

Single-Molecule Functional Chips: Unveiling the Full Potential of Molecular Electronics and Optoelectronics

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The main focuses of this account are our proposed molecular/interface engineering strategy including interface design using particular linkers, spacers, insulation, and functional centers and our device engineering strategy that covers the design of the device structure and electrode materials. These strategies adequately consider the coupling between functional centers and their external environment, thus affording the ability to evaluate and manipulate the intrinsic behaviors of target molecules. Specifically, a covalent molecule-electrode interface enables high device stability at a high bias voltage. Three nonconjugated methylene groups are inserted at the electrode-molecule interface to prevent the quenching of the excited state of the central molecule (e.g., diarylethene) by the graphene electrode, thereby achieving robust and reversible photoswitches. Cyclodextrins are introduced as insulating groups around molecular bridges to weaken the coupling of the bridges with the environment, which increases the quantum yield of light-emitting diodes. Additional reactive sites are introduced on the sides of the molecular bridges, providing the ability to add new functional centers. We show that using materials with a high dielectric constant as the dielectric layer enables efficient electrical manipulations of single-molecule electronics and optoelectronics by the gate voltage. We reveal that the use of ferromagnetic metal electrodes in single-molecule electronics and optoelectronics can meet the requirements for spin injection. In particular, the two-dimensional structure of graphene electrodes that can be tailored by etching enables high-density integration of molecules, paving the way for future logical manipulation and real-time communication.

These systematic investigations emphasize the importance of single-molecule electronics and optoelectronics for miniaturized device fabrication, intrinsic mechanism exploration, and advanced chip applications. Further interdisciplinary cooperative efforts, including micro- and nanoprocessing, organic synthesis, and theoretical calculation, will contribute to the rapid development of single-molecule electronics and optoelectronics that are suitable for practical applications.

1. INTRODUCTION

The interaction between light and matter, including control of light generation and regulation by a light field, is fundamental to current and emerging technologies that define our society.¹ Continuous effort is being devoted to optimizing electronic and optoelectronic devices using materials that range from bulk to two-dimensional (2D) materials^{2,3} and zero-dimensional quantum dots.⁴ In this regard, a potential ultimate solution to promote device performance, overcome the limits of device miniaturization, and achieve multiple functionalizations is a bottom-up strategy that directly uses opto- or

electroactive single molecules as functional centers; that is, single-molecule electronics and optoelectronics.⁵ To date, diverse single-molecule functional devices have been con-

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Figure 1. Schematic diagram of an integrated photoelectric detection system.¹⁶ Reprinted with permission from ref 16. Copyright 2023 Springer Nature.

structed to achieve both light generation and operation, such as switching,⁶ field effect,⁷ rectification,⁸ photoinduced current,⁹ and electroluminescence.^{10,11} Single-molecule functional chips and corresponding optoelectrical integrated detection technologies allow simultaneous multimodal measurements of the inherent photophysics of anchored molecules, which provide profound insights into molecular design and single-molecule device fabrication.

In recent decades, many types of single-molecule devices have been developed. Regardless of their preparation methods, achieving precise and reliable generation of either dynamic or static electrode pairs with nanoscale gaps is essential to connect individual molecules between electrodes. Dynamic single-molecule devices, such as scanning tunneling microscopy break junctions (STM-BJs)¹² and mechanically controlled break junctions (MCBJs),¹³ rely on a mechanical force to induce precise movements of electrodes and ensure that the bridging molecule is immobilized between electrode pairs. In contrast, static single-molecule devices, including electromigration junctions¹⁴ and carbon-based junctions,¹⁵ use different etching methods (such as oxygen plasma etching

and Joule thermal etching) to form fixed nanoscale gaps. Carbon-based single-molecule devices, especially graphenemolecule-graphene single-molecule junctions (GMG-SMJs), offer distinct advantages over other single-molecule devices such as controllable edge structures and stable properties. First, taking advantage of the rich chemistry of carbon, the formation of covalent amide bonds between graphene electrodes and individual molecules can be achieved, affording stable connections that enhance device durability during measurements in different environments. Second, the integrability and compatibility of GMG-SMJs with the complementary metaloxide-semiconductor (CMOS) technology facilitate their industrial application. Third, the GMG-SMJ platform provides the possibility of realizing integrated photoelectric detection (Figure 1).¹⁶ Specifically, the control cables among the microscope electron-multiplying charge coupled device, spectrometer, and single-photon counter are connected to the trigger of the lock-in amplifier. Based on the synchronous collection of optical and electrical signals, correlation analysis is employed to determine the basic metastable state of the photophysical process.



Figure 2. Diarylethene (DAE) single-molecule photoswitches based on photoisomerization. (A) Molecular structures of optimized DAEs for photoswitching.²² Reprinted with permission from ref 22. Copyright 2013 Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Schematic diagram of a robust and reversible single-molecule photoswitch.⁶ (C) Current–voltage (I-V) characteristics of DAE GMG-SMJs in open (black line) and closed (red line) forms.⁶ (D) Real-time switching of a single DAE upon cyclic exposure to UV and vis irradiation.⁶ Reprinted with permission from ref 6. Copyright 2016 American Association for the Advancement of Science.

In this Account, we systematically review our recent progress in the development of a series of functional devices with different functions, including photoswitching, field effect, rectification, light emission, spin switching, memristive effect, and unique electron transport, based on static GMG-SMJs and dynamic STM-BIs. Through straightforward interface engineering by inserting nonconjugated methylene (CH_2) moieties, reliable and reversible single-molecule photoswitches are constructed. Device engineering by introducing an ionicliquid gate and material with a high dielectric constant (k)allows light-controlled high-performance single-molecule fieldeffect transistors (FETs) and rectifiers to be developed. By adopting a molecular engineering approach that involves introducing cyclodextrins (CDs) as insulating groups, robust single-molecule light-emitting diodes (LEDs) that exhibit fluorescence and phosphorescence are constructed for realtime communication and full-order logic operation. Through rational designs of molecular materials, spin electronics and memristors based on single-molecule multifunctional devices are realized. In addition, several unique optoelectronic molecules that act as single-molecule wires are designed and their charge transport properties are investigated.

2. PHOTOINDUCED SWITCHING IN SINGLE-MOLECULE OPTOELECTRONICS

Control of electron transport through single molecules and regulation of the electronic properties of single-molecule devices using light, such as photoisomerization,⁶ plasmoninduced effect,¹⁷ and exciton dynamics,¹⁸ is the cornerstone of functional optoelectronic devices. Photoisomerization is a sensitive, convenient, and noninvasive way to create bistable states for switching. It is particularly attractive to use photochromic molecules such as diarylethene (DAE) and azobenzene derivatives in single-molecule junction applications because of their high thermal stability and fatigue resistance.

2.1. Diarylethene-Based Single-Molecule Optoelectronics

The 6π -electron triene cores of DAE derivatives can undergo a light-induced disrotatory ring closure; that is, they switch to the closed state upon exposure to ultraviolet (UV) light (300–400 nm) and switch back to the open state under visible (Vis) light irradiation (500–700 nm). The closed state of diary-lethene (*c*DAE) refers to the configuration that is planar, highly conjugated, and highly conductive, whereas the open state of diarylethene (*o*DAE) is the configuration that is distorted and has localized conjugation and low conduction. Therefore, reversible photoelectric switching between *c*DAE and *o*DAE has been observed. It is noteworthy that the slight length discrepancy between *c*DAE and *o*DAE of several angstroms enables the fabrication of stable devices on a chip.

The first DAE single-molecule switch was constructed using the MCBJ technology.¹⁹ The gold (Au)-based device achieved switching from conducting (*c*DAE) to insulating (*o*DAE) states when illuminated with Vis light, but failed to switch back upon irradiation with UV light. Because the calculated first excited potential surface of DAE is close to the Fermi energy of Au electrodes, this one-way switching phenomenon can be attributed to energy transfer from the first excited state of *o*DAE to Au electrodes, leading to the lack of ring closure. Charge-transport characteristics of several DAE devices based on STM-BJs have also been investigated at the single-molecule level.²⁰ To construct a reversible DAE single-molecule switch and overcome the quenching caused by Au electrodes, singlewalled carbon nanotube electrodes and amide bonds were introduced to tailor the DAE-electrode interface.²¹ However, although this device showed ring closure under UV irradiation, ring opening did not occur for the thiophene-based DAE molecule under Vis irradiation. This is because of the quenching effect of the excited state of the *c*DAE caused by the strong electronic coupling between electrode and DAE, emphasizing the importance of the DAE-electrode interface. Single-molecule carbon nanotube devices with pyrrole-based molecules switched to *c*DAE under UV irradiation and switched back to *o*DAE after being kept in the dark for 12 h.²¹

To further improve the DAE-electrode interface and construct a reversible switch, fluoro substituents were introduced onto the DAE core to narrow the gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), graphene point electrodes were constructed to tailor the Fermi energy, and a CH₂ group was included between the terminal amine group and DAE functional center on each side to restrict the delocalization of π electrons and decouple the molecule-electrode interface. All these features enabled the transition from *c*DAE to *o*DAE (Figure 2A).²² Both first-principle calculations and transition voltage spectroscopy measurements demonstrated that the CH₂ group weakened the molecule-electrode coupling to some extent. However, a reversible configuration change of DAE was still not achieved.

Two-way switching in DAE single-molecule switches was eventually achieved by inserting three nonconjugated CH_2 groups between the core and anchoring amine groups as linkers to optimize the molecule-electrode interface (Figure 2B and C).⁶ A robust and reversible DAE single-molecule switch was constructed with high accuracy (on/off ratio of 100), stability (operation for over a year), and reproducibility (46 devices with more than 100 cycles of photoswitching and ~10⁵ to 10⁶ cycles of stochastic switching) (Figure 2D).

2.2. Azobenzene-Based Single-Molecule Optoelectronics

Azobenzene, another typical photochromic molecule, can undergo reversible switching between *trans* and *cis* configurations when exposed to UV and Vis light, respectively. Upon UV irradiation, the planar *trans* configuration can photoisomerize to the twisted *cis* form, whereas Vis irradiation triggers the opposite process. The variation in the photoresponsive conductance of azobenzene upon photoisomerization is attributed to the modification of not only its frontier molecular orbitals (FMOs), but also its intramolecular dipole.

Under UV irradiation (254 nm), the azobenzene unit in the backbone of the molecular bridge in a single-molecule device undergoes a configurational change from *trans* (0 D) to *cis* (3 D) configurations, decreasing the conductance because the HOMO–LUMO energy gap increases and skews the energy-level alignment with the electrode Fermi energy. In contrast, Vis irradiation facilitates reverse photoisomerization, nearly restoring the original conductance.²³ By combining the light regulation of azobenzene units with the pH regulation of sulfonic acid units, such single-molecule devices show potential to function as logic gates.

Instead of an azobenzene group as the backbone, asymmetric devices with a side azobenzene unit also exhibited optical switching and stochastic conductance switching under a specific bias interval, which stemmed from switching between *trans* (1.22 D) and *cis* (6.59 D) configurations of azobenzene (Figure 3A).²⁴ Notably, such bias-control ability reveals the potential to manipulate molecular configurations using an electric field (Figure 3B). Single-molecule dynamic analysis



Figure 3. Azobenzene single-molecule photoswitches based on photoisomerization and their stereoelectronic effect. (A) Schematic diagram of a single-molecule photoswitch with an azobenzene substituent as a side group.²⁴ (B) Electrical control of a single-molecule azobenzene photoswitch.²⁴ Reprinted with permission from ref 24. Copyright 2019 Springer Nature. (C) Schematic diagram of the stereoelectronic effect of *cis*-azobenzene.²⁵ (D) Schematic diagram of the stereoelectronic effect of *trans*-azobenzene.²⁵ (E) Current–time (*I*–*t*) curves at 80 K for *trans* azobenzene and histogram of the two conducting states caused by left phenyl-ring rotation.²⁵ (F) *I*–*t* curves at 80 K for *cis*-azobenzene and histogram of the four conductance states caused by both left and right phenyl-ring rotations.²⁵ Reprinted with permission from ref 25. Copyright 2021 Wiley–VCH GmbH.

and theoretical investigations elucidated the role of bias voltage in adjusting the energy levels of *trans* and *cis* configurations of azobenzene, decreasing the activation energy and making the *cis* form thermodynamically favorable. Such bias-gated, fully reversible, two-mode, single-molecule devices provide useful insights for constructing logic gates. Moreover, incorporating an azobenzene moiety as a lateral substituent on a terphenyl central ring diversified its stereoelectronic polymorphism (Figure 3C and D). That is, the *cis* and *trans* configurations of the azobenzene substituent influenced the dihedral angle between the substituted phenyl ring and bilateral phenyl rings and corresponding rotational barriers, ultimately leading to eight distinct conformational states: four for the *trans* configuration and four for the *cis* configuration. At 80 K, the



Figure 4. Photoresponsive single-macromolecule devices with an azobenzene unit. (A) Schematic of a single-molecule photoresponsive peptide.²⁶ (B) Conductance changes of the photoresponsive peptide originating from photoswitching under UV (left) or vis (right) irradiation.²⁶ Reprinted with permission from ref 26. Copyright 2020 Wiley–VCH GmbH. (C) Schematic diagram of a photoresponsive single supramolecule.²⁷ (D) Interconversion dynamics of the single host–guest supramolecule between *trans* and *cis* configurations.²⁷ Reprinted with permission from ref 27. Copyright 2022 Wiley–VCH GmbH.

trans configuration displayed two conductance states upon rotation of the right phenyl ring (Figure 3E), whereas the *cis* configuration demonstrated four conductance states for both left and right phenyl-ring rotations (Figure 3F). This discrepancy primarily arose from the higher barrier of rotation of the right phenyl ring in the *trans* configuration in comparison with that of the right phenyl ring in the *cis* configuration. Thus, rational design of molecules can precisely tune the stereoelectronic effect in single-molecule devices.

The straightforward and easily constructible architecture of azobenzene facilitates its incorporation into supramolecules and peptides as a functional unit that is responsive to light. The azobenzene unit serves as a photoswitching moiety within cyclic peptides, triggering large geometric changes and enabling the study of structural dynamics in real time (Figure 4A).²⁶ Specifically, the peptide forms a secondary structure through hydrogen bonding and the dihedral angle changes simultaneously when the azobenzene unit isomerizes from trans to cis under UV irradiation. The opposite process occurs under Vis irradiation, leading to alternating conductance as the photoswitching peptide is exposed to UV or Vis light (Figure 4B). Real-time conductance measurements identified three distinct conformational states for each isomer. Each state was linked to a defined range of hydrogen bond lengths in the cis isomer and to specific dihedral angles in the trans isomer through molecular dynamics simulations. This deeper understanding of peptide structural dynamics can be used to explore the photoresponsive behaviors of proteins, facilitating the development of bioinspired optoelectronic nanodevices.

An azobenzene unit was introduced onto an axel of the pseudorotaxane supramolecule 1-[10-(4-phenylazophenoxy)-decyl] pyridinium bromide (AzoC10) as a photoresponsive guest and permethylated- α -cyclodextrin (PM- α -CD) was used as a host (Figure 4C).²⁷ Because of hydrophobic and van der

Waals interactions with the inner surface of the CD cavity, trans-AzoC10 is efficiently recognized by PM- α -CD. However, the transformation of planar trans-AzoC10 into the sterically bulky nonplanar cis-AzoC10 precludes the inclusion of cis-AzoC10 in PM- α -CD because of its shape mismatch with the CD cavity. Given that azobenzene groups transition selectively from trans to cis under UV irradiation and revert from cis to trans under Vis light, this property enabled the modulation of host–guest interactions and facilitated the study of singlesupramolecule dynamics (Figure 4D). Embedding lightresponsive units within supramolecules paves the way for developing advanced single-supramolecule optoelectronic devices, which could potentially act as powerful light-driven memristors with high information capacity.

3. FIELD EFFECT AND RECTIFICATION IN SINGLE-MOLECULE OPTOELECTRONICS

FETs and rectifiers are indispensable in modern electronics, highlighting their need for integration into optoelectronic chips. In particular, field-effect and rectification behaviors controlled by light are of interest for single-molecule optoelectronics.^{28,29} To this end, two ruthenium complexes $[AcS-C_6H_4-C \equiv C(dppe)_2Ru]^+ (dppe = 1,2-bis-$ (diphenylphosphino)ethane) were appended on each end of DAE (Ru-DAE) to decouple the electrodes and realize reversible photoswitching. The combination of the robust GMG-SMJ platform with the unique charge-transport characteristics and conductive orbitals of DAE endowed the Ru-DAE single-molecule devices with favorable field-effect and rectification behavior, as well as an original photoswitching effect. When UV irradiation induced the ring-closing reaction of Ru-DAE, the proximity of the perturbed HOMO of RuoDAE to the graphene Fermi level allowed it to be modulated



Figure 5. Light-controlled single-molecule FET and rectifier based on Ru-DAE. (A) Schematic diagram of a single-molecule Ru-DAE FET integrated with a photoswitch.⁷ Reprinted with permission from ref 7. Copyright 2022 Springer Nature. (B) Schematic diagram of a single-molecule DAE rectifier integrated with a photoswitch.⁸ Reprinted with permission from ref 8. Copyright 2021 American Chemical Society. (C) Field effect of a Ru-*o*DAE transistor.⁷ (D) Field effect of a Ru-*c*DAE transistor.⁷ (E) Rectification characteristics of a Ru-*o*DAE transistor.⁸ (F) Rectification characteristics of a Ru-*c*DAE transistor.⁸

by applying a gate voltage (Figure 5A).⁷ Specifically, upon using high-k metal oxides (5 nm of hafnium oxide HfO₂ and 5 nm of aluminum oxide Al₂O₃) as dielectric layers and applying a negative gate voltage, the dominant conducting molecular orbital (that is, the perturbed HOMO) of Ru-oDAE was elevated, thereby enhancing the conductance and maintaining the maximal on-state current at a low gate voltage (Figure 5C). In comparison, a Ru-cDAE transistor exhibited a weaker field effect (Figure 5D). A robust solid-state single-molecule FET with a maximum on/off ratio exceeding 3 orders of magnitude was constructed using high-k metal oxides; such an FET brings us a step closer to industrial application of single-molecule optoelectronics.

The localized characteristics of the FMOs of Ru-*o*DAE enable the high tunability of an individual part of the electron density by a gate electric field. Thus, UV irradiation to induce the ring-closing process accompanied by a gate electric field can markedly enhance the rectification behavior of Ru-*o*DAE. Specifically, the FMOs will shift asymmetrically under a gate electric field when an ionic liquid is used as the gate dielectric (7.5 Å-thick electrical double layer), while the strong conjugation and delocalization of the FMOs of Ru-*c*DAE constrain the FMOs to shift synchronously (Figure 5B).⁸ This

asymmetric orbital shift increases the degeneracy and the symmetry breaking induces intramolecular polarity, resulting in diode-like behavior with tunable rectification ratio. Overall, a gate-controlled rectifying function with an on/off ratio of ~60 and high-performance field effect with a maximum on/off ratio of >100 were simultaneously realized in a reversible Ru-DAE single-molecule photoswitch (Figure 5E). In contrast, RucDAE showed a relatively poor rectifying capacity because it did not exhibit an asymmetric orbital shift (Figure 5F). Notably, the remarkable field effect and symmetry-induced rectification of Ru-oDAE could be reversibly switched on and off by UV and Vis irradiations, respectively.

4. ELECTROLUMINESCENCE IN SINGLE-MOLECULE OPTOELECTRONICS

Multiple types of single-molecule electroluminescent devices have been developed to date, including devices with electroluminescence originating from electrode plasmons or individual molecules. In this section, we focus solely on the electroluminescence generated by an individual molecule. In comparison with single-molecule photoswitches controlled by light, generating light using electricity poses considerable challenges, necessitating greater efforts in device preparation



Figure 6. Single-molecule electroluminescence from GMG-SMJs. (A) Schematic diagram of a single-molecule LED.¹⁰ Reprinted with permission from ref 10. Copyright 2023 Wiley–VCH GmbH. (B) Emission color of devices protected with PDMS subjected to different cross-linking times. Inset: Proportions of donor and acceptor emission during PDMS cross-linking.¹⁰ (C) Schematic diagram of a single-molecule optoelectronic chip.³³ Reprinted with permission from ref 33. Copyright 2024 Elsevier Inc. (D) Superhigh-resolution optical imaging of the Pt-based molecular device.³³ (E) Output image (the logo of Peking University) reconstructed from the emitted photons from a single-molecule optical chip.³³ (F) One line of the output photons in E (top) and measured input electrical pulse sequence with 10 ms resolution (bottom).³³ (G) Schematic diagram of two single-molecule devices that enabled the combination of basic logic gates.³³ (H) Demonstration of a full adder, with the right device serving as the sum and the left device as carry-out.³³

and molecular engineering. From the design point of view, several considerations must be addressed: 1) adjusting the energy of luminescent molecules to emit light of specific wavelengths using substituents; 2) matching the energy level of molecules with the electrode Fermi energy to minimize energy loss caused by nonradiative recombination and enhance the conversion efficiency of electricity to light; 3) decoupling molecules from electrodes to prevent fluorescence quenching;

and 4) establishing a stable molecular device capable of withstanding high bias voltages (note that theoretically the voltage at which molecules can emit visible light cannot be lower than 1.4 V when the upconversion mechanism is not included).

The STM-BJ is the first technology used to investigate the electroluminescence properties of individual molecules. Various decoupling methods using oxide or sodium chloride



Figure 7. Spin regulation of a single radical molecule. (A) Schematic diagram of a single-molecule radical device with regulation of quantum spin.³⁶ (B) Direct regulation of spin using an external electric field.³⁶ (C) Direct regulation of spin using temperature.³⁶ (D) Direct regulation of spin using an applied magnetic field.³⁶ Reprinted with permission from ref 36. Copyright 2024 Springer Nature.

barriers have been developed, pushing the rapid progress of single-molecule LED technologies.^{30,31} Utilizing carbon materials such as carbon nanotubes³² and graphene as electrodes can improve the stability and CMOS compatibility. In particular, covalent bonds are ideal for reliably connecting electrodes with electroluminescent molecules and ensuring that the connections can withstand high voltages. Covalent bonding can be achieved by employing graphene point electrodes with edge carboxylation to form amide bonds with amino groups of electroluminescent molecules, facilitating charge transfer and decoupling the interaction between molecule and electrode. In a previous study,¹⁰ carbazole molecular bridges were used to construct GMG-SMJs, and a side chain was included on the molecular bridge to enable in situ substitution with a second fluorescent center to adjust emission light. Encapsulation of the molecular bridge in polydimethylsiloxane (PDMS) yielded a device that exhibited room-temperature electroluminescence (Figure 6A). Real-time optoelectronic detection of molecules revealed that the luminescence of individual molecules was guantized and

corresponded to changes in conductance. The proposed electroluminescence mechanism involves electrons jumping from the left electrode to the LUMO of the molecule and electrons on the HOMO of the molecule jumping to the right electrode, forming an excited state. The subsequent relaxation from the excited state to the ground state leads to photon emission. By controlling the Förster resonance energy transfer from the molecular bridge to the side fluorescent center, fluorescence switching between the two fluorescent centers can be achieved, enabling the regulation of the emission wavelength (Figure 6B).

In comparison with organic compounds, transition-metal complexes with π -conjugated ligands are renowned for their favorable fluorescence and phosphorescence properties. In GMG-SMJs, platinum (Pt) molecular bridges insulated by CD were covalently connected to the electrodes via amide bonds (Figure 6C).³³ The spin-orbit coupling of the heavy atom Pt enables effective transitions from singlet to triplet states and direct relaxation from triplet to ground states, which leads to bright emission (Figure 6D). Importantly, the CD insulation



Figure 8. Single-molecule memristors. (A) Schematic diagram of a single-molecule memristor driven by dynamical structure reconfiguration.⁴² (B) Read–erase–write–read operation in a chemically controlled single-molecule memristor. The first row shows para reconstruction catalyzed by polyphosphoric acid. The second row shows the corresponding applied operational voltages, and the third row shows ortho reconstruction catalyzed by TiCl₄.⁴² Reprinted with permission from ref 42. Copyright 2022 Wiley-VCH GmbH. (C) Schematic diagram of a single-molecule AIE device and the corresponding structural transitions, which provide great potential for the device to function as a memristor.⁴⁷ (D) Real-time *I*–*t* monitoring (top) of the structural transitions (bottom) of a single molecule.⁴⁷ Reprinted with permission from ref 47. Copyright 2022 Elsevier Inc.

on both sides of the Pt molecular bridge serves to weaken the coupling with the environment, thereby suppressing nonradiative processes. By adjusting bias and gate voltages, the device reliably emitted fluorescence or phosphorescence, enabling real-time optical imaging and chip communication (Figure 6E and F). Furthermore, two of these devices served as bits in logic operations (Figure 6G). By setting the dark state as '0' and light emission as '1', the devices executed 16 binary Boolean logic operations, as well as full adder (Figure 6H) and full subtractor operations. Moreover, by assigning the categories of emitted photons (fluorescence as '1' and phosphorescence as '2'), ternary logical operations can be achieved, offering novel prospects for the advance of optical chip technology. Beyond logical operations and information communication, multifunctional single-molecule optoelectronic chips provide valuable insights into single-molecule photophysical processes and serve as an alternative optoelectronic strategy for constructing integrated nanocircuits that break the confines of Moore's Law.

5. SPIN REGULATION IN SINGLE-MOLECULE ELECTRONICS AND OPTOELECTRONICS

The emergence of spintronic devices that facilitate logical operations, information storage, and information retrieval has catalyzed advances in electronic information technologies.³⁴ Meanwhile, single-molecule radical devices have revealed the interplay between unpaired electrons and conduction electrons at the molecular scale.³⁵ However, ensuring the stability and precise spin control of radical molecules at ambient temperatures remains a formidable challenge in the development of single-molecule radical devices. To address this challenge, a strategy developed recently involved the insertion of a biradical organic molecule naphtho[1,2-c:5,6-c]bis([1,2,5]thiadiazole) into graphene nanoelectrodes through covalent amide bonds, enabling the construction of single-molecule radical devices that were stable at room temperature (Figure 7A).³⁶ The transitions of electron configurations among the closed-shell singlet (closed-shell), open-shell singlet (singlet), and openshell triplet (triplet) states were effectively manipulated by temperature, electric field, and magnetic field (Figure 7B-D). Specifically, the increasing electric field decreased the potential energy disparity between these states, promoting the shift from the closed-shell state to the triplet state (Figure 7B). As the temperature increased, the probability of transition from the closed-shell state to the open-shell states rose and the transformation rate accelerated (Figure 7C). An applied magnetic field facilitated the transition from the closed-shell state to the triplet state and impeded the transition from the



Figure 9. Conductance regulation in optoactive single-molecule wires. (A) Schematic diagram of single-molecule A-D-A, D, and pA-D-A STM-BJs.⁵¹ (B) 2D conductance-displacement histograms for A-D-A junctions.⁵¹ (C) 2D conductance-displacement histograms for D junctions.⁵¹ (D) Conformational inversion barriers for pA-D-A.⁵¹ (E) 2D conductance-displacement histograms for pA-D-A junctions. The purple trace (high conductance state) corresponds to pA-D-A(S), and the green trace (low conductance state) corresponds to pA-D-A(CN).⁵¹ Reprinted with permission from ref 51. Copyright 2023 Wiley–VCH GmbH. (F) Schematic diagram of a DPP single-molecule FET based on a GMG-SMJ.⁵⁴ (G) Transmission spectra of a series of DPP, which exhibit an odd–even effect.⁵⁴ Reprinted with permission from ref 54. Copyright 2020 Wiley–VCH Verlag GmbH and Co. KGaA, Weinheim.

closed-shell state to the singlet state (Figure 7D). This singlemolecule electrical technique can quantitatively decipher corresponding thermodynamic and kinetic mechanisms and enable simple and efficient characterization of open-shell species.

Spin injection using ferromagnetic metal (nickel) leads has been achieved in GMG-SMJs.³⁷ Foreseeably, injected spin electrons could interact with single-molecule radicals to regulate their spin. Full clarification and regulation of the intrinsic characteristics of the electron (spin) and charge transport in single-molecule radical devices could facilitate the combination of spintronic and optoelectronic devices. Such detection and regulation of electron spin could be naturally expanded into optoelectronic molecules to realize effective control of phosphorescence and fluorescence.^{38,39}

6. MEMRISTIVE EFFECTS IN SINGLE-MOLECULE ELECTRONICS AND OPTOELECTRONICS

The development of memristive devices can be regarded as a promising avenue for sustaining Moore's law because no additional gate electrodes are required.⁴⁰ Over the past few decades, scientists have made considerable progress in the miniaturization of memristive devices, especially memristor arrays at the nanoscale.⁴¹ Recently, a reliable single-molecule memristive effect from dynamic structural reconstruction of

phenol, rather than typical electrochemical doping or charge capture, was reported (Figure 8A).⁴² Specifically, based on the electric field-driven Fries rearrangement (Figure 8B), precise manipulation of the potential energy surface by the bias voltage enabled the desired species to be maintained or switched along the reaction coordinate to achieve a memristive effect. This phenol memristor can be erased by a bias pulse of +0.6 V (-0.6 V), and written and read by a bias of 0.05 V (-0.05 V). The covalently connected solid-state single-molecule memristor demonstrates a remarkable performance by enduring over 2000 high-frequency write-erase operations within a brief 10-s period, showing the stability of resistance switching through structural reconstruction. The precise manipulation of optoelectronic molecules using electric fields not only enables effective control over properties, but also inherently forms a pathway for constructing logic gates and facilitating in-memory computing.^{43,44} Such innovation is integral to the development of storage and computation integration within optoelectronic materials, and will contribute to the miniaturization of devices across multiple dimensions. Consequently, single-molecule optoelectronic memristors face large growth prospects in future technological landscapes.⁴⁵

The ability of an external electric field to tune the activation barrier in single-molecule junctions applies not only to chemical reactions, but also to the transformation of molecular



Figure 10. Conductance regulation in electroactive molecules. (A) Schematic diagrams of charge transport in *ac*-HBC and *zc*-HBC.⁵⁶ (B) Conductance of *ac*-HBC-based GMG-SMJs.⁵⁶ (C) Conductance of *zc*-HBC-based GMG-SMJs.⁵⁶ (D) 2D conductance-displacement histograms for *ac*-HBC junctions with a conductance peak at ~1.6 × 10⁻⁴ G_0 (12.3 nS).⁵⁶ (E) 2D conductance-displacement histograms for *zc*-HBC junctions with a conductance peak at ~1.6 × 10⁻⁴ G_0 (12.3 nS).⁵⁶ (E) 2D conductance-displacement histograms for *zc*-HBC junctions with a conductance peak at ~1.3 × 10⁻⁵ G_0 (1.0 nS).⁵⁶ Reprinted with permission from ref 56. Copyright 2023 American Association for the Advancement of Science. (F) Schematic diagram of an azulene-based single-molecule device with a PNP structure.⁵⁹ (G) *I–V* characteristics of azulene-based and naphthalene-based single-molecule devices at 5 K.⁵⁹ (H) Plot of ln *I/V*^{0.5} versus 1/*T* for azulene-based single-molecule devices, showing the temperature (10 K) of the change of the electron-transport mechanism from thermal emission to tunneling.⁵⁹ (J) Calculated thermal emission barrier of azulene-based and naphthalene-based single-molecule devices, showing the temperature (140 K) of the change of the electron-transport mechanism from thermal emission to tunneling.⁵⁹ (J) Calculated thermal emission barrier of azulene-based and naphthalene-based single-molecule devices.⁵⁹ Reprinted with permission from ref 59. Copyright 2022 American Chemical Society.

configurations and conformations. By embedding tetraphenylethylene derivatives, which are typical aggregation-induced emission (AIE) units,⁴⁶ in GMG-SMJs (Figure 8C), the intrinsic dynamic behaviors of conformation transitions, including alkene (C=C) bond twisting, phenyl rotation, cyclization, and side phenyl rotation, as shown in red, green,

blue, and purple (Figure 8D), respectively, were visualized *in situ* and deciphered through precise measurements of the molecular conductance at cryogenic temperatures.⁴⁷ Similar to the phenol memristor, manipulating the electric field allowed us to regulate intramolecular vibrations and rotations. In particular, the activation energy was lowered to facilitate C==C bond twisting. Because the luminescence of AIE molecules is strongly connected to the molecular vibration, integrating the single-molecule luminescence with electric field-controlled intramolecular vibration will fully elucidate the intrinsic AIE mechanism and provide efficient light sources.⁴⁸ More valuable is that the direct manipulation of the molecular conformation using electric fields will break through traditional understanding and regulate "AIE" properties at the single-molecule level to achieve memristive effects.

7. CONDUCTANCE REGULATION IN SINGLE-MOLECULE ELECTRONIC AND OPTOELECTRONIC WIRES

Single-molecule wires are the archetypal elements in molecular electronics. The design of efficient molecular wires with a controlled relationship between conductance and structure, the effective regulation of energy levels, and known effects of photoelectronics on charge transport is still a subject of intense research.⁴⁹ Elucidating the relationship between molecular structure (energy levels, spin state, configuration, and conformation) and carriers (behavior of electrons and excitons) is critical for the development of single-molecule wires. Therefore, in combination with molecular structures, here we review the charge-transport properties and future functionalization of a series of candidate molecules for single-molecule wires.

7.1. Acceptor–Donor–Acceptor Molecule

In the past decade, considerable advances have been achieved in organic photovoltaics primarily because of the development of innovative semiconductor materials. A typical example is donor-acceptor-donor (A-D-A) molecules, which have unique electronic properties that influence the photoelectric process.⁵⁰ To delve into such properties, we used the STM-BJ technique to measure the electron-transport properties of the whole A-D-A molecule and the role of bilateral acceptor groups (Figure 9A).⁵¹ We found that protonation can break the S-O noncovalent conformational lock and expose both S and CN anchoring sites, allowing the direct detection of solely the central donor unit (Figure 9E). Overall, the STM-BJ-based devices ranked from high to low conductance as follows: protonated A–D–A with S anchoring sites (pA-D-A(S)), A-D-A with CN anchoring sites (A-D-A(CN)), protonated A–D–A with CN anchoring sites (pA-D-A(CN)), and only the donor part with S anchoring sites (D(S)) (Figure 9B–D). The higher conductance of A-D-A(CN) than that of D(S)was caused by the orbital hybridization of the central donor unit with the acceptor groups on both sides and the participation of additional transport LUMOs. The higher conductance of pA-D-A(S) than that of D(S) demonstrated that the acceptor groups on both sides of the donor group provided conductive orbitals that were delocalized across the entire A-D-A molecule. Moreover, the higher conductance of A–D–A(CN) than that of pA–D–A(CN) was ascribed to the decreased conjugation in the A-D-A molecule caused by protonation-induced reversion. The higher conductance of pA-D-A(S) than that of A-D-A(CN) indicated that

opposite dipole moments between the donor and each acceptor can establish dual barriers in the charge-transport pathway of the A–D–A junction, effectively suppressing biasdependent charge movement. Exploring the electronic properties of single A–D–A-type molecules with a particular focus on the effect of acceptor groups can provide valuable insights essential for the innovative design of molecules with adaptable features to enable the construction of high-performance optoelectronic devices.

7.2. Diketopyrrolopyrrole Molecule

Within the realm of optoelectronic materials, diketopyrrolopyrrole (DPP) is distinguished by its chemical adaptability, durability, and exceptional photoelectrical characteristics. As a result, DPP has been used in many semiconductor electronic devices.⁵² Charge transport through LUMO+1 and LUMO+2 orbitals of DPP at room temperature has recently been probed using the combination of an ultrafast laser and STM-BJs.⁵³ To further unveil the structure-activity relationship of DPP, we synthesized four DPP molecular bridges (AM_n -DPP, n = 0-3) with different methylene linkers to investigate the effects of the electrode-DPP interface on gate-controlled charge transport in DPP-based single-molecule FETs constructed as GMG-SMJs with ionic liquid gating (Figure 9F).⁵⁴ The insertion of methylene groups efficiently weakened electrode-DPP interface coupling. The alignment of the HOMOs of AM₀-DPP and AM_1 -DPP with the graphene Fermi level (Figure 9G) meant that the perturbed FMO energy levels remained static relative to the graphene Fermi level because of the pinning of the HOMO under negative gate voltages. In contrast, positive gate voltages released the pinning effect, leading to an obvious downward adjustment of the perturbed FMO energy levels. Even at a gate field of 1 V, the perturbed HOMO remained closer to the graphene Fermi level than the perturbed LUMO, acting as the dominant conducting channel and resulting in a continuous decrease in conductance. Regarding AM2-DPP and AM3-DPP, the ambipolar transport behavior of their single-molecule junctions was explained by the position of the graphene Fermi level in the middle of the perturbed HOMO and perturbed LUMO at zero gate voltage. This comprehensive study deciphered the effect of the electrode-DPP interface on the charge-transport properties of photoactive DPP single molecules, providing essential knowledge for the development of practical single-molecule optoelectronic devices.

7.3. Polycyclic Aromatic Hydrocarbon

Graphene-like polycyclic aromatic hydrocarbons resemble functional carbon-based materials and offer a tunable and compatible HOMO-LUMO gap for photoregulation and luminescence.⁵⁵ A fused-ring aromatic molecule hexabenzocoronene (HBC) with a discoidal structure displays armchair (*ac*-HBC) and zigzag (*zc*-HBC) forms, which can affect charge transport properties, and generate quantum effects (Figure 10A).⁵⁶ Using both GMG-SMJ (Figure 10B and C) and STM-BJ platforms (Figure 10D and E), the inherent influence of ac-HBC and zc-HBC on charge transport was studied. The measurements on GMG-SMJ platforms show that the conductance of ac-HBC is 2 orders of magnitude larger than the conductance of zc-HBC. 2D conductance-displacement histograms of ac-HBC (12.3 nS) and zc-HBC (1.0 nS) from STM-SMJ also support the relative conductance relation. The measurements revealed that charge carriers were preferentially transported along ac-HBC, resulting in a current ten times higher than that along zc-HBC. In addition, zc-HBC exhibited

a smaller HOMO-LUMO gap and superior field-effect performance with lower off-state conductance than was the case for *ac*-HBC. Investigation of the charge-transport behavior of *ac*-HBC and *zc*-HBC contributes valuable insight into the electronic characteristics of π -conjugated systems, which is crucial for the development of high-performance molecular nanocircuits for use in optoelectronics.

7.4. Azulene Molecule

Azulene possesses a partially negatively charged five-membered ring and partially positively charged seven-membered ring. This structure endows azulene with favorable optical properties, such as anti-Kasha fluorescence, arising from its unique FMOs.⁵⁷ Moreover, the intrinsic dipole moment of the azulene-based π -conjugation system facilitates the formation of electrochromic and fluorescent materials.⁵⁸ A molecule with two back-to-back azulene units has been used to construct single-molecule devices with a PNP structure (n-type or electropositive region sandwiched between two p-type or electronegative regions) (Figure 10F).⁵⁹ At cryogenic temperatures, the PNP structure exhibited bidirectional rectification because of its inherent dual-direction dipole moment (Figure 10G). In addition, the inherent dipole moments within the single-molecule PNP structure effectively lowered the transition temperature of charge-transport switching from thermionic emission to tunneling (Figure 10H and I) and lowered the transport barrier (Figure 10J). The introduction of two opposing dipole moments into single-molecule PNP FETs, along with increasing polarizability, also boosted the on-off current ratio and gate modulation.⁶⁰ The study of the electrical properties of azulene, in combination with single-molecule luminescence, establishes a foundation for subsequent research on the optoelectronic properties of azulene, including protontransfer dynamics and anti-Kasha luminescence.⁶¹

8. CONCLUSION AND OUTLOOK

In this Account, we systematically review different strategies developed for constructing single-molecule functional devices based on GMG-SMJs and STM-BJs. Considering interface engineering, robust and reversible single-molecule photoswitches and photoresponsive single-macromolecule devices based on DAE and azobenzene units were constructed. In combination with the unique Ru-DAE molecule, the device engineering strategy has provided light-controlled highperformance FETs and rectifiers. Based on the molecular engineering strategy, precise single-molecule LEDs have been developed, which paves the way for further practical applications including real-time communication and logic operation; spin electronics, including spin injection and room-temperature spin regulation, and memristive devices based on external electric-field regulation reveal the potential to realize multifunctional devices; and charge-transport characteristics of typical optoelectronic molecules have been investigated with the aim of developing single-molecule wires.

These systematic studies consistently show that an opto- or electroactive single molecule can indeed work as the main component of functional ultraminiaturized molecular nanocircuits. Compared to macroscopic devices, these singlemolecule devices have special advantages. First, the concomitant enormous electric field in the nanoscale conductive channel of a single-molecule device could effectively modulate the potential barrier of molecular reconstruction, isomerization and conformation change, which inherently forms a pathway

for constructing a single-molecule memristive effect and logic gate. Moreover, since molecular photophysics is strongly related to molecular motions including vibration and rotation, integrating the single-molecule luminescence with electric field controlled molecular motions will elucidate the intrinsic luminescence mechanism and provide tunable light sources. Second, the discovery of remarkable quantum effects (such as quantum interference and entanglement) at the molecular scale provides promising opportunities to achieve unprecedented optoelectronic functions. Third, the straightforward structures of single-molecule devices (e.g., no depletion layer and low capacitance) lead to ultrafast response capabilities, laying the foundation for ultrafast optoelectronic operations. Finally, applying multifield manipulation (light, electricity, magnetism, and phonon) to single-molecule optoelectronic devices can increase their logical computing capability, thereby surpassing traditional silicon-based devices. For example, one goal is to realize the regulation of the quantum spin in singlemolecule radical devices through a magnetic field at room temperature, which is potential to facilitate logical operations and information storage.

However, there are still several formidable challenges that need to be addressed. First, it is paramount to develop different universal methodologies capable of producing stable, uniform, and high-yield single-molecule functional devices with atomic precision. This highlights the precise regulation of the molecule-electrode interface. Second, only through integrated functional chips can we achieve industrial production and application of single-molecule devices. Therefore, it is extremely significant to promote the integration of singlemolecule devices, including rational designs of integrated circuit patterns and efficient protocols for single-molecule junction integration. Based on intermolecular interactions, wiring supramolecules into nanocircuits may be one of the promising strategies. We believe that strong collaborative efforts across various disciplines, encompassing micro- and nanoprocessing, organic synthesis, and theoretical calculation, will ultimately provide practical single-molecule electronics and optoelectronics for real-world applications.

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Notes

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