and conductive states due to their importance for future quantum information processing and storage. In addition, this article mainly elaborates the experimental advances, including the stimuli-responsive materials and device structures. It should be noticed that the theoretical simulation also plays an important role in revealing the underlying mechanism of single-molecule electrical or spin switches. The readers who are interested in this aspect can read some corresponding excellent theoretical reviews.39-41

2 | STIMULI-RESPONSIVE MATERIALS FOR ELECTRICAL SWITCHES

In the past century, synthetic chemistry and materials have been extensively developed. This great progress provides people the guidance in the design and synthesis of functional molecules for building single-molecule switches. From the sight of switching mechanism, switching effect can be classified into three types: conformation-induced, electronic state regulation, and spin state regulation. In this paper, we will summarize single-molecule electrical switches in this section and spin switches in the next section mainly in terms of the way of external stimuli.

2.1 | Light stimuli

Light, as an easily producible and controllable stimulus, has been widely utilized in single-molecule electrical switches. Usually, there are two possible principles for conductance switching based on light: light-induced reversible structural or conformational change and lightinduced electron transition or intramolecular electron transfer. Many photochromic molecules have been used to build molecular switches in solution, which could help us to design and synthesize molecules for single-molecule electrical switches. But it should be kept in mind that the behaviors of photochromic molecules in single-molecule devices might significantly differ from those in solution and solid-state bulk materials due to the coupling between the molecular core and electrodes, or other possible reasons. Figure 1 shows the commonly used chemical structures, including diarylethene, azobenzene, stilbene, spiropyran, dimethyldihydropyrene, and dihydroazulene, that can be reversibly switched between two stable structures under light stimulation or heating.

Diarylethene derivatives can undergo reversible photoswitching between open and closed conformations in solution, resulting in considerable changes in molecular energy level and electron delocalization, but a small change in molecular length, which makes them as potentially ideal materials for single-molecule switches. In 2003, Wees et al connected a diarylethene derivative into a nanoscale circuit with gold electrodes, as shown in Figure 2A.⁴² They observed switching of the molecules from the conducting (closed) to the insulating (open) state when illuminated with visible light, but fail to observe the reverse process upon exposure to UV light. This phenomenon is attributed to quenching of the excited state of the molecule in the open conformation by gold electrodes. Afterward, thiophene-based and pyrrolebased diarylethene molecules were introduced into single-molecule junctions with single-walled carbon nanotube (SWCNT) electrodes by Guo et al.43 On the contrary, they found that the thiophene-based molecule was able to undergo a photocyclization from the open state to closed state under UV light simulation, generating a current increase (Figure 2B,C), but the device was unable to switch back due to the quenching effect of the excited state of the closed form by SWCNTs. For the pyrrole-based molecule, the device could switch on as UV light was applied and thermally switch back in the dark overnight, and the cycle between the open and closed states is shown in Figure 2C. Both the abovementioned works highlight that the behavior of photochromic molecules in solution is significantly different from that in single-molecule junctions.

After many years of continuous efforts, this challenge was finally solved by Guo's group in 2016 (Figure 3).⁷ By incorporating three non-conjugated methylene groups between the diarylethene core and the anchoring amine group to decrease the molecule-electrode coupling strength, they enabled the realization of a fully reversible, two-mode, single-molecule electrical switch with excellent levels of accuracy, stability, and reproducibility.

Guo et al first introduced azobenzene group into the electron transport pathway in a graphene-moleculegraphene junction for the construction of single-molecule electrical switch.44 Due to the fact that the reversible photoisomerization of azobenzene between its trans and *cis* conformations will result in large changes in both shape and molecular length, the molecular structures need to be specially designed. Otherwise, the reversible in situ conformation changes in singlemolecule junction are difficult due to the mechanical restriction. Later, they further exploited the azobenzene core as a side-group chemical gating via reversible optical and electric control to realize the single-molecule switching effects.⁴⁵ This strategy makes the molecular structure stable, as the switching of azobenzene in the side chain has no mechanical restriction in the molecular junction. Wandlowski et al demonstrated a reversible photothermal switch based on dimethyldihydropyrene/ cyclophanediene photochromic system by using a mechanically controlled break junction.46 Distinct conductance changes between the fully conjugated ON state (closed form) and the broken non-conjugated OFF state (open form) were observed, with an ON-OFF ratio as



FIGURE 1 Basic chemical structures of commonly used photochromic molecules in single-molecule devices



FIGURE 2 Typical optical single-molecule switches. A, Schematic representation of photoswitching from closed to open states upon exposure to visible light, but failed to return back under UV light in an MBCJ device. Reproduced with permission.⁴² Copyright 2003, American Physical Society. B-D, Schematic representation of single-molecule switches based on SWCNT electrodes; current changes induced by UV light; switching circles as the device is exposed to UN light and left in dark overnight. Reproduced with permission.⁴³ Copyright 2007, American Chemical Society

high as 10^4 and excellent reversibility of conductance switching. Another single-molecule didydroazulene/ vinylheptafulvene switch was developed by Broman, and the switching effect can be remarkably enhanced by reducing the coupling between the switching core and electrodes through modifying the switching core with *p*-MeSC₆H₄ end-groups.⁸ A set of characteristic Coulomb blockade diamonds was observed in the differential conductance curves taken at different gate voltages, implying that the transport through the molecule goes by sequential tunneling.

Except for the light induced conformational change, the other possibility by using light stimuli to establish single-molecule electrical switches is to induce electron transition or intramolecular electron transfer. As displayed in Figure 4A, Dubi et al measured the conductance histograms of perylene tetracarboxylic diimide molecules attached to Au-electrodes, in the dark and under illumination.⁴⁷ A significant and reversible change in conductance was observed, which was attributed to the formation of a bound exciton in the molecule and in turn caused a shift in the local energy of the frontier orbitals. This implies that a single-molecule junction with an exciton binding energy similar in magnitude to the HOMO-Fermi level energy difference may work as a photoswitch with excellent ON-OFF ratio. Another new concept for a metal-molecule-semiconductor device employing Au tip/molecule/GaAs substrate was achieved by Nichols et al⁴⁸ With low doped GaAs, molecular junctions displayed rectification ratios as particularly high as >10³ in the dark and a high photocurrent in reverse biases. It should be noticed that the replacement of gold electrodes with conventional GaAs or silicon semiconductor materials reduces the gap between molecular electronic and traditional microelectronics.⁴⁹⁻⁵² Figure 4B shows a porphyrin-C60 dyad molecule in the gold-ITO (indium tin oxide) tunnel junction. A considerable fraction of illuminated molecules exhibited the high conductance and returned to the low conductance in the dark.⁵³ The reason is that the absorption of light led to the formation of a long-lived charge separated state (Porphyrin* +-C60^{•-}) by photoinduced electron transfer.

2.2 | Electric field stimuli

In traditional microelectronics, a transistor as an electronic component constitutes the heart of electronic circuits, which is typically a three-terminal electrical device. The current through one pair of the terminals can be regulated by applying a voltage to the third terminal. One of the most important functions of a transistor is to act as an amplifier or an electrical switch. Although the regulation principles are different from traditional transistors, a gate voltage is also the most commonly used and efficient approach for constructing single-molecule electrical



FIGURE 3 Reversible optical single-molecule switches. A, Schematic view of a graphene-diarylethene-graphene junction. B, Real-time measurement of the current through a diarylethene molecule that reversibly switches between the closed and open forms, upon sequential exposure to UV and Vis lights. Reproduced with permission.⁷ Copyright 2016, AAAS

switches. Single-molecule transistors consist of solid-state gating and electrochemical gating according to the methods of generating the gate voltage. Generally, the switching mechanism with gate electrodes can be classified into two types: (a) tuning the frontier orbital energy with respect to the Fermi level of the contacts and (b) changing their charge state of electrochemically active molecules. In addition to three-terminal devices, switching effects can also be achieved in the two-terminal devices with the electric field stimuli to induce chemical reactions or conformational changes.

2.2.1 | Solid-state gating switches

Building a gate-controlled three terminal device at the molecular level is of great challenge since the inception of molecular electronics. Strictly insulating the gate from the molecule and source/drain electrodes is essential to ensure that the gate couples only electrostatically to the molecule. The main challenge in fabrication lies in the contradiction between reducing the gate leakage as much as possible and maximizing the electric field reaching the molecule. After many years of constant efforts, several approaches have been established for the fabrication of solid-state single-molecule transistors, including electromigration break junctions,^{17,18,26,54,55} gated MCBJs,⁵⁶⁻⁵⁹ and transistors with carbon-based electrodes (carbon nanotube and graphene).⁶⁰⁻⁶⁴

Solid-state single-molecule transistors were first reported by two separated groups in 2002 by using the electromigration-induced break junctions.^{26,54} Ralph et al thermally grew 30 nm SiO₂ insulating layer on top of a degenerately doped Si substrate used as a gate electrode.²⁶ Nanometer scale gold wires were prepared on the SiO₂ layer by electron beam lithography, which were then broken by electromigration to produce a nanogap of about 1-2 nm width. A single-molecule complex of Cobalt ion coordinated with two organic ligands was connected to gold electrodes as the conducting channel. The conductance of molecules with long organic ligands can be regulated by a gate voltage. In addition, the Coulomb blockade, in which the flow of electrons is controlled by the sequential charging of a molecule, was observed. Molecules with short organic ligands couples strongly with the electrodes, allowing the observation of Kondo effect, in which conducting electrons interact with a local spin. The device structure by Park et al is similar except that an aluminum pad with a 3 nm oxide layer serves as a gate electrode.54 Kondo effect was also observed and could be tuned reversibly by using the gate voltage to alter the charge and spin state of the molecule. Lee et al reported the observation of direct molecular orbital gating by exploiting a three-terminal break junction formed through electromigration.¹⁸ Figure 5A shows representative I-V curves at different V_G values, indicating an obvious increase of molecular conductance as V_G becomes increasingly negative, which means their potential application as an electrical switch. Two distinct transport regimes are evident in the Fowler-Nordheim plots (Figure 5B), and the transition voltage, V_{trans} , exhibits a clear gate dependence. As the V_{trans} value allows an experimental determination of the relative position of the molecular orbital energy and the electrode Fermi level, the change of molecular conductance results from the molecular orbital regulation by the gate voltage. van der Zant et al investigated electron transport through an anthraquinone-based junction, and achieved a 10-fold increase in the off-resonant differential conductance due to the electric field induced reduction of the molecule.⁵⁵ Interestingly, this redox-induced conductance switching can be performed reversibly, enabling the realization of an electrical switch.



FIGURE 4 Electrical switches based on electron transfer. A, Schematic illustration of the target molecule trapped in an STM-BJ setup and illuminated with laser light (top), conductance histograms in the dark and under illumination (bottom left), and examples for the conductance traces (bottom right). Reproduced with permission.⁴⁷ Copyright 2018, American Chemical Society. B, Schematic illustration of a porphyrin-C60 dyad molecule in the gold-ITO tunnel junction. Reproduced with permission.⁵³ Copyright 2011, American Chemical Society



FIGURE 5 Gate-controlled charge transport characteristics of an Au-molecule-Au junction. A, Representative *I-V* curves for different gate voltages. B, Fowler-Nordheim plots demonstrating the gate-variable transition from direct to Fowler-Nordheim tunneling. Reproduced with permission.¹⁸ Copyright 2011, Nature Publishing Group

Furthermore, solid-state single-molecule transistors can also be obtained via an MCBJ. Ralph et al prepared the gated MCBJs that provided the ability of simultaneously adjusting the spacing between the electrodes

mechanically and tuning the energy levels of C₆₀ molecules via a gate electrode.⁵⁹ The conductance regulation by a gate voltage was dependent on the spacing between the electrodes, which is mainly because the spacing affects the coupling of the molecule and electrodes. Van der Zant et al investigated charge transport through a single porphyrin molecule by using electrically gateable MCBJs.⁵⁷ They found that both the occupied and unoccupied levels moved significantly toward the Fermi level upon reduction of the electrode spacing, suggesting that the image-charge effects played a dominant role in the large spread in conductance values. The same group used similar back-gate approach to realize a gate-tunable single-molecule rectifier with rectification ratios as high as 600.56 The rectification mechanism arose from the asymmetrical two parts of the molecule which was weakly coupled through a saturated linker.

Figure 6A shows the device structure of a singlemolecule transistor based on graphene electrodes.⁶¹ By using standard lithography and evaporation techniques, few-layer exfoliated graphene flakes in a two-terminal configuration with top-contact source and drain electrodes were prepared on a degenerately doped silicon substrate as a back gate, with a 285 nm silicon dioxide as the dielectric layer. The graphene nanogaps were ⁹⁸ ↓ WILEY-

obtained via a feedback-controlled electroburning method. Obvious Coulomb blockade was observed as depicted in Figure 6B, indicating that the transport current can be effectively regulated via a gate voltage in this three-terminal device. In comparison with the other fabrication methods, one of the important advantages of this technique is that the device can operate at room temperature. Except for covalently bonding, the molecules can also be inserted to the graphene nanogaps via π - π stacking interaction for constructing single-molecule transistors. Mol et al demonstrated a robust grapheneporphyrin-graphene transistor by using large π -conjugated structure as anchoring groups.⁶³ Multiple redox states were observed at room temperature under gate voltage tuning, enabling their application as an electrical switch.

2.2.2 | Electrochemical gating switches

One disadvantage of solid-state single-molecule transistors is usually the weak coupling between the molecule and gate electrode, which means that the actual electric field strength reaching the molecule under unit gate voltage is low. To solve this issue, one approach is to build a planar device and make the insulated dielectric layer as thin as possible. But this is challenging in the technique and a too thin dielectric layer may result in the leakage current of the gate electrode. An alternative solution is to fabricate an electrochemical gating single-molecule transistor. The formed electrical double layer by applying a gate voltage can be extremely thin, usually a few angstroms, regardless of the position of the gate electrode, which can enable much more efficient electrostatic coupling. For those non-redox active molecules, applying a gate voltage can change the molecular orbital energy levels relative to the electrode Fermi level, and thus the molecular conductance will be efficiently regulated.^{19,65-70} The effect of a gate voltage is not only to tune the energy levels of electrochemically active molecules, but also to reversibly oxidize and reduce the molecules at the redox potential, exhibiting conductance switching effects.20,71-82

Electrochemically non-redox active molecules: As early as in 2005, Tao et al investigated the charge transport of non-redox active molecules, such as 4, 4'-bipyridine and 1, 4'-benzenedithiol, under the tuning of an electrochemical gate voltage.⁷⁰ Only slight change of transport current (less than 30%) was observed due to the large LUMO-HOMO gaps of the molecules and the screening



FIGURE 6 Electrical switches based on dielectric gating. A, Illustration of the device structure of a single-molecule transistor based on graphene electrodes. B, Transporting current as a function of the bias voltage and gate voltage. Reproduced with permission.⁶¹ Copyright 2017, American Chemical Society

of the gate field by the electrodes. Many years later in 2019, the same group reported the direct observation of anti-resonances in single-molecule charge transport measured by a gate-controlled STM break junction.⁶⁵ As depicted in Figure 7B, an anti-resonance in the transmission function located inside the HOMO-LUMO gap was predicted for Meta and thus the transmission function of Meta displayed a strong energy dependence. In contrast, no anti-resonance was expected for Para. As a result, the transmission function was less energy dependent. This theoretical prediction was experimentally proved by the measured conductance vs gate voltage for Para and Meta, as shown in Figure 7C. The sharp drop in the conductance of Meta as the gate voltage decreased to -0.55 V and the increase at more negative potentials after the conductance minimum, provided a direct observation of the anti-resonance signature in the transmission function. By controlling the quantum interference, the

conductance of a single molecule could be tuned over two orders of magnitude with a subthreshold swing of ~17 mV dec⁻¹, excellent features for high-speed and lowpower electronics. Almost at the same time, Hong et al also observed the anti-resonance features of the destructive quantum interference in single-molecule thiophene junctions via electrochemical gating by using a modified electrochemical MCBJ technique, as shown in Figure 7D,E.⁶⁶

By changing aqueous electrolytes into ionic liquids, Guo et al realized gate-controllable charge transport of non-redox molecules on the basis of the platform of graphene-molecule-graphene single-molecule transistors.¹⁹ Ambipolar charge transport characteristics were observed for both triphenyl and hexaphenyl molecular junctions, arising from the change of dominant conducting orbital from HOMO to LUMO as the gate voltage changed from negative to positive. This is the first time of



FIGURE 7 Switches formed from gate-controlled STM break junctions. A, Schematic view of the gate-controlled measurement of single-molecule charge transport. B, Top: adjusting the gate voltage shifts the molecular energy levels relative to the electrode's Fermi energy level; bottom: adjusting the gate voltage changes the relative alignment between molecular energy levels and Fermi level. C, Conductance of *Para* (black circles) and *Meta* (red triangles) as a function of the gate voltage. Reproduced with permission.⁶⁵ Copyright 2019, Nature Publishing Group. D, Schematic view of the electrochemically gated MCBJ technique and molecular structures of thiophene derivatives with anchoring groups of thioacetyl (–SAc). E, Tendency of the molecular conductance of 2,5-TP-SAc (purple) and 2,4-TP-SAc (orange) vs electrode potentials from –0.6 to 1.3 V. Inset shows the magnification from –0.6 to 0 V. Reproduced with permission.⁶⁶ Copyright 2019, Nature Publishing Group

realizing ambipolar charge transport with a small gate voltage ($|V_G| < 1.5$ V) in electrochemically inactive molecular systems with a large energy gap ($E_G > 3.5$ eV). Duan et al fabricated molecular transistors by employing vertical cross-plane graphene/self-assembled monolayer/ gold heterostructures and ionic liquid gating.⁶⁴ Destructive quantum interference effects were exhibited in pseudo-*p*-bis((4-[acetylthio]phenyl)ethynyl)-*p*-[2,2]

cyclophane (PCP), which were absent in 1,4-bis(([4-acetylthio]phenyl)ethynyl)benzene (OPE3). As a result, the zero-bias differential conductance of the former is only about 2% of the latter. By the modulation of an ionic liquid gate, PCP transistors can reach a maximum ON-OFF ratio of up to 330, about one order of magnitude higher than that of OPEs. In addition, these stable switching operations worked up to room temperature.

Electrochemically redox active molecules: For electrochemically redox active molecules, the molecular energy levels can be tuned, when the gate electrode potential is outside the redox-active region. As the potential enters the redox region, the molecules will undergo the reversible oxidization/reduction process, accompanied by the changes of molecular energy levels and the molecular conjugation extent. Based on the redox couple of anthraquinone/hydroanthraquinone (AQ/H₂AO), a novel AQbased norbornylogous bridge tetrathiol, 5AQ5, was connected into an electrochemical single-molecule transistor by using the STM-BJ by Row et al.⁷⁵ The AQ moiety in 5AQ5 can be electrochemically and reversibly switched in situ between the high-conducting H₂AO form and the low-conducting AQ form, with a conductance ON-OFF ratio of an order of magnitude. Furthermore, Bryce et al investigated two π -conjugated molecules, isomeric AQ-1,5 and AO-1.4, by using the same technique.⁷³ For both molecules, the transport current can be tuned over one order of magnitude by varying the gate potential over a range of ~1 V. Outside the redox-active potential region, the gating effect is to shift the molecular energy levels relative to the metal Fermi level, thus leading to a modest change in conductance. While entering the redox-active region, large and reversible jumps of the conductance were observed due to the change in the redox state, accompanied by the changes in the conjugation pattern. In addition, the change in conductance upon changing the redox state was larger for AQ-1,5 than for AQ-1,4, due to the larger suppression of the conductance in oxidized AQ-1,5 as a result of the destructive quantum interference.

Campos et al developed an electrochemically gating single-molecule switch based on activated antiaromaticity by using the STM-BJ technique.⁷¹ As depicted in Figure 8A, a 8,8'-biindeno[2,1-b]thiophenylidene (BTP) molecule could be reversibly switched between the

neutral state and the 6-4-6 electron state with antiaromatic character upon oxidation/reduction. As the gate voltage changed from positive to negative, the conductance increased modestly at first, which was consistent with the HOMO dominated charge transport. Once the gate voltage was beyond -1.4 V, a significant conductance change was observed, resulting from the occurrence of the charge state (Figure 8A, bottom left). They further revealed that the switching was reversible by changing the gate voltage between negative (<-1.5 V) and positive (>1 V) values, yielding an average ON-OFF ratio value of ~70. This work demonstrated the exploitation of antiaromaticity to create single-molecule devices that are highly conducting. Besides the two-state switch, Wandlowski et al achieved conductance switching among three well-defined charge states in the core-substituted naphthalenediimide (NDI)-based single-molecule transistor through electrochemical gating, as shown in Figure 8B.²⁰ An ON-OFF ratio of around one order of magnitude between the most conductive NDI-R and the least conductive NDI-N state was obtained. What is more, as the NDI anion was present in a radical state, this kind of materials could be exploited as spin switches as well.

2.2.3 | Two-terminal switching devices

In the earlier discussion, the switching processes are controlled with a gate electrode. In fact, single-molecule electrical switches can be constructed with an electric field between source and drain electrodes. With the singlemolecule STM-BJ conductance measurements, Coote et al investigated the electrostatic catalysis of a Diels-Alder reaction.⁸³ As displayed in Figure 9A, the diene (a furan) was attached to the STM tip via a thiol group while the dienophile (a norbornylogous, NB) was attached to a flat gold surface via two thiols. The inset in the right panel showed the STM current response before (1), during (2), and after (3) the formation of a single blink, respectively. When the electric field was present and aligned so as to favor electron flow from the dienophile to the diene, a fivefold increase in the formation frequency of the blinks was observed. This work provided the experimental evidence of the non-redox, bondforming process being accelerated by an oriented electrostatic electric field. With the similar device structure (Figure 9B), a static electric field was used to trigger alkoxylamine dissociation to release a nitroxide and carbocation.⁸⁴ In the electrochemical experiments, an alternative means of homolysis, albeit to nitroxides and carbocations, were obtained. This work suggested a redox on/off switch to guide the cleavage of alkoxyamines at an electrified interface. In addition, they concluded that



FIGURE 8 Typical electrochemical switches based on redox-active molecules. A, Model of the electrochemically activated BTP switch (top); logarithm-binned 1D histograms for thiochromatin BTP as a gate voltage of +2, -0.5, -1.4, and -1.5 V (bottom left); cyclic on/off conductance values determined by switching between the positive gate voltage and negative gate voltage chosen to be beyond the oxidation/ reduction thresholds (bottom right). Reproduced with permission.⁷¹ Copyright 2017, AAAS. B, Schematic illustration of the electrochemically gated break junction and molecular structure of NDI-BT in the neutral state (NDI-N), radical-anion state (NDI-R), and dianion state (NDI-D). Reproduced with permission.²⁰ Copyright 2015, Wiley-VCH



FIGURE 9 Two-terminal electrical switches. A, Schematic illustration of the stages encountered during a blinking event (left), and a real-time data capture of blinking events (right). The inset shows the STM current response before (1), during (2), and after (3) the formation of a single blink. Reproduced with permission.⁸³ Copyright 2016, Nature Publishing Group. (B) Schematic depiction of the STM-BJ setup for investigating the effect of an external electric field on the breaking of a C—ON bond (left), and breaking probability of single molecules (right). Reproduced with permission.⁸⁴ Copyright 2018, American Chemical Society

even in the electrochemical process of the C—ON cleavage step directional electrostatic effects are possible in solution, highlighting their previously overlooked role in organic electrochemistry. Readers interested in the electrostatic catalysis in single molecule are recommended to read two corresponding excellent review articles, one about experiments⁸⁵ and the other about theories.⁸⁶

With a graphene-molecule-graphene junction, Guo et al investigated the charge transport of a molecule comprising an azobenzene side group orthogonal to the electron transport channel.⁴⁵ They reported an unusually discovery of unambiguous conductance switching upon two external stimuli (light and electric field). As is well known, the light can induce reversible isomerization of azobenzene between *cis* and *trans* forms. The significance of this work lies in the discovery that an external electric field exhibited the efficient adjustment of the energy alignments among *trans, cis,* and transition states, which plays a crucial role in the *trans-cis* isomerization of the azobenzene unit.

2.3 | Mechanical force stimuli

In the STM-BJ technique, the formation and break of single-molecule junctions are controlled by changing the tip-substrate distance. Surprisingly, reversible binary switching in single-molecule junctions can also be achieved by mechanically controlling the metal-molecule contact geometry. As displayed in Figure 10A, Venkataraman et al reported a 4,4'-bipyridine-gold singlemolecule junctions, where two conductance states could be reversibly switched through repeated junction elongation and compression.⁸⁷ At the beginning of separating the tip and substrate, the molecule existed in a high G geometry. As the elongation happened, the nitrogengold bond would be perpendicular to the conducting π -system, resulting in a low G geometry. Similarly, Tao et al investigated the electromechanical properties of a 1,4'-benzenedithiol molecular junction as the junction was stretched and compressed.⁸⁸ However, they found a counterintuitive result in comparison with the abovementioned conclusion. In their experimental



FIGURE 10 Electrical switches based on stereoelectronics. A, Examples of junction geometries relaxed at different tip-sample distances (top panel), and schematics illustrating the high *G* and low *G* configurations, respectively. Reproduced with permission.⁸⁷ Copyright 2009, Nature Publishing Group. B, Newman projections for the A-A (purple), O-A (yellow), and O-O (green) dihedral configurations from the perspective of the sulfur-methylene σ bond in the Au-Si4-Au system. Reproduced with permission.⁸⁹ Copyright 2015, Nature Publishing Group

measurements, the conductance increased by more than an order of magnitude during stretching and decreased back as the junction was compressed. This finding was attributed to a strain-induced shift of the HOMO energy level closer to the Fermi level of the electrodes, leading to a resonant conductance enhancement. In another attempt, by simply lengthening or compressing the molecular junction, permethyloligosilanes ([SiMe2]n, n = 1-10) with methylthiomethyl electrode linkers exhibited a reversible switching behavior that operated through a stereoelectronic effect (Figure 10B).⁸⁹ Elongation of the molecular junction resulted in an increase of conductance, while compression led to a low G state. This work exploited the strong Si-Si σ conjugation in oligosilanes that exhibited stereoelectronic effects, which are not accessible in the week conjugation of C-C σ bonds. Theoretical calculations supported the existence of three distinct dihedral conformations, which influenced the coupling between the oligosilane backbone and the sulfur-methylene σ bond, thus producing two conductive states.

In addition, a mechanical force can also shift the redox potential of a molecule, change its redox state, and thus allow the tuning of the single-molecule conductance. By using the STM-BJ technique, Tao et al studied the electron-transfer reaction of 1,1'-ferrocenyl diester (Fc-Lip) by tracking its conductance while mechanically stretching the molecule under electrochemical control.⁹⁰ As the stretching distance between two electrodes increased, more and more oxidation state conductance appeared. However, the reverse process that compresses the molecule to induce the change from oxidation to reduction states has not been realized so far. This work revealed that a mechanical stretching could regulate the redox state of single metal complex compounds, leading to the conductance switching.

2.4 | Chemical stimuli

An external chemical stimulus can induce the conformational change or structural change of conducting molecules in single-molecule junctions, and thus it will apparently result in the conductance change. Although an electrical switch based on chemical stimuli is not suitable for integrated circuits, it is of great importance as a single-molecule chemical/biological sensor. As displayed in Figure 11A, Guo et al studied the reversibility of coordination reactions by using a graphene-moleculejunction.⁹¹ The introduction graphene of ethylenediamine tetraacetic acid (EDTA) destructed the coordination between Co²⁺ and ligands, leading to an open circuit. Once adding Co²⁺ to the system again, it turned back to a close circuit. Two stable and distinctive conductance states can be reversibly switched under sequential treatments of EDTA and cobalt ions.

Single-molecule sensing of environmental pH was reported by Borguet et al by using an STM-BJ approach (Figure 11B).²¹ Two pH-sensitive dye molecules of malachite green (MG) and pararosaniline (PA) were chosen as molecular sensing units, both of which exist in a high conjugated state in acidic solution and a weak conjugated state in basic solution (pH > 13). Therefore, the conductivity can be reversibly switched in responding to environmental pH with a high ON-OFF ratio of ~100. Density functional theory indicated that the HOMO-LOMO gap of the dyes in weak conjugated state was nearly twice as large as in the high conjugated state.

2.5 | Multiple stimuli

In the above-mentioned examples, we discussed about different kinds of electrical switches that only respond to a single type of external stimuli. By smartly designing the molecular structure, several functions can be integrated into the same single-molecule junction. Several groups have reported single-molecule switches controlled by different external stimuli.^{45,92-96} As shown in Figure 12A, a spiropyran derivative that undergoes rapid and reversible isomerization under either UV light or chemical stimuli was incorporated into a single-molecule device via the STM-BJ technique, providing a bifunctional electrical switch.92 The unique multiple response of this singlemolecule electrical switch places spiropyran derivatives as key candidates for molecular circuitry. However, the switching process in this system occurred ex situ in solution and the molecules were caught by gold electrodes either in their open or closed states. Future work should try to develop in situ switches, where the switching events happen while the molecule is still attached to both electrodes. Recently, Darwish et al reported the utilization of a spiropyran derivative as the active unit for the construction of single-molecule electrical switches that responded to both chemical and mechanical stimuli.93 The mechanically controlled isomerization of the closed spiropyran to the open merocyanine state resulted from the C-O bond breaking of the spiro center via physically pulling the ends of the molecule. Therefore, robust anchors to the electrodes are required so that the contact bonds should be stronger than, or at least comparable to, the spiro C–O bond.

In another multiple stimuli-responsive system that was achieved via chemically fabricated nanogaps (onwire lithography) functionalized with dithienylethene (DTE) units bearing organometallic ruthenium



FIGURE 11 Electrical switches based on chemical stimuli. A, Strategy for studying the reversibility of coordination reactions (top) and I_{sd} vs V_G data of a rejoined device under sequential treatments of EDTA and cobalt ions. Inset: three representative switching cycles for the same device when alternately treated with EDTA and cobalt ions (bottom). Reproduced with permission.⁹¹ Copyright 2012, Wiley-VCH. B, Molecular structures of pararosaniline (top) and malachite green (bottom) at different pH values, and corresponding sequential cycles of pH-induced condunctance modulation between ON and OFF states. Reproduced with permission.²¹ Copyright 2013, Wiley-VCH



FIGURE 12 Electrical switches based on multiple stimuli. A, Molecular structures of the investigated spiropyran derivatives and schematic illustration of a single-molecule switching device reversibly responding to UV light and chemical stimuli. Reproduced with permission.⁹² Copyright 2014, American Chemical Society. B, Schematic view of molecular isomerization within nanogap devices under different inputs (light and electrolysis); the electronic symbol and a truth table of the OR logic gate. C, Schematic view of molecular isomerization under various inputs (E_1 , E_2 , and light); the electronic symbol and a truth table of the AND-OR logic gate. Reproduced with permission.⁹⁴ Copyright 2014, Nature Publishing Group

fragments, the addressable and stepwise control of molecular isomerization could be repeatedly and reversibly completed with a combination of electrochemical stimuli and light irradiation to realize the controllable switching of conductivity between two distinct states.⁹⁴ As displayed in Figure 12B, either an input of UV light or

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electrolysis induced the transformation of DTE from the open state to the closed state, accompanied by a significant conductance increase, thus affording a two-input OR logic gate. In addition, the unique electronic structure of the longer molecule combining two DTE units offered the achievement of stepwise modulation, allowing the fabrication of a three-input AND-OR logic gate (Figure 12C). Importantly, these organometallic molecular wire-based logic gates could be simply reset upon exposure to visible irradiation, ensuring the cycled setreset operation. One weakness of this kind of switching devices is the long response time, 30 minutes for UV light and 2 hours for reset by visible light.

3 | STIMULI-RESPONSIVE MATERIALS FOR SPIN SWITCHES

Molecular magnetic switches, or spin switches, are one of the most important components in molecule-based spintronics for future quantum information processing and storage. To build single-molecule spin switches, one key challenge is to find bistable materials that can reversibly switch between two distinct magnetic and conductive states in response to an external stimulus. The most commonly used molecules for spin switches contain spincrossover metal complexes and organic radical molecules. In this part, we will summarize the progress of singlemolecule spin switches in terms of external stimuli that trigger the switching process, including electric field,⁹⁷⁻¹⁰⁴ magnetic field¹⁰⁵⁻¹⁰⁹ and mechanical force.^{110,111}

3.1 | Electric field stimuli

By using an MCBJ technique, Weber et al investigated the charge transport of a molecule containing two coupled spin centers that were confined on two Co²⁺ ions, where the magnetic coupling path was orthogonally oriented to the conduction channel.¹⁰¹ By applying a finite bias, they were able to repeatedly switch between the pseudo-singlet state and the pseudo-triplet state. As depicted in Figure 13A, an electric field could also be directly used to manipulate the single nuclear spin resonance and thus reversible conductance switching could be observed.¹⁰⁰ In fact, there is no direct coupling between the spin and the electric field. But a moving object in an external field could see a magnetic field that interacts with the spin magnetic moment of electrons, which is the physical origin of the hyperfine Stark effect. To perform the experiments, they connected a $TbPc_2$ (Tb^3) ⁺ ion sandwiched between two phthalocyanine ligands) single-molecule magnet into a three terminal nuclear



FIGURE 13 Typical spin switches based on an external electric field. A, Artist's view of a nuclear spin qubit transistor based on a single TbPc₂ molecular magnet. Reproduced with permission.¹⁰⁰ Copyright 2014, AAAS. B, Structure of a neutral diradical molecule, differential conductance (red) and corresponding redox center spin value *S* (blue) as a function of V_{g} . Reproduced with permission.⁹⁷ Copyright 2017, American Chemical Society. C, Idealized sketch of the voltage-triggered spin crossover switch in a single-molecule junction. Reproduced with permission.⁹⁹ Copyright 2015, Wiley-VCH



FIGURE 14 Spin switches based on magnetic fields. A, Schematic view of the electron transport process through a FePc molecule absorbed on an Au(111) surface at different magnetic fields. Reproduced with permission.¹⁰⁵ Copyright 2019, Nature Publishing Group. B, Schematic illustration of a single-molecule junction for TEMPO-OPE under magnetic field (top panel), and corresponding magnetoresistance curves (bottom panel). Reproduced with permission.¹⁰⁷ Copyright 2016, American Chemical Society. C, Topographic image of a Ho and an Fe atom on bilayer MgO, and the magnetic states of Ho are controlled and probed with an STM by using spin-polarized tunneling (left panel). The magnetoresistive tunnel current I recorded on top of a Ho atom shows switching between two magnetic states of a long residence time. Reproduced with permission.¹⁰⁶ Copyright 2019, Nature Publishing Group

spin qubit transistor fabricated via the electromigration technique. At constant source-drain and gate biases, the electron spin changes between the $|\uparrow$ and $|\downarrow$ states by sweeping the magnetic field, resulting in а conductance jump.

Apart from spin-crossover metal complexes, the charge transport of all-organic radical molecules has also been explored in single-molecule junctions that showed switching effects. Three terminal devices based on a 2,4,6-hexakis(pentachlorophenyl)mesitylene diradical molecule were fabricated by using feedback-controlled electromigration (Figure 13B).97 The neutral diradical molecule could undergo reversible and stable charges by means of a gate voltage. An inelastic electron tunneling spectroscopy in the two stable redox states revealed that the added electron magnetically coupled to the two radical spins, preserving their open-shell character, while changing the magnetic state of the molecule from a singlet state to a doublet state with three unpaired electrons. In this way, the exchange interactions between the added electron and the two radical spins were

switched on and off by controlling the occupation of the redox center.

Differing from the utilization of an electric field to directly manipulate spin electrons, Mayor et al reported a new mechanism to build single-molecule spin switches based on voltage-triggered distortion of the ligand (Figure 13C).⁹⁹ Fe^{II} terpyridine complexes, in which one ligand fixed the complex in the junction and the other one exhibited an intrinsic dipole moment responding to the strength of the applied electric field, have been designed. At a threshold voltage, the central Fe^{II} ion changed from a low-spin state to a high-spin state due to the distortion of the coordination sphere under a high electric field, resulting in a bistability in the currentvoltage curves.

Magnetic field stimuli 3.2

A magnetically sensitive negative differential resistance (NDR) effect for iron phthalocyanine (FePc) molecules



FIGURE 15 Spin switches based on mechanical forces. A, Schematic view of a Fe^{II}-based SCO molecular junction in the ideal arrangement to trigger the LS to HS switch by separating the electrodes by Δx (left) and Fe^{II} 3d levels involved in the spin-crossover phenomenon (right). Reproduced with permission.¹¹¹ Copyright 2016, American Chemical Society. B, Schematic illustration of varying the gap width of a molecular junction by varying tip height (top) and dI/dV spectra acquired in a molecular junction undergoing multiple tip upward and downward displacement cycles. Reproduced with permission.¹⁰⁰ Copyright 2017, American Chemical Society

on a single-layer copper nitride on a Cu(001) surface was observed by using the low-temperature STM technique.¹⁰⁸ The effective shift of the NDR with the magnetic field was enhanced by the inherent voltage division across the two asymmetric tunneling barriers, allowing for the creation of novel magnetoresistance phenomena. Here, the magnetic field plays the role of the gate electrode to control the charge transport. By using the similar device structure but just replacing the Cu_2N capped Cu(001) substrate with an Au(111) surface, Gao et al measured the charge transport of the same FePc molecule.¹⁰⁵ By varying the magnetic field, the electron pathway could be switched between two molecular orbits, as shown in Figure 14A. At a weak magnetic field, the spin direction of Fe was in plane and currents flowed by the d_{xz}/d_{vz} orbital, while at a strong magnetic field, Fe spin was aligned to the magnetic field and electrons tunneled preferentially through the d_{τ^2} orbital, giving rise to a tunable anisotropic magnetoresistance up to ~93%. This unique tunability of the electron pathway arose from the reorientation of the magnetic moment on the transition metal center, resulting in a re-hybridizaiton of the d orbitals. This work indicated that the multi-orbital nature and the spin-orbit coupling could be exploited to construct single-molecule spin switches. Díez-Pérez et al achieved single-molecule electrical switches with an ON-OFF ratio of >100 through spin-dependent transport at

room temperature.¹¹² In their Ni tip/spin crossover Fe^{II} complexes/Au substrate devices, the Ni electrode was magnetically polarized, either an α -up or a β -down spin-polarized Ni, providing a large conductance change between the two distinct states.

As shown in Figure 14B, a novel single oligo(pphenyleneethynylene) (OPE)-based radical molecular junction was successfully prepared by Scheer et al with an MCBJ technique at a low temperature of 4.2 K.¹⁰⁷ Different from those single-molecule junctions where the magnetic center locates in the charge transport channel, the employed molecule in this work had a radical group as a side chain. Surprisingly, the huge impact of magnetic field on electron transport of the OPE radical molecule was observed with magnetoresistances of 16%-287% at a magnetic field of 4 T, while the values in the non-radical pristine OPE were only found to be 2%-4%. The results revealed that the unpaired electron could reduce the electronic coupling between the current-carrying molecular orbital and the electrodes with increasing the magnetic field. Reversible spin switches based on single-atom was realized as well by Lutz et al, as depicted in Figure 14C.¹⁰⁶ The magnetic bistability of individual Ho atoms on MgO was observed, where the switching was induced by tunneling electrons. The magnetic origin of the long-lived states was confirmed by single-atom electron spin resonance on a nearby iron sensor atom.

3.3 | Mechanical force stimuli

As displayed in Figure 15A, van der Zant et al. developed an approach to induce the change of the spin state of Fe^{II} ions by an external stimulus of mechanical force by using the MCBJ technique.¹¹¹ In these molecules, the relative arrangement of the two terpyridine ligands within homoleptic Fe^{II}-complexes could be mechanically controlled. Upon mechanical pulling of source and drain electrodes, the Fe^{II} coordination sphere might be distorted, and thus the spin state of the central metal ion switched from low spin to high spin states. According to the statistics of conductance measurements, a large fraction of molecular junctions formed with the spin-crossover Fe^{II}-complex displayed a conductance increase of one to two orders of magnitude during stretching the electrodes. Although the reversible process that the Fe^{II} ion changed from high spin to low spin states by pushing the electrodes was not yet realized, the concept in the work showed the possibility of building single-molecule spin switches by mechanical force stimuli. With the STM-BJ technique, Lin et al achieved the mechanically controlled reversible spin crossover of single Fe-porphyrin molecules (Figure 15B).¹¹⁰ By mechanically stretching or squeezing the junctions by adjusting the tip height, the center Fe^{II} ion underwent a spin state change between S = 2 and S = 1 reversibly for multiple times.

4 | SUMMARY AND PERSPECTIVE

Single-molecule electrical and spin switches are electronic components of the greatest importance in molecular electronics and spintronics. In this article, we summarize the recent progress of various electrical switches and spin switches in single-molecule junctions according to different external stimuli that induce the switching process. Thanks to the development of synthetic chemistry and device processing techniques, single-molecule switches have been successfully realized in many stimuli-responsive systems and different device structures, which operate by different working principles. Meanwhile, theoretical physic and chemistry also play an important role in explaining the switching mechanism and novel physical phenomena. Unexpectedly, the stimuli-responsive single-molecule device platform also offers unique opportunities for photodetectors, chemical sensors, and biosensors, which are not mentioned in this paper.

We have witnessed various great breakthroughs in molecular electronics in the past two decades. However, there are still some challenges that need to be overcome in future. First, the stability and reproducibility of molecular devices remain challenging, due to the fact that precise control of the contact geometry between the molecule and electrodes is currently difficult. Second, both STM-BJ and MCBJ are exploited as very powerful tools in the fabrication of single-molecule junctions. But these systems require harsh operating conditions, such as high vacuum and ultra-low temperature, which limits their potential for practical applications. Carbon electrodes, including carbon nanotube and graphene, show the priority over gold electrodes, as devices based on carbon electrodes are usually able to work at ambient condition. Third, sometimes controversial issues exist in single-molecule devices arising from the complex fabrication process, special testing condition, and sensitivity to the environment of the devices. However, as the rapid progress of physical characterization technologies, various more complex and precise measurements have been performed, providing more abundant details to support the conclusion repeatedly. In addition, different robust single-molecule device fabrication methods have also achieved considerable developments, which allow the confirmation and comparison of the same physical mechanism in various types of electrical devices and thus provide more solid experimental data. At last, the standard for evaluating single-molecule electrical and spin switches is not completely established, and the further integration of electronic components into digital circuits still stays in the embryonic stage. We have enough confidence to believe that molecular electrical and spin switches have a promising future for bridging hard electronics to the soft molecular world.

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ORCID

Fei Huang https://orcid.org/0000-0001-9665-6642 *Xuefeng Guo* https://orcid.org/0000-0001-5723-8528

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AUTHOR BIOGRAPHIES



Guojun Ke received his BS degree in 2012 and PhD degree in 2017 from the School of Chemistry, Sun Yat-Sen University, under the supervision of Prof. Marcel Mayor and Daibin Kuang. From 2013 to 2016, he was a visiting Student at the University of

¹¹² ₩ILEY-

Basel. He is currently working as a Postdoctoral Fellow in the State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, under the supervision of Prof. Fei Huang and Prof. Xuefeng Guo. His current research is focused on device physics of single-molecule junctions.



Fei Huang received his BS degree in chemistry from Peking University in 2000 and gained his PhD degree in materials science from the South China University of Technology in 2005 under the supervision of Prof. Yong Cao. After postdoctoral work at

the University of Washington with Prof. Alex K.-Y. Jen, he began his academic career in 2009 as a Full Professor at the South China University of Technology. His main interests are in the fields of organic functional materials and devices for opto-electronics.



Xuefeng Guo received his PhD degree in 2004 from the Institute of Chemistry, Chinese Academy of Sciences, Beijing. From 2004 to 2007, he was a Postdoctoral Research Scientist at the Columbia University Nanocenter. He joined the Faculty as

a Professor under the "Peking 100-Talent" Program at Peking University in 2008. His research is focused on functional nanometer/molecular devices.

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