Invited Review

Optical and charge transport characteristics of photoswitching plasmonic molecular systems

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ABSTRACT

Probing the optical and charge transport characteristics in molecular junctions not only provides fundamental understanding of light–matter interactions and quantum transport at the atomic and molecular scale, but also holds great promise for the development of molecular-scale optical and electronic devices. Herein, an overview of recent progress in fabricating and characterizing photoswitching molecular systems using both the current measured from single molecule circuits as well as the light signals monitored in photodetectors is presented. We review four groups of azobenzene, diarylethene, dihydroazulene, spiropyran photoswitching molecules that have been used to construct photoswitching molecular devices by scanning tunneling microscope-based or mechanically controlled break-junction techniques, focusing on the impact of light-induced reactions on the charge transport processes at the single molecule level. We also discuss key optical properties of photoswitching systems, uncovered by a range of optical methods including transient absorption and ultrafast spectroscopies, that are critically related to structural symmetry or nonlinear optical effects.

1. Introduction

The phenomenon of photochromism was first discovered by Fritzsche in 1867 [1]. Since then, with the efforts made in synthesizing photochromic molecules as well as the development of fatigue-resistant spirooxazines and diarylethenes, the field of photochromism research has experienced an explosive growth in the 20th century [2–4]. In recent years, researchers start to study single molecule charge transport properties of photochromic molecules with the potential to expand functions in molecular devices with light (Fig. 1 left). Due to the versatile nature of light stimuli, it has become a unique tool for regulating the conductance of molecular junctions by inducing photophysical or photochemical processes that alter the electronic structure and/or conformation of the molecule. Advantages of light over gate voltage as an external control include an improved efficiency for nanoscale systems, fast speed and high selectivity. On the other hand, such photoswitchable molecular systems serve as a powerful platform for probing emerging optical properties (Fig. 1 right).

Here we aim to bridge the two seemingly separate but closely-connected research areas of molecule electronics and plasmonics by discussing recent progress in understanding photoswitching molecular systems from both of these two perspectives. Molecular

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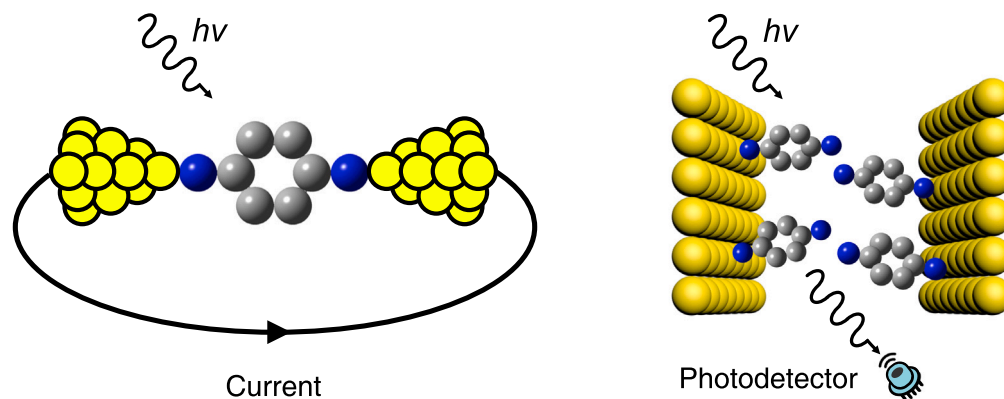[1] These authors contributed equally to this work.

Fig. 1. Graphical illustration of photoswitching molecular junctions probed by the tunneling current (left) and optical signal (right).

electronics is a research field that focuses on utilizing single molecules or self-assembled monolayers (SAMs) as active electronic components. In recent years, plasmonic phenomena in molecular electronics attracted attention since plasmonics lies at the intersection of the macroscopic photonics and nanoelectronics, and these molecular systems have the capability of confining light to dimensions far below the diffraction limit. Plasmonic resonances, especially those in molecular junctions, provide the ability in both tuning the local electromagnetic environment of the molecular junction and modifying the charge transport characteristics in the quantum mechanical tunneling regime. Combining molecular electronics with plasmonics presents opportunities to study both charge transport processes and plasmonics in the quantum regime.

Single molecules are considered as the ultimate constituents of nanodevices [5–9]. To date, single molecule or self-assembled monolayer devices with a variety of functions have been realized, including molecular switches, molecular memories and field–effect devices. Over the past decades, single-molecule optoelectronic devices have shown great potential in building memories and logic components for next-generation circuits. In particular, photochromic (or photoswitching) molecules, the electronic properties of which can switch under light irradiation, have received considerable attention as compared with molecules that undergo changes under other stimuli, such as magnetic fields, pH, and temperature; light provides a non-invasive, low-cost and clean method to switch the molecule in molecular devices.

Photoisomerization not only leads to spatial redistribution of the electron density of the molecule, it also inevitably manifests in variations of the optical properties. Indeed, in many photo-switchable molecules, this isomerization is accompanied by breaking (or opening) a particular bond, whereas in the opposite process, the bond is formed anew (closed). Then, the photo-induced transition to the "closed" state often results in the formation of an absorption band in the visible spectral range, which is visually perceived as a distinct color. In what follows, in lieu of discussing the chemical mechanisms of colorization, we focus on more intricate optical properties, e.g. pertinent to fundamental symmetry or nonlinear effects.

Some valuable insights into the interplay of electronic density in photoswitchable molecules and nonlinear-optical effects are summarized in the recent reviews [10,11]. Emphasizing on the close connections between molecular electronics and plasmonics, our discussions center on the photoswitching systems that are extensively investigated in both fields. Efforts have been made from both the electronic and plasmonic communities to study the same fundamental light-induced chemical change in the same molecular materials. Here we overview the present state of the art of this field, focusing on several key phenomena and applications of optical and charge transport characteristics of photoswitching single-molecule junctions. Section 2 is focused on the recent development of using photoswitching molecules as active components for creating single molecule junctions following the four types of diarylethenes, azobenzenes, dihydropyrenes, and spiropyrans. Sections 3.1 and 3.2 provide a discussion of the optical studies of supramolecular self-assembling photoswitching systems and photo-responsive hybrid plasmonic nanostructure systems, respectively. Section 3.3 provides a brief description of nonlinear-optical processes observed in photoswitching systems, including Raman scattering, second harmonic generation, and third-order nonlinear effects. In addition, in Section 3.4, we review the ultrafast dynamics of photochemical switching reactions with the development of transient absorption or Raman spectroscopies with femtosecond or picosecond temporal resolution. A brief conclusion and outlook appear in Section 4.

2. Charge transport through photoswitching single-molecule junctions

2.1. Types of photoswitching molecules in forming molecular junctions

In a phototransformation reaction, chemical bonds in a molecule are rearranged, resulting in changes in not only the chemical structure but also the electronic structure of the molecule. Such sensitive response to light enables the molecules to work as photoswitches, memory devices, or light-driven actuators [12]. Therefore it becomes critical to probe and understand the details of how we alter the charge transport phenomena across photoresponsive molecules by photoirradiation. Single molecule junctions, commonly fabricated by scanning tunneling microscope break-junction technique (STM-BJ) [13,14] or mechanically controlled
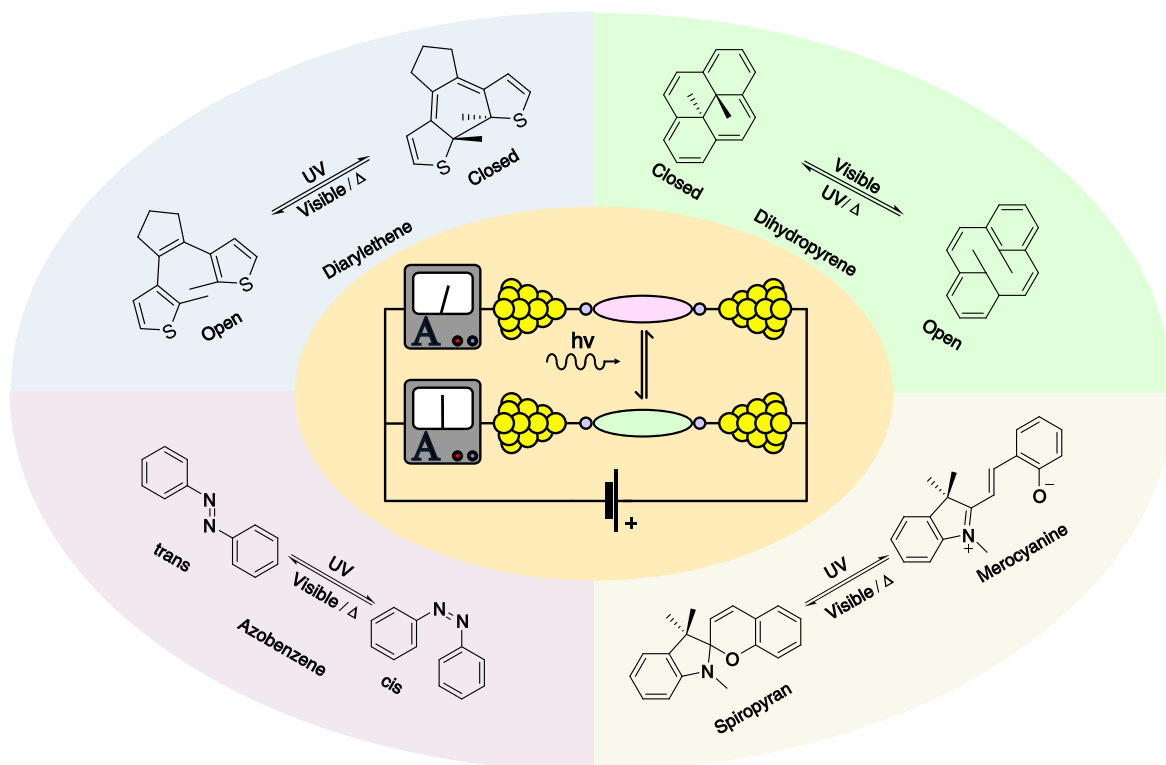
Fig. 2. A schematic of single molecule junctions in response to light and four representative photoresponsive molecules with their corresponding phototransformation reactions.

break-junction technique (MCBJ) [15], provide a unique platform for probing charge transport processes as well as light-induced reactions at the single molecule level. In both of these two techniques, a single molecule junction is repeatedly formed and ruptured in a solution of the target molecule at high efficiency, and data of thousands of single molecule junctions are analyzed for obtaining a statistically-significant result. Below we discuss single molecule charge transport studies of photoresponsive diarylethenes, azobenzenes, dihydropyrenes, and spiropyrans as shown in Fig. 2, and showcase the interplay between photoswitching events and the electronic properties of such single molecule devices.

2.2. Diarylethenes

Diarylethenes are derivatives of stilbenes with the two phenyl rings in silbenes replaced by thiophenes (dithienylethenes) or furans (difurylethenes). Diarylethenes are photochromic and have advantages of being thermally stable and resistant to fatigue. The structure of diarylethene undergoes open⟷closed form transitions under UV/visible light illumination (Fig. 2), accompanied by the changes of molecular properties such as optical absorption spectrum and single molecule conductance. Specifically, the molecular structure of diarylethene changes from a non-conjugated open state to a conjugated closed state under ultraviolet light, and the molecular conductance is expected to change from a low to a high state accordingly. Most notably, the change in molecular length under isomerization is negligible, which makes diarylethene an ideal structure for single-molecule devices.

In 2003, Dulić and co-workers reported one-way photoswitching of a diarylethene molecule (referred to as DAE-1 in this discussion) using a mechanically controlled break junction technique [18]. DAE-1 is terminated with thiol groups for anchoring to the gold electrodes. When the DAE-1 junction was exposed to visible light, the molecule configuration was changed from the conjugated closed state to the non-conjugated open state, and a sharp increase of three orders of magnitude in resistance was observed at the same time. For the Au-DAE-1-Au, the switching occurred only from closed to open form, whereas the reverse process was not observed. Specifically, the calculated potential curve of the first excited state came very close to the Au electrode Fermi level. In order to overcome the molecular excited state quenching caused by the strong electronic coupling between molecules and electrodes, Guo and coworkers reported a new method to reduce the electronic interaction by introducing three methylene (-CH₂-) groups into each side of the molecule [19]. The introduction of non-conjugated methylene groups between the terminal amine group and the functional diarylethene core enables a fully optimized molecule–electrode interface coupling. As a result, the altered molecule has outstanding performance in terms of accuracy (on/off ratio of 100), stability (over a year), and reproducibility (46 devices with more than 100 cycles for photoswitching and $\sim 10^5$ to 10^6 cycles for stochastic switching). A further discussion about the influence of plasmonic metal structures on the reversibility of the switching of diarylethenes is provided in Section 3.2.
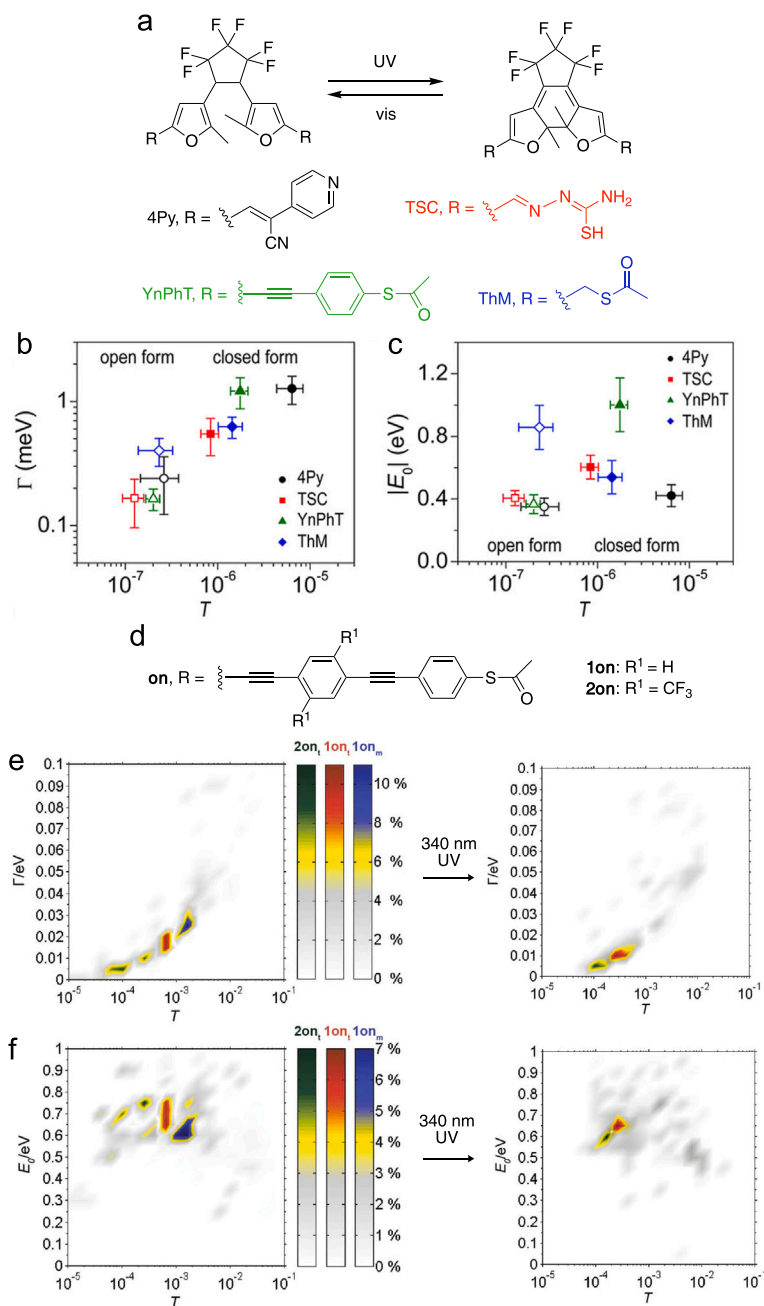
Fig. 3. Closed form of diarylethene compounds has a higher coupling strength with the Au electrodes than that of the open form. (a) Open and closed forms of difurylethenes that are terminated with an R group, and the chemical structures of the R groups for 4Py (black), TSC (red), YnPhT (green), and ThM (blue) molecules. (b) Level broadening $\Gamma = \Gamma_L + \Gamma_R$ and (c) molecular level alignment E_0 obtained from 20 I–V curves by the use of the single-level model. Γ_L (Γ_R) is the coupling strength between the molecule and the left (right) electrode. (d) Chemical structure of the R group for molecule 1on and 2on. Histograms of (e) Γ and (f) E_0 plotted against transmission T for junctions formed with 1on and 2on pre- and post-illumination with UV light. $2on_t$ and $1on_t$ denote measurements performed in solvent toluene, and $1on_m$ denotes measurements performed in mesitylene. (a–c) are reprinted with permission from Ref. [16], copyright (2012) American Chemical Society. (d–f) are reprinted with permission from Ref. [17], copyright (2012) Wiley.

Using the technique of STM-BJ, Tam et al. investigated the conductance of photoswitchable diarylethene molecules in both their conducting (closed) and non-conducting (open) configurations [20]. In this work, the molecular junction was formed *via* the adsorption of terminated pyridine groups on the Au surfaces. The conductance for the closed state was $(3.3 \pm 0.5) \times 10^{-5} G_0$ through fitting the conductance histogram with a Lorentzian function, where $G_0 = 2e^2/h$ is the conductance quantum. For the non-conjugated

open state, however, the specific conductance of the fully stretched molecule was below the experimental noise floor ($10^{-6}G_0$). As a result, the obtained on/off ratio of the diarylethene conductance was at least 30, consistent with the results of DFT calculations.

In addition to the on/off ratio of the single molecule conductance, further information regarding the electronic coupling between DAE and the metal leads as well as the molecular frontier orbital alignment with the metal Fermi level have also been investigated. In such efforts, Kim et al. reported single molecule conductance measurements of four diarylethene compounds (chemical structures in Fig. 3a) using MCBJ technique and observed a higher molecular conductance for the closed forms than that of the open forms for all compounds [16]. Furthermore, authors performed I–V measurements and extracted the molecule–electrode coupling strength (or level broadening $\Gamma = \Gamma_L + \Gamma_R$) and the molecular level alignment E_0 following a single-level model based on the Landauer formalism:

$$T(E) = \frac{4\Gamma_L\Gamma_R}{[E - E_0]^2 + [\Gamma_L + \Gamma_R]^2} \tag{1}$$

These two parameters Γ and E_0 are plotted against transmission in Fig. 3b and 3c, respectively. The authors found that the coupling Γ increases by more than three times from the open to the closed form for the conjugated compounds 4Py, TSC, and YnPhT, but remains similar from the open to the closed form for ThM (Fig. 3b). In contrast, the frontier molecular orbital was not observed to be closer to E_F for the closed form than that of the open form, as both increase and decrease of E_0 was observed from open to closed forms for the four compounds (Fig. 3c). The authors concluded that this switching ratio of the conductance between closed and open forms is largely determined by the change in coupling strength with the electrode rather than the molecular level alignment.

Following this work, the same team investigated another diarylethene derivative (chemical structure in Fig. 3d) [17]. Different from the work described above where molecules were illuminated with UV light *ex situ* prior to forming the molecular junctions, here the authors *in situ* illuminated the junctions with 340 nm UV light for 10 min to switch the open form molecule into a closed form. From I–V measurements, the authors obtained the Γ and E_0 using a single level model as described above, and found differences between *in-situ* and *ex situ* switching. For *in situ* switching as shown in Fig. 3e and 3f, $1on_t$ displays one transmission state both pre- and post-illumination, whereas $2on_t$ shows two distinct transmission states with different Γ and E_0 pre-illumination, and only one state post-illumination. In addition, if the open-form was prepared *ex situ* and assembled on the device, two transmission states were observed. The authors attributed the two conductance states observed for $2on_t$ prepared *in situ* and *ex situ* to the two different conformations of the molecular junction. In cases of *in situ* switching, the initial position of the S–Au bonds remain unchanged therefore only one state was observed when the ring is closed and the molecule has less conformational freedom. In comparing 1on with 2on, the electron-withdrawing CF_3-group has an impact on the coupling strength, level alignment, and the conformational freedom of the junction. The authors also performed measurements of 1on in toluene ($1on_t$) and in mesitylene ($1on_m$) (Fig. 3e and 3f left panels), and showed that solvent can influence Γ and E_0. Another interesting observation from this work is that authors observed the *in situ* switching from close to open form, but were not able to switch the open form back to the closed form by illuminating the junction with visible light, agreeing with other works on DAE molecules [18,21].

2.3. Azobenzenes

Azobenzene undergoes an isomerization reaction between a *trans* and a *cis* conformation in response to light, and this phenomenon has been probed at the single molecule level. In Henzl et al., scanning tunneling microscopy (STM) images of an azobenzene derivative with $-NO_2$ and $–NH_2$ substituents (structure in Fig. 4a) showed that a voltage-induced isomerization reaction occurred [22]. As shown in Fig. 4b–d, configuration of the monomer Azo-1 changed between elongated (*trans*) and bent (*cis*) forms upon an applied voltage bias. This isomerization reaction is evidenced by the sharp change of tunneling current (Fig. 4e), and the authors determined the isomerization yield at different bias voltages (Fig. 4f). A threshold of about 650 mV for isomerization reaction is determined, which is much lower than the energy required for photoisomerization reaction in gas phase (ultraviolet light of 3.55 eV for trans→cis and blue light of 2.82 eV for cis→trans), highlighting the impact of a weakly-interacting metal surface on the isomerization of the molecule.

For a single molecule that is attached to two Au electrodes, Kim et al. reported a higher conductance measured of *cis* conformation than that of *trans* for Azo-2 (Fig. 4g and 4h) [23]. Further, the authors performed inelastic electron tunneling spectroscopy (IETS) measurements under 4.2 K using MCBJ, and observed a clear peak at ~160 meV for *trans* isomer but a peak at ~190 meV for *cis* isomer experimentally, agreeing with the calculations (Fig. 4i and 4j). The authors concluded that the N=N stretching vibrational mode likely contributes to these peaks that show a different IETS fingerprint between *cis* and *trans* isomers. This work demonstrates that between the two structurally similar isomers of azobenzenes, their vibrational modes detected at the single molecule level are different.

In situ switching of an azobenzene unit by light has also been realized in a single molecule device. Meng et al. reported a single molecule junction of Azo-3 (structure in Fig. 4k) connected to graphene electrodes where the azobenzene unit is a side group of the molecular backbone [24]. By *in situ* applying sequential ultraviolet and visible light, authors observed a real-time corresponding conductance switch with an on/off ratio of ~2.1 (Fig. 4l) and attributed this conductance switch to the *trans–cis* isomerization of the azobenzene unit. We note that this on/off ratio of single molecule conductance between the two isomers of azobenzene is considerably lower than the reported on/off ratios reported for open/closed forms of DAEs [19] and DHPs [25].
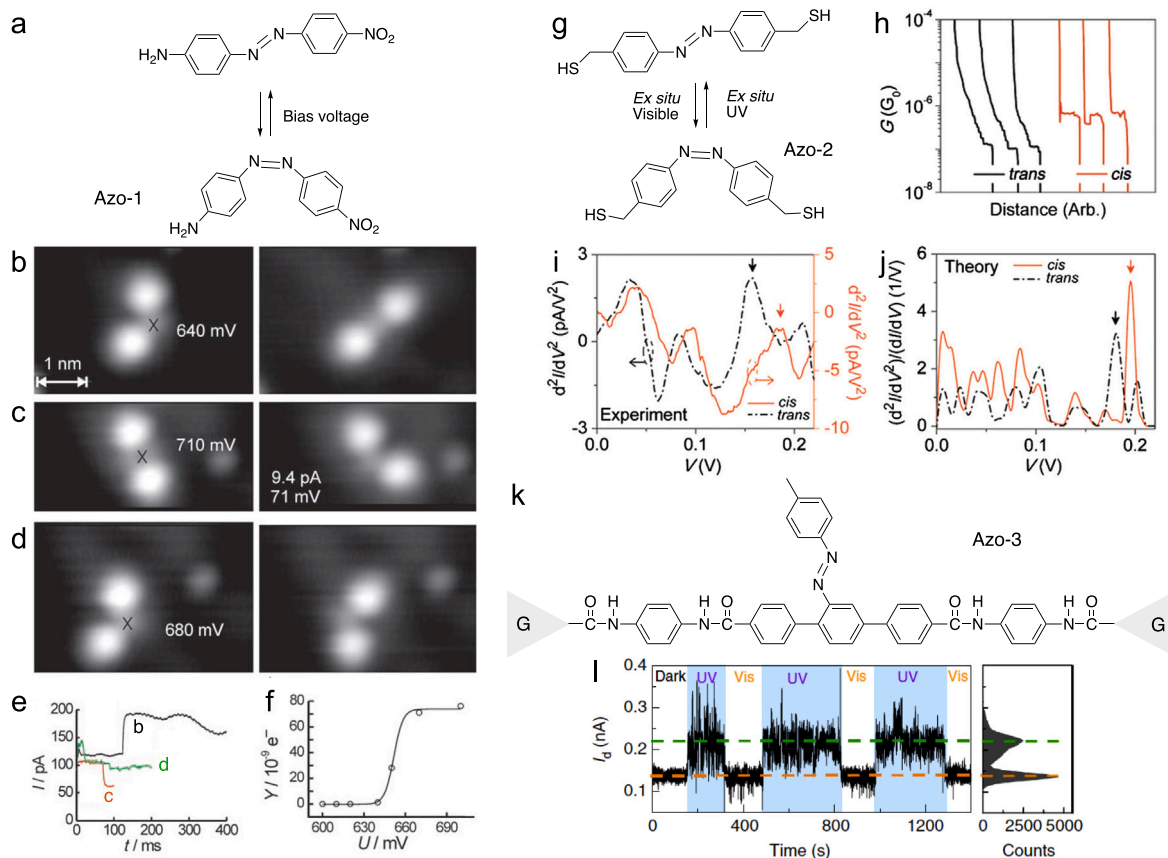
Fig. 4. Isomerization of azobenzenes between a *trans* and *cis* conformation. (a) Chemical structure and isomerization reaction of Azo-1. (b–d) STM images of Azo-1 before (left) and after (right) electron injection at the specified bias voltage at the position marked with a cross. (e) Current *vs.* time trajectories for b–d where the sharp change corresponds to the isomerization reaction. (f) Isomerization yield *vs.* applied bias voltage for Azo-1. (g) Chemical structure and isomerization reaction of Azo-2. (h) Representative conductance traces of Azo-2 *trans* and *cis* isomers. IETS spectra (i) measured under 4.2 K and 6 meV and (j) calculated at 5 meV for Azo-2 *trans* and *cis* isomers. (k) Chemical structure of Azo-3 connected to graphene electrodes. (l) Current *vs.* time measured for Azo-3 under 10 mV under sequential exposure to UV and visible light; the corresponding histogram is shown on the right. (b–f) are adapted with permission from Ref. [22], copyright (2006) Wiley. (h–j) are adapted with permission from Ref. [23], copyright (2012) American Physical Society. (l) is adapted with permission from Ref. [24], copyright (2019) Springer Nature.

2.4. Dihydropyrenes

Dihydropyrene (DHP) is another photochromic structure that can be reversibly switched between a π-conjugated state and a state where the π-conjugation is broken in the center. When exposed to visible light, DHP is converted into cyclophanediene (CPD) when a C–C bond is ruptured. The reverse reaction process can be achieved under UV radiation or thermal activation.

By using the MCBJ technique, a reversible single-molecule photoswitch based on a DHP motif with very high on/off ratio ($>10^4$) was achieved by Roldan and co-workers [25]. Specifically, pyridine anchoring groups were introduced on opposite sides of a DHP scaffold (molecule D-1, structure in Fig. 5a) to ensure an efficient binding of the molecule on the gold electrodes and an optimized electronic transport through the molecular junction. The authors showed that the molecular configuration changed from DHP (closed-form) to CPD (open-form) when exposed to visible light *in situ* (Fig. 5b and 5c), and heat was applied for the reverse process from CPD to DHP as undesired side reactions could occur in the presence of UV light. As shown in Fig. 5b, 2D histogram of D-1 displays three different conductance features [high (H), middle (M), and low (L)], which were attributed to the sequential formation of different configurations between the single molecule and the electrodes. In detail, immediately after the breaking of the Au–Au contact, a nanogap formed. A molecule first jumped in between the two contacts and slid along the two leads with its π-system in contact with the metal leads (H), then assumed a tilted orientation between the two electrodes (M), and finally transformed into a fully extended molecular conformation (L) just before the rupture of the junction. In contrast, no molecular features were observed in conductance experiments with C-1 (Fig. 5c). The authors also demonstrated a sequential and reversible switching between D-1 and C-1 by *in situ* visible light illumination and heat at room temperature, and a photothermally-triggered switching between DHP/CPD was fully reversible and stable over more than five sequential cycles (Fig. 5d).

In another work, Max and co-workers explored the charge transport properties of the same DHP/CPD derivatives D-1 and C-1 in single-molecule junctions by employing the STM-BJ technique [26]. Upon visible light illumination, the DHP molecule configuration
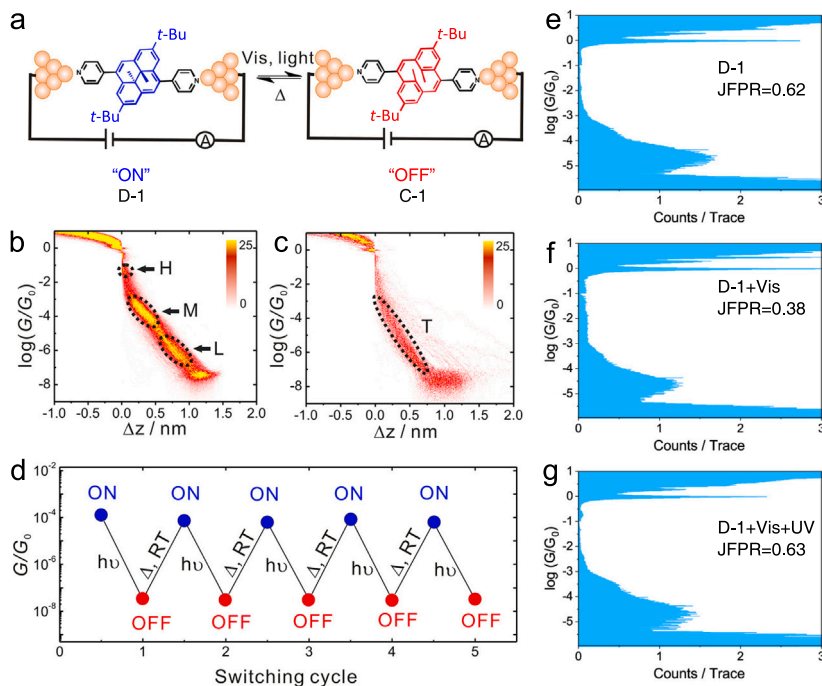
Fig. 5. (a) The schematic of D-1 and C-1 photochromic molecular junctions. (b,c) 2D conductance histograms of (b) D-1 and (c) C-1. (d) Five sequential, fully reversible cycles of the photothermally triggered *in situ* conductance switching between D-1 and C-1. (e–g) Conductance histograms for D-1 (e) pre-light exposure, (f) after 30 min light exposure and (g) after 30 min UV light exposure. (a–d) are reprinted with permission from Ref. [25], copyright (2013) American Chemical Society. (e–g) are reprinted with permission from Ref. [26], copyright (2022) American Chemical Society.

changes from the π-conjugated planar state to the less π-conjugated CPD isomer, which results in DHP being more electrically conductive. In this work, a dimensionless value called junction formation probability ratio (JFPR) was used as an approximate semiquantitative guide to the formation probability of single-molecule junctions, as listed in each 1D conductance histograms in Fig. 5e–5g. JFPR was determined by dividing the molecular peak height by the $1G_0$ peak height. Smaller JFPR value means that the molecular junctions were formed with less probability or were less defined. Irradiation experiments on C-1 showed that the JFPR decreased from 0.62 (Fig. 5e) to 0.38 (Fig. 5f) after the molecular solution in the STM substrate was exposed to visible light for 30 min (Fig. 5a), which was attributed to the partial conversion of DHP to the open CPD form. There were no conductance features for CPD since the conductivity value was predicted to fall below the experimental noise floor, agreeing with the results reported in Rolden et al. [25]. Furthermore, the JFPR value was reverted to 0.63 after *in situ* UV light irradiation for 30 min of the same STM sample, which indicated that the molecules were switched back to the original DHP isomer (Fig. 5g).

2.5. Spiropyrans

Spiropyrans (SPs) are another type of unique photochromic molecules responsive to various stimuli, including light irradiation, pH changes, mechanical force, different solvents, and changes in temperature. SPs mainly consist of two heterocyclic functional groups, linked through a spiro C–O bond. Upon irradiation with UV light, SP transforms into its highly conjugated merocyanine (MC) form when the spiro C–O bond is ruptured.

Darwish and co-workers reported a dual photo- and chemo-responsive spiropyran single molecule junction constructed with molecule SP-1 using STM-BJ technique (Fig. 6a) [27]. The electrical properties of the single-molecule switching operation for molecule SP-1 under both UV and acid stimuli are shown in Fig. 6b–d. SP-1 closed form showed two clear conductance peaks at $0.023G_0$ and $0.051G_0$ under dark conditions (Fig. 6b–c). The presence of multiple peaks were ascribed to different binding geometries of the $-NO_2$ groups to the gold electrode surface. Upon UV light irradiation, an additional high conductance state at $0.15G_0$ was observed (Fig. 6b), which was assigned to the merocyanine MC-1 open form. This high conductance was attributed to the high current flow due to an efficient electrical MC-1/electrodes coupling. The yield from the OFF state (closed form) to ON state (open form) conversion was estimated to be 15%–35%, which was obtained from comparing the area under the histogram peaks. The disappearance of the $0.15G_0$ conductance peak after the UV LED being turned off demonstrated that the conductance switching was reversible. The reversible conductance switching between SP-1 and MC-H-1 controlled by acid/base was also verified by addition of trifluoroacetic acid (TFA) and triethylamine (TEA). A high conductance peak at $0.11G_0$ was observed upon addition of TFA, which came exclusively from the open and protonated MC-H-1 form, and no low conductance peaks were observed, indicating that a more
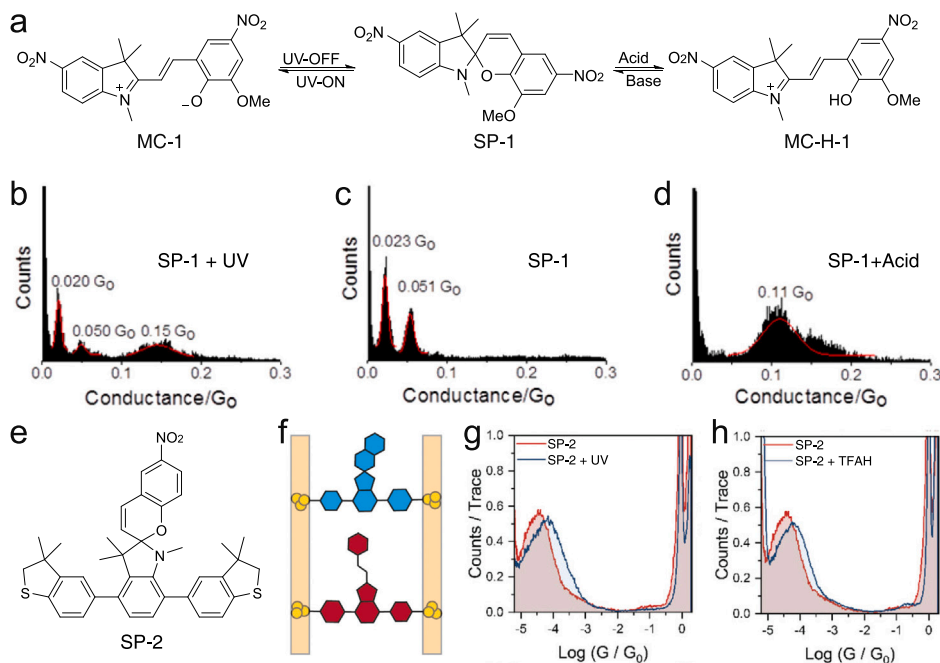
Fig. 6. (a) Light-induced and acid-induced isomerization of spiropyran. (b–d) 1D histograms obtained from hundreds of current traces are shown, respectively, for SP-1 (b) in the presence of UV light, (c) in the absence of any stimuli, and (d) in the presence of TFA. (e) Chemical structure of SP-2. (f) An orthogonal conductance pathway in spiropyrans displays no backbone change upon isomerization of the side group of SP (blue) to MC (red). (g–h) Comparison of conductance histograms of SP-2 before and after (g) *in situ* irradiation with UV light and (h) *in situ* addition of trifluoroacetic acid (TFA). (a–d) are reprinted with permission from Ref. [27], copyright (2014) American Chemical Society. (e–h) are reprinted with permission from Ref. [28], copyright (2023) Wiley.

complete conversion of SP-1 to MC-H-1 was stimulated by the presence of acid in comparison to the generation of MC-1 induced by UV light.

While testing series of spiropyran compounds, David and co-workers designed and synthesized the T-shaped spiropyran SP-2 terminated with 3,3-dimethyl-2,3-dihydrobenzo[b]thiophen-5-yl (DMBT) contact groups (chemical structure in Fig. 6e), in which the side chain of SP-2 can undergo an SP to MC conformational change upon UV light or acid exposure (Fig. 6f) [28]. In single molecule junction conductance measurement of SP-2, an increase of approximately half an order of magnitude (from $10^{-4.51}G_0$ to $10^{-4.08}G_0$) was observed after irradiating the molecule under UV for 20 min (Fig. 6g). Similarly, after the addition of a dilute solution of trifluoroacetic acid, authors observed an modest increase in conductance (from $10^{-4.51}G_0$ to $10^{-4.22}G_0$) (Fig. 6h). Theoretical calculations show that the conductance increase in SP-2 from the SP-form to MC-form is is due to the change in the torsional rearrangement of the three phenyl rings in the backbone leading to increased orbital overlap between the anchor groups and the central functional core unit of the junction. In other words, the major effect in the overall transmission is a result of conformational changes in the conducting backbone, which is influenced by the structure of the side group.

3. Optical effects in photoswitchable molecular systems

3.1. Supramolecular self-assembling systems

Under light irradiation, photoswitchable molecules undergo a structural change, leading to the corresponding switching of observed optical properties such as their absorption spectra and fluorescence intensities [29–32]. However, in bulk systems where average behavior is registered, this effect becomes obscured due to the inherent experimental averaging. Experimental data gradually change upon photoirradiation due to the presence of a large number of molecules in the system, with only the total switched/unswitched ratio being affected by photoirradiation. Real digital photoswitching is anticipated if the photochromic reaction can be detected at the single-molecule level. Therefore, efforts have been made to achieve measurements of fluorescence change at the single-molecule level, and the fluorescence change has been observed in single-molecule photochromism.

Changes in fluorescence intensity from single molecules are not normally controllable, manifesting themselves as repeated cycles of emission ('blinking') or as spectral diffusion [33–37]. Masahiro Irie et al. have designed and synthesized a fluorescent photoswitching molecule in which photochromic 1,2-bis(2-methoxy-4-phenyl-3-thienyl) perfluorocyclopentene and fluorescent 1,5-dimethoxy-9,10-bis(phenylethynyl) anthracene are linked through an adamantyl spacer [29]. Fig. 7a shows the chemical structure of this fluorescent photochromic molecule and the relative energy levels of the component chromophores. The fluorescence spectrum well overlaps the absorption spectrum of the closed-ring isomer of the diarylethene unit, so the bis(phenylethynyl)anthracene
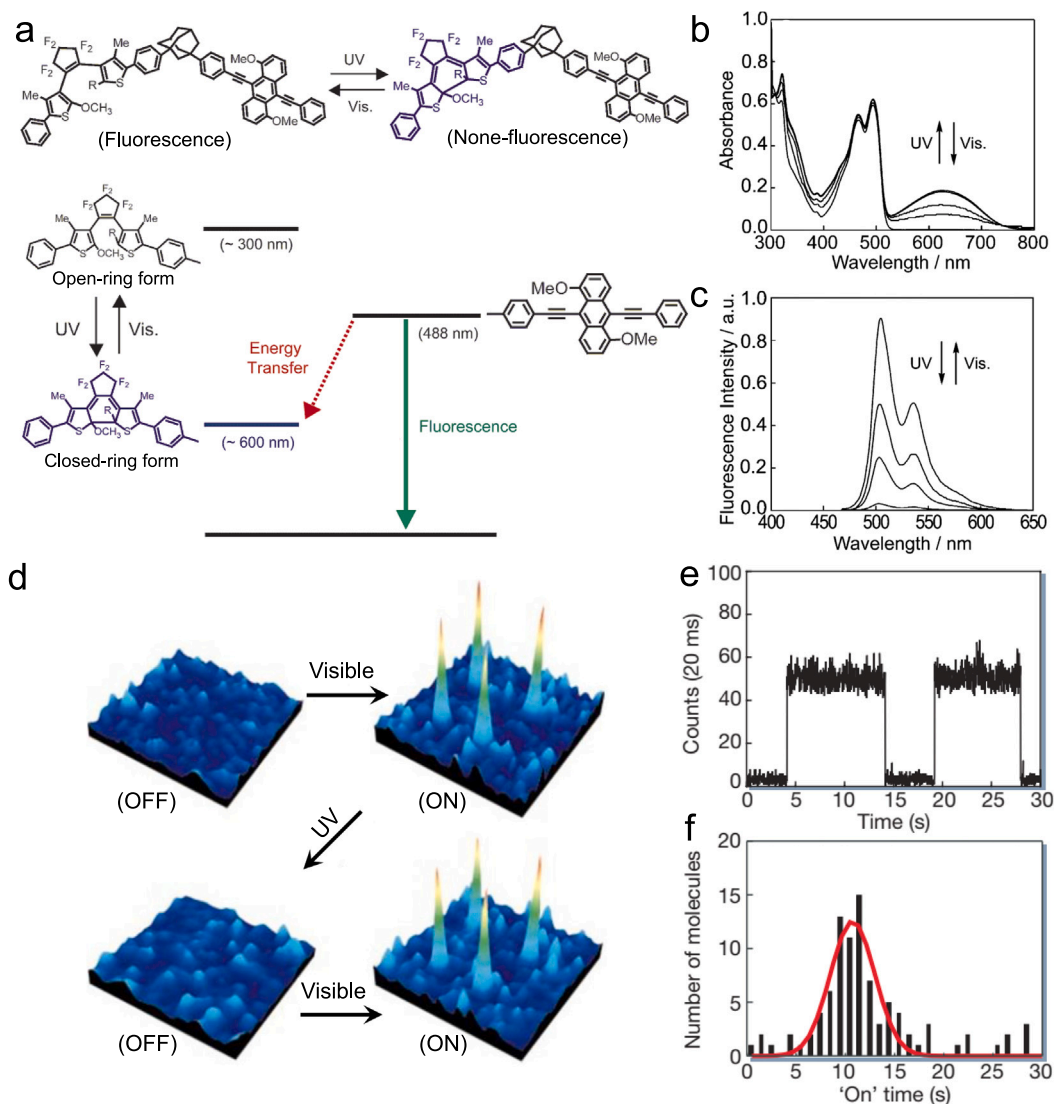
Fig. 7. Photo-induced switching of fluorescence efficiency. (a) Structural design of fluorescent photochromic molecules and relative energy diagram of the chromophore components. (b) Absorption and (c) fluorescence spectra for molecule shown in (a) upon irradiation with 313 nm light. (d) Photoswitching images of four single molecules upon alternate irradiation with 488 nm and 325 nm light. (e) Fluorescence intensity from a single molecule embedded into Zeonex thin film changes upon irradiation with 325 nm and 488 nm light. (a–c) are reprinted with permission from Ref. [30], copyright (2004) American Chemical Society. (d–f) are reprinted with permission from Ref. [29], copyright (2002) Nature Publishing Group.

fluorescence is efficiently quenched when the diarylethene unit converts from the open to the closed ring isomers. On the other hand, when the diarylethene unit is in the open-ring isomer, its energy level is higher than the level of the bis(phenylethynyl)anthracene unit and the fluorescence quenching does not take place. The changing of fluorescence and absorption intensities in ensemble solution both show changes between two discrete states in Fig. 7b and c [30]. Additionally, confocal microscopy reveals the fluorescence images and digital switching behavior of single molecules embedded in a polymer film (Fig. 7d). This switching was observed in detail by measuring the response time of a single molecule to irradiation with strong visible and very weak ultraviolet light (Fig. 7e). To confirm that this switching was indeed due to photo-isomerization, the 'on' and 'off' times for 50–100 molecules were measured by changing the power of the ultraviolet and visible light (Fig. 7f). The average 'on' and 'off' times was decreased in proportion to the reciprocal power of the radiated light, indicating that the switching effect is indeed photochemical. The on/off switching between two discrete states was observed on polymer films at the single-molecule level, which provides unequivocal evidence that the photochromic reaction takes place between two discrete states.

Metal–organic frameworks (MOFs) are an emerging class of porous materials and contain multiple functional moieties inside the framework. Thus, MOFs are ideal candidates for realizing cooperative functionalities based on periodic arrangement on a
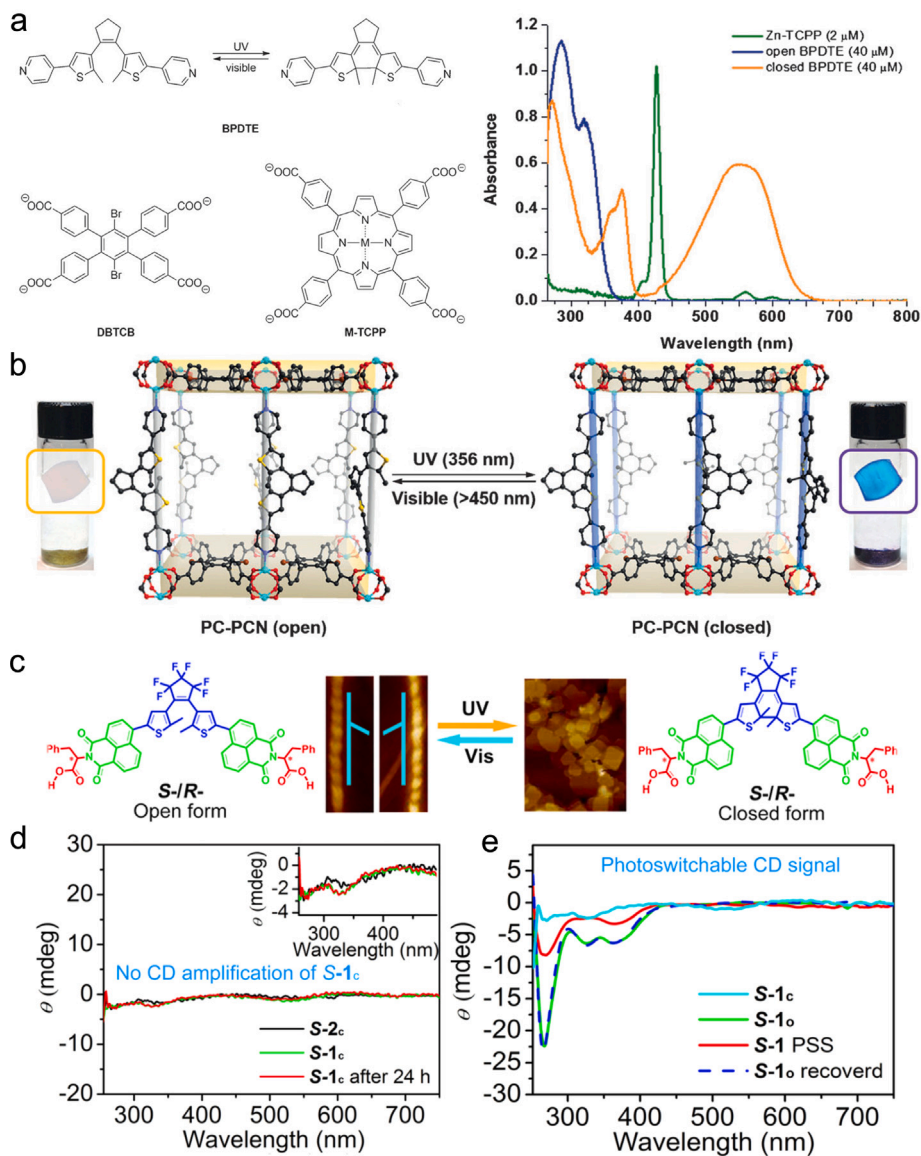
Fig. 8. MOF and chiral supramolecular systems. (a) Photoisomerization of BPDTE under UV and visible light and structures of ligands consisting of two-dimensional layers in PC-PCN and SO-PCN, respectively. UV/Vis spectra of H_4Zn-TCPP and two different forms of BPDTE. (b) Illustration of reversible photochromic reaction in PC-PCN. (c) Molecular model of helical nanostructures. (d–e) The effect of 24 h aging (d) and of irradiation with 365 nm and with visible light (recovered) $\lambda > 510$ nm (e) on the circular dichroism (CD) spectra of helical self-assembly shown in (c). (a–b) are reprinted with permission from [41], copyright (2015) Wiley. (c–e) are reprinted with permission from [42], copyright (2016) American Chemical Society.

molecular scale [38–40]. Two MOFs, namely PC-PCN (photochromic porous coordination network) and SO-PCN (singlet oxygen-generating porous coordination network) which contain 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene (BPDTE) as a photochromic switch are presented in Fig. 8a and b [41]. Notably, a molecular dyad system which contains a photochromic switch and a photosensitizer was well established with SO-PCN. The reversible control over $^1O_2$ generation through a competition of energy transfer pathways upon irradiation at specific wavelengths in SO-PCN was studied. Also, SO-PCN was demonstrated as a heterogeneous catalyst for photooxidation of 1,5-dihydroxynaphthalene (DHN).

In the context of molecular photoswitches, chirality is understood as a distinct response to circularly polarized light, giving rise to *e.g.* circular dichroism [42,43]. In order to achieve this, either intrinsically chiral molecules with photo-switchable properties need to be utilized, or extrinsic chirality must be introduced into the system by proper spatial arrangement of the photo-switchable molecular building blocks. The second route was taken in Ref. [42], where a three-component assembly was employed for designing a chiral switch. In the open form, the molecule demonstrates pronounced circular dichroism in the UV range. Interestingly, the sign of the reversibly enabled and disabled dichroism is inherited from the parent enantiomer, reiterating the external nature of the

observed chirality. In the future, this approach can be utilized for designing large-scale chiral glasses, similar to the photo-written holographic gratings based on diaminobiphenyl with azo groups [44].

A different approach in introducing chirality in a controllable way consists in modifying the macroscopically chiral arrangement of liquid crystals by means of photoswitching. Allowing the bipolar handedness switching (*i.e.* from right to left, instead of chiral to achiral), this design strategy is based on the equilibrium shifting between multiple chiral contributions of the opposite signs in a single molecule [45]. Upon UV irradiation, the trans–cis isomerization of the azoarene reduced the right-handed contribution, while a comparable left-handed contribution of the two binaphthyl units was retained. As a result, photo-induced dichroism changes of about 200% were registered, corroborating the high promise of the equilibrium shift strategy for future photoswitching applications. This method has been further improved by extending the functionality over the IR spectral range [46].

Since the first study that reported a light-regulated binding ability of the azobenzene-capped β-cyclodextrin (β-CD), the use of azobenzene compounds in supramolecular systems has been extensively expanded. One particular property of azobenzene is that the geometric structure of azobenzene compound is relatively small for fitting into the cavities of many macrocycles, which is quite different from other photochromic compounds such as diarylethenes and spiropyrans. Recently, Zhu and co-workers reported a unique helical self-assembly that processed dynamic amplification of chirality with photo-reversibility at supramolecular level. They introduced naphthalimide chromophore and α-chiral amino acid to photo-responsive DAE, shown in Fig. 8c and d [42]. The open isomer forms helixes and expresses a dynamic circular dichroism amplification in CCl_4, as the terminal chiral carboxylic group works as helicity generator and provides intermolecular hydrogen bonding. Upon irradiation of the open isomer at 365 nm, the disassembly of helixes occurred, and the circular dichroism signal decreased remarkably. This was presumably due to the formation of closed isomer, which was more planar and rigid in molecular conformation and lacks flexibility for helical self-assembly. Interestingly, the assembly and disassembly of this helical supramolecular architecture were reversibly controlled by alternative UV and visible light.

3.2. Photo-responsive hybrid plasmonic nanostructures

The excitation of light in molecular junctions can induce surface plasmon modes in nanostructures and nanogaps, generating highly confined fields that effectively modify the local electromagnetic environment as charge carriers traverse across molecular junctions. The modification in charge transport across a junction resulting from the absorption of light in the electrodes can be described as photon-assisted transport (PAT). Theoretical studies have predicted that the conductance of molecules could be enhanced upon illumination via PAT mechanisms [47–51]. Furthermore, experimental observations showing enhanced current in molecular junctions by coupling the fields to localized surface plasmons at both on- and off-resonances have been attributed to PAT [52–55]. Similarly, the contribution of PAT has also been observed in photoswitching molecule junctions [56]. Another widely discussed mechanism for explaining the increased current induced by light in molecular junctions is the generation of hot electrons; the population and transport of such hot electrons and how to experimentally distinguish hot electrons transport and PAT continues to be investigated [57,58].

To improve the switching efficiency, multiple nanophotonic geometries have been suggested for taking advantage of the light confinement at the nanoscale. In particular, a promising approach consists in utilizing surface plasmon-induced localization of the optical intensity in hot spots in the close vicinity of metallic (usually Au or Ag) nanostructures. The implementation of photo-switchable molecules in electronic devices not only enables miniaturization but also introduces novel functionalities to the devices. However, when a minute entity like a molecule is affixed to macroscopic surroundings, it is not inherently evident that its functionalities remain conserved.

As a prominent example, controllable switching of transport in photochromic molecules, from an "open" state into an "close" state, was often observed to be unidirectional [18] . The reverse switching process does not occur, which can be attributed to the quenching of the first excited state of the open form of the molecule under the influence of gold nanoparticles. In the absence of gold, the closed form exhibits a broad absorption peak around 550 nm. Upon irradiation with light at 546 nm, this peak completely disappears (indicating complete conversion to the open form) but reappears upon illumination with 313 nm light. The observed background absorption is characteristic for gold colloids (Fig. 9a and b). Since then, many molecular switches have been investigated [59–61], and only a few studies have demonstrated reversible switching [21,62].

It has been shown that the molecule–electrode coupling strength plays a key role in determining the device performance. The opposite unidirectional photoswitching of single diarylethenes (from the insulating open form to the conducting closed form) has been observed, where the molecules were used to bridge the nanogaps between carbon electrodes either single-walled carbon nanotubes [21] or graphene sheets [19]. In this configuration, owing to the energy transfer from the photo-excited molecule to the extended p-electron system in the electrodes, the molecule remains locked in its closed form. This quenching effect originates from the strong molecule–electrode coupling ensured by the covalent amide linkages. These results have stressed the crucial importance of the molecule–electrode coupling strength in determining the device performance. To address this issue, efforts were made to decrease the effective molecule–electrode coupling. In particular, one study has shown that incorporating three methylene (-CH_2-) groups into each side of the molecular backbone reduces the electrode-molecule coupling to a level that effectively prevents the quenching of the molecular excited state by the electrodes (Fig. 9c–e). The system is thus shifted from the Landauer regime when no spacer was introduced into close to the Coulomb blockade regime, in which the molecule can reversely switch between closed and open conformations.
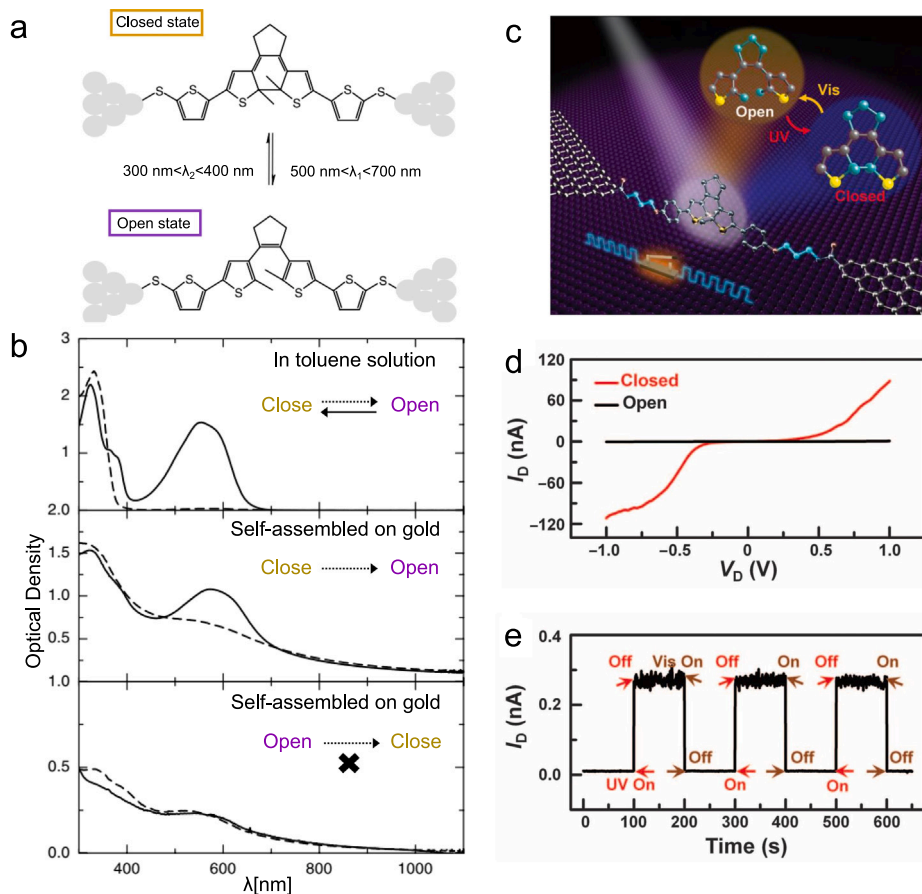
Fig. 9. Plasmonics with photochromic molecules. (a) Photochromic molecular switching between two Au contacts in closed state and open state. (b) Absorption spectra of the molecular switches. Solid line: closed form; dashed line: open form. (c) Schematic of a graphene–diarylethene–graphene junction that highlights the expansion of the molecular bridge by methylene groups. (d) I–V characteristics of individual diarylethenes in open and closed form. (e) Real-time measurement of the current through a diarylethene molecule that reversibly switches between the closed and open forms. (a–b) are reprinted with permission from Ref. [18], copyright (2003) The American Physical Society. (c–e) are adapted with permission from Ref. [19], copyright (2016) AAAS.

3.3. Nonlinear-optical processes

3.3.1. Raman scattering

Surface enhanced Raman scattering (SERS) has developed into a powerful analytical technique for obtaining the detailed structural information in the vibrational spectra of absorbed molecules due to interactions between the substrate surface and the surface analytes typically through electromagnetic mechanism (EM) or chemical mechanism (CM). The latter deals with non-resonant efficiency enhancement that can be achieved through light modulation of molecular systems by the interactions with the metal surface [63]. The CM enhancement of Raman efficiency in a molecular system interacting with a small gold cluster can be controlled by toggling the photoswitch from its closed form to the open form. When adsorbed on the surface of Au cluster metal, the photoswitchable molecules in open form exhibit the strongest Raman scattering, while for the free molecule, it is reversed (Fig. 10a–c). The integrated Raman intensity of open-Au is found to be almost 3 times stronger than that of the closed-Au. At the same time, for bare closed molecules the Raman intensity is about 10 times stronger than that of the open-form ones. This trend can be qualitatively explained using a two-state approximation that demonstrates how CM enhancement scales approximately as $(\omega_X/\omega_e)^4$, where ω_X represents the HOMO–LUMO gap of the free molecule and $\overline{\omega_e}$ denotes an average excitation between the HOMO of the photoswitch and the LUMO of the adsorbed metal [64]. The reversible switching ability of these molecules between open and closed forms makes it an excellent probe for controlling the CM enhancement of SERS and for providing accurate estimates for the magnitude of the enhancements.

SERS also serves as a valuable tool for investigating photochromic switches, which necessitates immobilizing the switch at an interface distinct from its solution state. It is crucial to comprehend how this immobilization impacts their switching behavior. Concerning photochemically induced switches, certain systems exhibit a thermal barrier during the ring-opening process, leading to a significant reduction in the rate of opening within the temperature range of 100–200 K [66]. As previously reported, the introduction of asymmetry into the π-system could reduce the thermal barrier by changing the connectivity of one of the thiophene
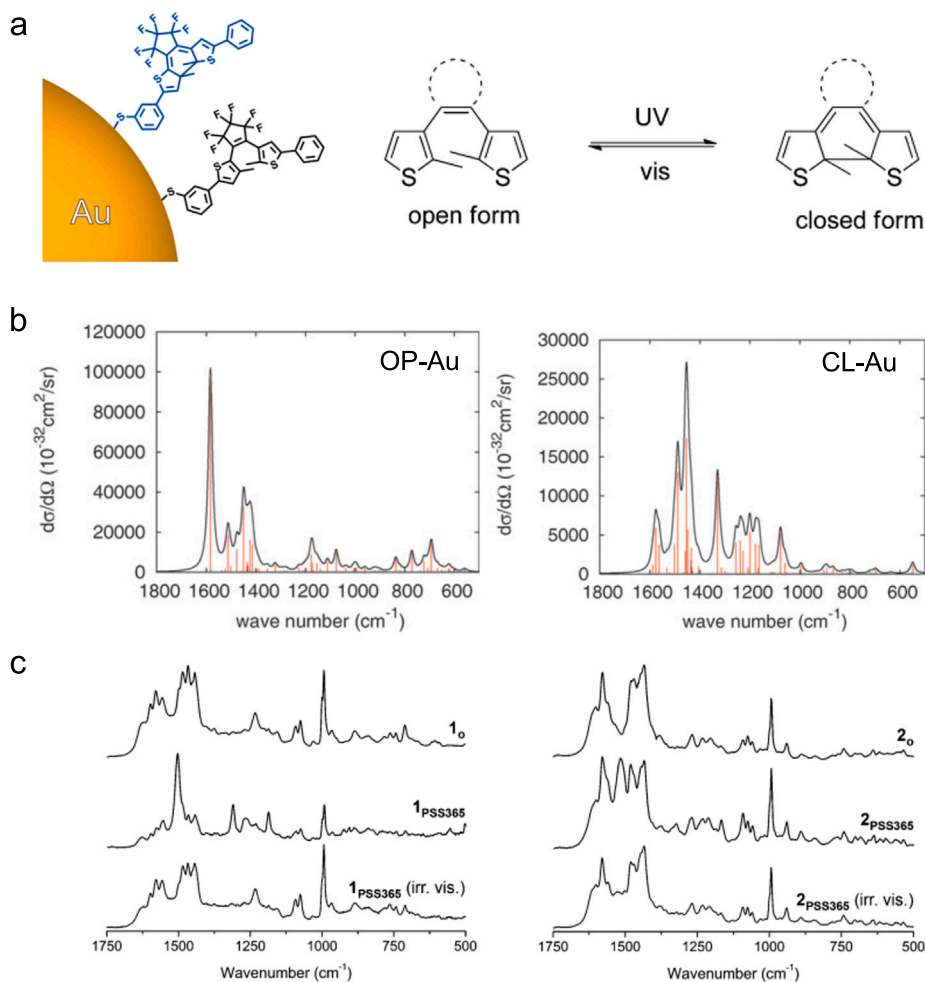
Fig. 10. SERS study of dithienylethene molecular photoswitch. (a) Representation geometries of the free open and closed photoswitch molecules bound on gold cluster (left) and the photoswitching reaction process (right). (b) Simulated normal Raman spectra of OP-Au complex and CL-Au complex. Spectra have been broadened by a Lorentzian with a width of 20 cm^{-1}. (c) Experimentally obtained SERS spectra of symmetry DAE 1 (left) and asymmetry DAE 2 (right) on roughened gold beads. 1_o and 2_o represent open forms. 1_{pss365} and 2_{pss365} represent 1_o and 2_o after being irradiated at 365 nm. 1_{pss365} (irr. vis.) and 2_{pss365} (irr. vis.) represent 1_{pss365} and 2_{pss365} after being irradiated at visible light. (a) and (c) are reprinted with permission from Ref. [63], copyright (2009) Royal Society of Chemistry. (b) is reprinted with permission from Ref. [65], copyright (2013) American Chemical Society.

parts [67]. Thomas et al. selected two kinds of DAE photochromic switches (1_o and 2_o in Fig. 10c) immobilized on Au spontaneously. By taking advantage of SERS on interfaces and the ability to combine SERS with electrochemical means, the authors studied the temperature-dependent effects of the DAE system [65]. 1_o is "symmetric" at the center and 2_o has an "asymmetric" design where the two thiophene units are connected at different positions when compared with each other. As demonstrated in SERS spectroscopy, the switching characteristics of the asymmetric DAE 2_o in solution differ from those of 2_o when fixed on gold. Specifically, the immobilization of 2_o on Au leads to excited state quenching of the closed form isomer and suppresses photochemical ring opening, which is an effect not observed for 1_o on gold. In addition, the immobilization on gold affects the thermal barrier of photochemical ring opening for 2_o. In order to investigate the photochemical ring opening of DAE 1_c and 2_c at low temperatures, roughened gold beads carrying SAMs were cooled and characterized by SERS spectroscopy. As observed, ring opening did not occur for DAE 1_c at 100 K while occurred at 200 K and 300 K, indicating that a thermal barrier in the ring-opening process was present when 1 was tethered to a gold surface. For DAE 2_c, at 100 and 200 K, no evidence showed for ring opening, indicating a higher thermal barrier for both than that of DAE 1_c. These findings provide insight into the photochemically and electrochemically driven isomerization of dithienylethenes and provide an example of how these molecules can behave differently in the solution phase from when adsorbed onto a metal surface. The potential for adjusting SERS through PAT in a nanocavity offers hope, as it enables the modification of molecular junction transmission by absorbing energy from the optical field.

3.3.2. Second harmonic generation

Second harmonic generation (SHG) is a lowest-order nonlinear-optical process of frequency doubling. The ongoing interest to SHG is motivated by its unparalleled sensitivity to the microscopic symmetry of atomic arrangements: in the dipole approximation, SHG from centrosymmetric media is forbidden. Moreover, in dielectrics SHG can be enhanced by resonant excitation and detection, thus being a convenient tool for probing eigenmodes of materials in the spectral domain. Conventionally, the second-order nonlinear response is characterized by the susceptibility $\hat{\chi}^{(2)}$ which is a third-rank tensor in the general case. It gives rise to the electric polarization at the double frequency $\mathbf{P}(2\omega)$: $P_i(2\omega) = \hat{\chi}^{(2)}_{ijk} : E_j(\omega)E_k(\omega)$, where $\mathbf{E}$ is the electric field at the fundamental frequency ω. In systems with high symmetry, the $\hat{\chi}^{(2)}$ tensor can be reduced to a small number of its components, enabling quantitative comparison of nonlinear-optical properties across a wide range of materials through an "effective" susceptibility $\langle \chi^{(2)} \rangle$. A closely related quantity is the hyperpolarizability $\hat{\beta}_{ijk}$ which determines the second-order dipole moment $\mathbf{p}^{(2)}$ induced by the fundamental field. It might prove more useful in the context of individual atoms or molecules rather than continuous media.

Upon a photo-induced transition from an open into a closed state, the electronic orbitals usually conjugate, enabling large-scale electron motion. This delocalization of the excited electron states usually results in a larger induced dipole moment and thus a higher polarizability. Whereas this mechanism has been extensively discussed for the first-order (linear) polarizability α [68,69], the same holds true for the hyperpolarizability $\hat{\beta}_{ijk}$. In particular, more than an order of magnitude increase has been observed in CH_2Cl_2-based photochromic metal complexes [70]. A more intricate scenario has been observed in benzazolo-oxazolidine (BOX) chains connected by π-linkers [71]. Upon the first switching into the closed state, the electron conjugation indeed leads to a drastic increase of the second-order polarizability. However, consecutive switching in various BOX units demonstrates mixed results, *i.e.*, an increase or a decrease of $\hat{\beta}$ was observed, depending on the symmetry of a particular compound. In particular, 2D compounds exhibit inversion symmetry in the open–open phase, which strongly hampers their dipole hyperpolarizability. This result clearly indicates a significant difference between linear and nonlinear (even-order) optical properties, which is intimately related to the unequal sensitivity to the symmetry.

These symmetry considerations add an extra dimension to the photo-induced second-order nonlinear-optical switching properties of molecular species. Another important exemption from the general rule mentioned above is related to the renormalization of the energy levels upon the photoswitching. Indeed, density functional theory calculations have predicted an order of magnitude higher second-order polarizability in the open phase of polyoxometalate derivatives than that in the closed form [72]. Intriguingly, owing to the calculated structures of the molecules, the inversion symmetry considerations are inapplicable here. Instead, energy renormalization was invoked by the authors: upon the photoswitching, the orbital conjugation changes the energy level structure, and in specific spectral ranges the optical transitions in the closed form do not involve the newly created delocalized electron states. As a result, frequency-dependent hyperpolarizability is governed by the matrix elements of a different dipole transition which turns to exhibit smaller anharmonicity. The ubiquity of this phenomenon remains however to be proven experimentally: the opposite trend was registered upon *trans−cis* photoisomerization of azobenzene-functionalized self-assembled monolayers [73]. A more complex interplay of multiple factors was theoretically demonstrated to enable hyperpolarizability modulation in meso-substituted hexaphyrins [74]. Notably, instead of a photoinduced transition between the closed and open forms, both geometry and electronic density are changed in the course of the switching, thus confirming the topological nature of the observed modulation.

Lastly, we touch on the intricate geometries where the photo-switchable elements are embedded into larger systems. In particular, modulation of the optical properties (and thus electrical conductance) can be exploited in nonlinear plasmonics [56]. The photo-induced molecular transition effectively changes the tunneling current and thus the losses in plasmonic cavities. This results in a stronger enhancement of the local electric field and thus higher nonlinear-optical effects (Fig. 11 a–b). In a broader context, the switching of molecular junctions with photo-induced current remains an attractive perspective with numerous applications in nonlinear nanophotonics [75–77]. Further, photo-switching enables an interesting approach to the design of large-scale nonlinear-optical glass with tunable properties [78]. In particular, incorporation of azobenzene complexes into glass was suggested and realized long ago [79], allowing photo-induced manipulation of the nonlinear-optical properties. In particular, adding Disperse Red 1 (DR1) allowed periodic poling of the glass: two-photon absorption of the 1064 nm radiation and one-photon absorption of the (much weaker) 532 nm beam interfere, creating polar selective excitation for the DR1 and an in-plane polar order. The SHG response measured in the absence of the 532 nm excitation revealed considerable nonlinearity which can be controlled by enabling and disabling the poling. By a comparative analysis of SHG response, the authors further inferred that this approach is capable of inducing high optical nonlinearities by replacing DR1 with a nonlinear optical chromophore with even higher hyperpolarizability. A somewhat similar approach resulted in the realization of photo-switchable polymer films containing platinum(II) complexes [80].

3.3.3. Third-order nonlinear-optical effects

Modulation of the third-order hyperpolarizability $\hat{\beta}_{ijkl}$ in the photo-switchable systems is conceptually quite similar to the second-order one. One essential difference is pertinent to the lack of sensitivity to the inversion symmetry operation, which reduces the number of active modulation mechanisms. The increase of dipolar polarizability in the electron-conjugated state of a photo-switchable molecule, however, remains intact, which can be visualized by stimulated Raman scattering. This third-order nonlinear-optical process was employed to demonstrate the photo-switching kinetics in diarylethenes [81,83]. As a result of the photo-induced switching of the molecular state, a few Raman-active phonon modes disappear (Fig. 11c). The sub-microsecond timescale of the photo-switching dynamics was inferred from these experiments.

Furthermore, $\hat{\beta}^{(3)}$ is responsible for the self-action effects, including self-focusing and two-photon absorption. The third-order nonlinear response of molecular species in solutions is often characterized and quantified with a relatively simple experimental z-scan technique [84]. Majority of the systems exhibiting photo-switched third-order nonlinear-optical properties contain azobenzene
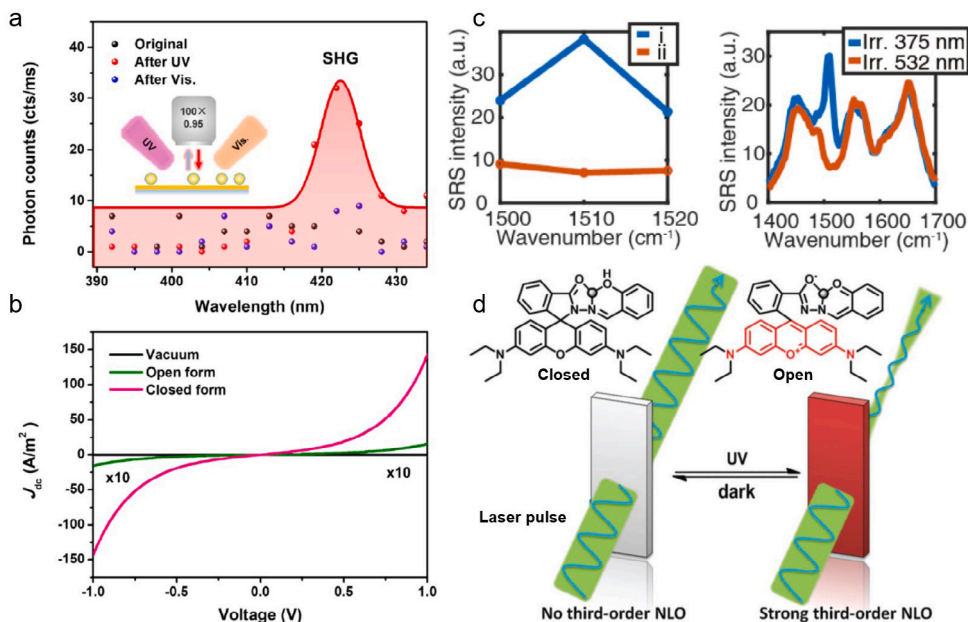
Fig. 11. (a) Active tuning of the SHG output in photoactive plasmonic molecular nanocavity. The black, red, and blue symbols represent measured SHG spectra in the original state of the host (thiol-β-CD)-guest (DAE) molecular complex, after UV exposure, and after visible light illumination, respectively. (b) Tunneling current density in the nanocavity calculated within the Simmons model at different barrier heights. (c) Photo-switchable stimulated Raman spectra after spatial averaging: measured on live HeLa cells (left) and measured with hyperspectral imaging of stained live HeLa cells ranging from 1400 to 1700 cm^{-1} (right). (d) Tautomerism of rhodamine B salicylaldehyde hydrazone metal complexes (1-Zn) before and after UV irradiation and the corresponding modulation of the third-order nonlinear-optical properties resulting in the self-focusing of transmitted radiation (right). (a) are adapted with permission from Ref. [56], copyright (2023) American Chemical Society. (c) is adapted with permission from Ref. [81], copyright (2021) Optical Society of America. (d) is adapted with permission from Ref. [82], copyright (2016) Royal Society of Chemistry.

(AB) or its derivatives [85]. Undergoing trans–cis isomerization when irradiated with UV light, these molecules were found to demonstrate not only a varied $\hat{\beta}^{(3)}$ but also reversed saturated absorption [86]. Two-photon absorption efficiency which was also modulated within this transition was also found to originate in the energy renormalization, thus showing a frequency-dependent behavior. Another example of photo-tunable nonlinear-optical refraction was observed in rhodamine B-based organic/metal complexes [82]. Subnanosecond relaxation of the highly nonlinear open state that emerged after UV irradiation was registered, accompanied by a gradual disappearance of the third-order nonlinear response. These results allowed the authors to conclude on the superiority of organic/metal complexes compared to traditional organic dyes for the development of photo-controllable third-order nonlinear-optical switches (Fig. 11d).

Similar to the second-order nonlinearity, third-order $\hat{\beta}^{(3)}$ of continuous media can also be enhanced by embedding nonlinear photochromic molecules into the system. In many practical situations with multiple contributing factors, their intriguing interplay can be expected. For example, the introduction of photo-switchable AB derivatives into Langmuir–Blodgett polymer films allowed the observation of a continuous transition from positive to negative self-action [87]. This behavior in multilayer films was attributed to the competition between the two-photon absorption and reversed saturation of the linear absorption. In turn, the enhanced nonlinear optical susceptibility originates in the *trans–cis* photo-isomerization of the AB derivatives and is associated with the electron density conjugation. Although the latter is generally considered to play the dominant role in the photo-induced variations of the nonlinear-optical properties, recent studies [88] indicate a strongly enhanced role of charge transfer for the third-order nonlinearity of oligothiophenes, as compared to the second-order effects. The authors further concluded that both linear and nonlinear-optical properties follow the structural changes induced by photochromism: a somewhat intuitively expected result which has been confirmed by DFT calculations employing hybrid exchange–correlation functional B3LYP [89].

3.4. Ultrafast dynamics of photochemical switching reactions

A large number of transient absorption spectroscopic (TAS) studies have been performed to determine the ultrafast dynamics of DAE derivatives associated with cyclization and cycloreversion reactions. These studies reveal the rate of cyclization and cycloreversion, which is crucial for both the quantum yield and the fatigue resistance (in competition with other radiative and nonradiative relaxation channels) [90]. Table 1 summarizes the photocyclization and photocycloreversion reaction rates in the

Table 1
The photocyclization and photocycloreversion reaction rates in the crystal and solution phase of typical DAE molecules.

Reactions	Structure	Phase/solution	Timescale	Method	Ref
Cyclization	1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl) perfluorocyclopentene	single-crystal	5.3 ± 0.3 ps	fs-TAS. Pump: 343 nm. Probe: white light.	[92]
	1,2-bis(5-phenyl-2-methylthien-3-yl) perfluorocyclopentene	cyclohexane	0.9 ± 0.1 ps	fs-TAS. Pump: 310 nm. Probe: white light.	[93]
	1,2-bis(2-methyl-3-benzothienyl) perfluorocyclopentene	n-hexane	0.45 ps	fs/ms-TAS. Pump: 310 nm. Probe: white light.	[94]
	poly-1,2-bis(2-methylthien-3-yl) perfluorocyclopentene	chloroform	$\approx$0.2 ps	fs-TAS. Pump: 260 nm. Probe: white light.	[95]
	1,2-bis(3,4-dimethyl-5-phenyl-2-thienyl) perfluorocyclopentene	1-butanol	<4 ps	ps-TR S&AS RS Pump: 310 nm. Probe: 568 nm.	[96]
	1,2-bis[5-formyl-2-methyl-thien-3-yl] perfluorocyclopentene	dichloromethane	2.3 ± 0.2 ps	fs-TAS. Pump: 308 nm. Probe: white light.	[97]
Cycloreversion	1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl) perfluorocyclopentene	cyclohexane	9 ps	fs-TAS & PP. Pump: 500 nm. Probe: white light.	[98]
	bis(2-methyl-5-phenylthiophen-3-yl) perfluorocyclopentene	n-hexane	12 ps	fs-TAS. Pump: 600 nm. Probe: white light.	[99]
	1,2-bis(2-methylbenzo[b]thiophen-3-yl) hexafluorocyclopentene	n-hexane	22 ps	fs-TAS. Pump: 530 nm. Probe: white light.	[100]

crystal and solution phase of typical DAEs. The majority of ultrafast studies have been carried out in solution, indicating that the cyclization occurs on subpicosecond to picosecond (ps) time scales. Most studies have been performed with femtosecond (fs-TAS) or picosecond transient absorption spectroscopy (ps-TAS), or picosecond time-resolved Stocks and anti-stocks Raman spectroscopy (ps-TR S&AS RS) systems to observe the ultrafast dynamic processes. However, the presence of open-ring isomers with parallel conformation can weaken our ability to interpret spectral features related to newly formed closed-ring molecules. DAEs in the crystalline phase are usually composed entirely of antiparallel conformation, and their periodic structure allows all excited molecules to undergo cyclization in the same local environment. The disadvantage of crystalline phase measurements is that the periodic crystal structure and intermolecular contacts will presumably have an unknown effect on the reaction pathways, which leads to a significantly slower cyclization. The cyclization reaction is sensitive to the substituents at both ends of the molecule with the same intermediate backbone unit [91]. The coupling strength between the electron system of the intermediate backbone unit and that of the substituents are affected by the geometry, alignment and π electron system of the substituents, resulting in the different time constants of the reaction.

In contrast to the photocyclization reactions mentioned above, directly measuring the time constants of the ring-opening reaction of closed-ring isomers is challenging due to overlapping absorption spectra with open-ring isomers in the UV region. To estimate these time constants, one need to observe the decay of transient absorption and fluorescence signals from the excited closed-ring isomers. As summarized in Table 1, the cycloreversion reaction is typically slower than the cyclization reaction and different photoswitching molecular systems have certain differences, which is related to the reaction mechanism [90]. As depicted in Fig. 12a and b, upon UV irradiation, the open-ring isomer transitions to the 1BFC(o) state, close in energy to the 2 A state, followed by rapid internal conversion. The excited wavepacket progresses along the 2 A surface, accessing the 2A/1ACI(o) conical intersection through orthogonal vibrations, leading to decay to the ground state and formation of the closed-ring isomer. In contrast, the ring-opening reaction under visible light involves excitation of the closed-ring isomer to the 1BFC(c) state. The wavepacket moves away from the Frank-Condon region along the 1B surface, then falls rapidly to the 2 A surface via the 1B/2ACI(c) conical intersection. Molecules excited with shorter wavelength light, possessing excess vibrational energy on the 2 A surface, cross the energy barrier 2ATS1 more readily, reaching the 2A/1 A conical intersection (2A/1ACI(o)). Here, rapid deactivation to the ground state produces the open-ring isomer, indicating the need for thermal activation or excess kinetic energy for the ring-opening reaction.

Photoswitching devices have attracted considerable attention for their characteristic properties, which are different from those of photoswitching molecules in solution and in bulk crystal. Particularly attractive is the possibility of ultrafast dynamics studies of photochemical switching reactions by using femtosecond optical spectroscopy. Molecular compounds with photoswitchable magnetic properties and plasmonic hybrid photo-addressable nanodevices have been intensively investigated over the last decades due to their prospective applications in the fields of nanoelectronics, sensing and magnetic data storage. In 2014, Kaszub et al. reported the
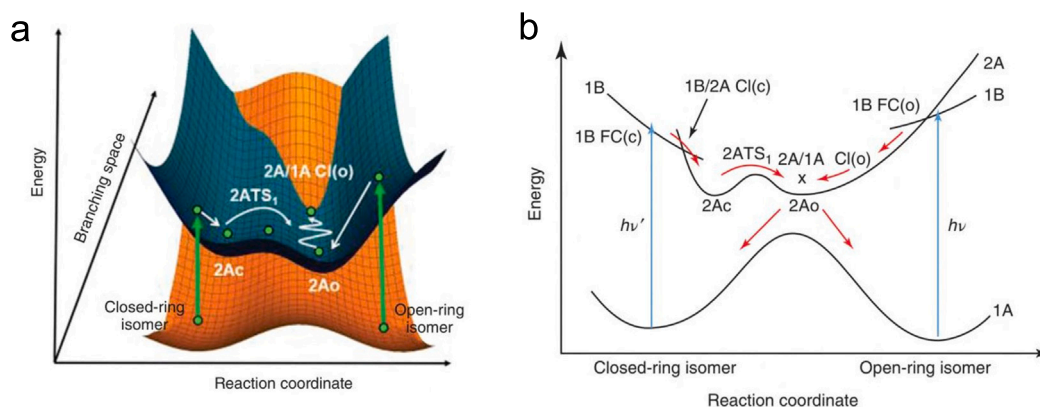
Fig. 12. (a) Schematic representation of the structures of S_0 (orange) and S_1 (green) potential energy surfaces corresponding to the photoisomerization between open- and closed-ring isomers of a diarylethene. (b) Outline of two reaction paths corresponding to ring-opening and ring-closing reactions of a diarylethene. (a-b) are adapted with permission from Ref. [90], copyright (2021) Wiley.

first appealing study of coppernitroxide-based molecular magnets photoswitchable compounds systems using femtosecond optical spectroscopy, which unveiled the mechanism of ultrafast (< 50 fs) spin state photoswitching and established its principal differences to other photoswitchable magnets (Fig. 13a–c) [101]. These copper-nitroxide-based molecular magnets undergo reversible magneto-structural rearrangements between weakly and strongly exchange-coupled states of spin triads nitroxide–copper(II)–nitroxide (WS/SS states). This kind of photoswitching is different from that occurring in classical SCO compounds, as it proceeds on the larger scale of exchange-coupled cluster and, hypothetically, could be noticeably slower. Notwithstanding such expectations, the observed photoswitching time is very short and similar to the values found in several coordination compounds. Another finding is that the photoswitching mechanism can basically be described by three-state dynamics involving ground SS state, intermediate excited state, and final WS state (Fig. 13b). The transition from excited to WS state is partly spin-allowed, therefore the overall SS→WS photoswitching represents an interesting alternative for developing ultrafast photo-magnetic materials, thus promoting breathing crystals for applications in spintronics.

Photoswitchable hybrid plasmonic nanosystems based on photoswitchable molecules and plasmonic nanostructures enable observations of photochromism-plasmonic coupling. On the one hand, the photochromic reaction of the diarylethene molecules greatly modifies the surface plasmon resonance (SPR) mainly through a change of the local refractive index. On the other hand, the enhanced electromagnetic field at the surface of the GNPs induces an enhancement of the photochromic kinetics under visible light irradiation. These cross talk interactions providing new tools to investigate the molecular-plasmonic coupling experimentally and theoretically. Liu et al. [102] conducted a real-time study of all-optical modulation of localized surface plasmon resonance (LSPR) coupling in a hybrid system that integrates a photoswitchable optical grating with a gold nanodisk array (Fig. 13c–e). In this azo-dye-doped holographic polymer-disperse liquid crystals (HPDLC) system, the diffraction of the grating can be continuously tuned in real time by an external pump light. As demonstrated that the trans–cis transformation of the azo dyes embedded in the grating structure results in the nematic-isotropic (N–I) phase transition of the liquid crystals (LCs), thus changing the plasmonic properties of the Au nanodisk array. Although long response times for the "ON" and "OFF" photoswitching processes estimated as 3.4 s and 2.9 s need further optimization (as influenced by multiple factors including grating structure, working temperature, the amount of azo dyes, and the power of the pump light), this proposed all-optical modulation system demonstrated here can be conveniently integrated with other plasmonic systems in future nanophotonic devices.

By achieving a strong coupling between the electronic energy levels of molecules and light in plasmonic photoswitch-nanoantennae system, we can efficiently manipulate the photochemical properties of the system. Realization of this control on the ultrafast time scale is expected to lead to many new applications combining ultrafast optics and optically driven chemistry. Recently, Kuttruff et al. designed a platform consisting of a dual-mode anisotropic plasma antenna array and a spiropyran optical switch, which can selectively access weak and strong coupling regions and follow polariton dynamics after pulsed femtosecond laser excitation (Fig. 13f and g) [103]. In both weak and strong coupling regimes, experiments show the potential to affect the chemical energy landscape of the hybrid system on sub-picosecond timescales, revealing a significantly faster dynamics of the excitation with respect to the purely molecular relaxation time. This observed faster dynamics cannot be explained by simple plasma non-radiative decay, which occurs in the first few tens of femtoseconds but originates in the complex intramolecular dynamics within the coupled plasmon molecular systems. These results provide an exciting foundation for further exploring the synthesis and characterization of strongly coupled optical switching systems, paving the way for a comprehensive control of nanoscale ultrafast chemical processes.

4. Conclusions and perspectives

A variety of molecular electronic and plasmonic materials have been developed for device applications, thus, it becomes critical to probe and understand the details of how we alter the charge transport and optical phenomena across photo-responsive molecules
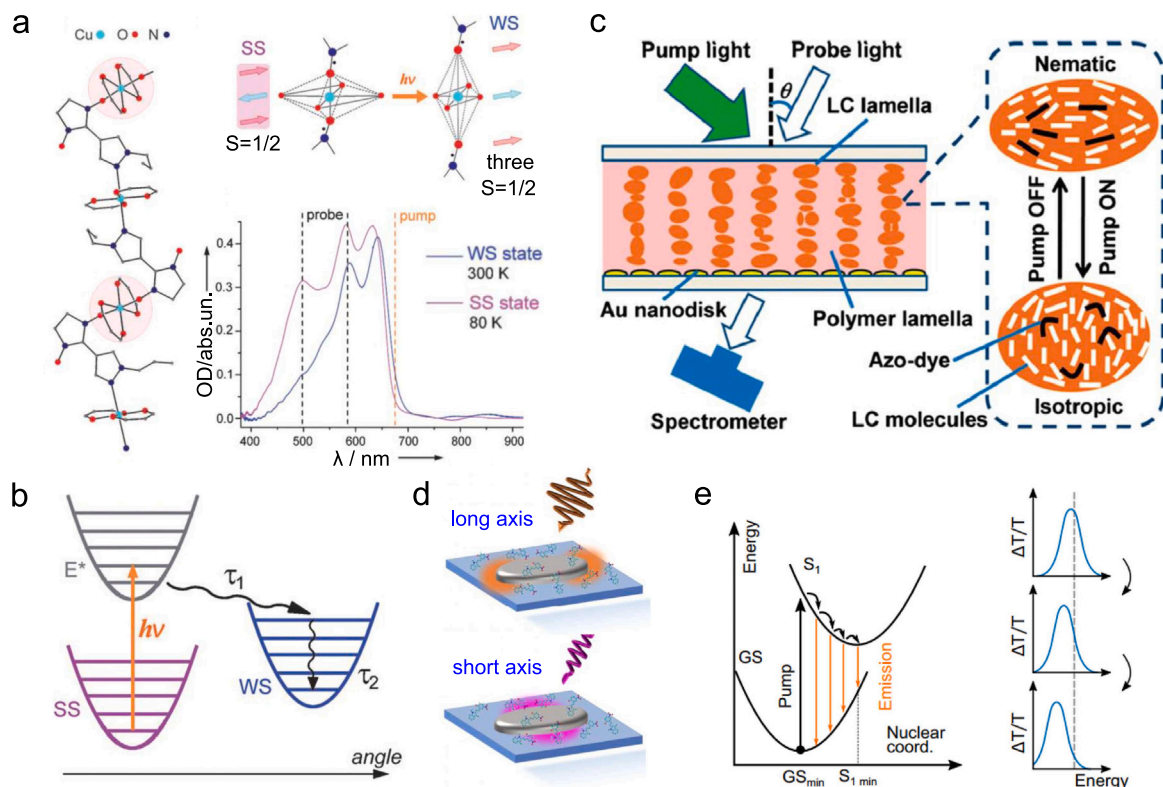
Fig. 13. Photoswitchable hybrid nanosystem ultrafast dynamics studies. (a–b) Ultrafast photoswitching in a copper-nitroxide-based molecular magnet: (a) Polymer chain structure, key properties and optical absorption spectra of molecular magnet [Cu(hfac)2L^{Pr}] (pump and probe positions in femtosecond experiment are indicated). (b) Photoswitching scheme of [Cu(hfac)2L^{Pr}] . (c) All-optical modulation of localized surface plasmon resonance (LSPR) coupling in a hybrid system that integrates a photoswitchable optical grating with a gold nanodisk array. (d–e) Hybrid system consisting of photo-switchable molecules and aluminum nanoellipse: (d) Sketch of the localized plasmon dipolar excitation along the long and short axes of the nanoantenna; (e) Ultrafast dynamics of the MC isomer. (a–b) are adapted with permission from Ref. [101], copyright (2014) Wiley. (c) is adapted with permission from Ref. [102], copyright (2011) American Chemical Society. (d–e) are adapted with permission from Ref. [103], copyright (2023) Springer Nature.

by photoirradiation. In this review, we have discussed optical and charge transport characteristics of photoswitching single-molecule junctions probed primarily by scanning tunneling microscope break-junction or mechanically controlled break-junction technique. These studies provide fundamental understanding of nanoscale charge transport processes as well as light-induced interactions at the single-molecule level. Despite the great progress made in both the experimental and theoretical aspects of single-molecule optoelectronic devices, challenging tasks still exist in extensive application of the research results. On one hand, in order to get high-yield well-defined single-molecule junctions, it is vital to prepare controllable and reliable nanogap electrodes as well as to precisely regulate the target molecules at the molecular or even atomic scale. Towards this end, it is necessary to develop fabrication as well as characterization methods used in the field to explore the photoelectric interaction processes. Such methods can potentially lead to construction of integrated molecular electronic devices with high stability and reproducibility. On the other hand, there are still challenges in rational molecular junction design. It remains to be explored as how to make more complex structures of molecular junctions to achieve multifunctional detection and regulation.

Next, the designing strategies and applications of supramolecular self-assembling systems and plasmonic hybrid nanostructures with photochromic compounds as photo-responsive units are reviewed. In what follows we provide an overview of the several nonlinear-optical processes of photoswitching single-molecule junctions including Raman scattering, second harmonic generation and third-order nonlinear-optical effects. The reversible switching ability of these photoswitching molecules between open and closed forms make them an excellent probe for controlling the chemical mechanism enhancement of SERS and these photoswitching molecules help enable accurate estimates for the magnitude of the enhancements, providing insights into the photochemically and electrochemically driven isomerization. Although several types of plasmonic hybrid nanostructures have been demonstrated as potential photoswitching molecular electronic components [104–107], those that can be used for practical applications are still very limited. Firstly, it remains a challenge to construct stable single-molecule plasmonic hybrid nanostructures with uniform distribution, which typically requires the integration of electronic control technology for achieving effective single-molecule capture. In the investigation of all-optical systems involving plasmonic hybrid nanostructure systems, for instance, while it is feasible to fabricate single molecule junctions through Raman techniques, verifying the presence of single-molecule within the system can be accomplished by examining spectral characteristics such as SERS spectral "blinking" behaviors during tens to hundreds of

seconds of continuous laser exposure time period [108–111]. However, prolonged laser irradiation also induces alterations in molecular conformation or changes in spectral characteristics due to oxidation–reduction reactions that impede observations related to molecular switching behaviors. Moreover, there may exist novel mechanisms based on plasma-assisted effects that influence the photoswitching behavior of single-molecule plasmonic nanojunctions, which requires more in-depth systematic verification and exploration by researchers in this area. Besides, the nonlinear optical investigations of plasma nanocavity systems, such as second and higher harmonics, typically involve single molecule layers. Currently, there is considerable research on the combination of bulk materials, two-dimensional (2D) materials, and plasmonic nanocavities. For example, studies have focused on the enhancement of dark excitons photoluminescence (PL) [112] as well as the improvement of organic light-emitting diode device performance induced by the Purcell effect [113]. Other areas of interest include the control of 2D excitonic states [114] and phase transitions induced by hot carrier injection [115]. However, there exists a research gap in the exploration of single-molecule plasmonic nanocavities, thus limiting the depth of research based on the quantum conductance transmission mechanism. The exploration of quantum charge transport theory and the development of advanced fabrication techniques are imperative for gaining novel physical insights into the mechanism of charge transport in conducting photoswitching molecules on single-molecule plasmonic nanojunctions.

Finally, considering the ultrafast dynamics and excitement in this area of research, the rapid progress in transient absorption and Raman spectroscopies with femtosecond or picosecond time-resolved resolution made over the past few years strongly suggests that in the not-too-distant future, photoswitching molecules will provide an important fundament for novel devices and advanced materials. However, currently, a plethora of studies predominantly focus on solution systems and single crystal photoswitching molecular systems, with limited reports on the ultrafast dynamics of integration of plasmonic hybrid systems. The latter indicates a promising future direction for molecular optoelectronics. Moreover, the significant challenge in effectively controlling ultrafast time scales still exists, which requires the comprehension of the interplay between collectively coupled molecular excitation and light modes. By means of collaborative experimentation and quantum mechanical modeling, we can further elucidate a deeper understanding of the light regulation mechanism in plasma nanocavities controlled by intramolecular dynamics under potential plasma interactions, thereby facilitating the advancement of optical devices with enhanced conversion efficiency. Furthermore, the single-molecule nanojunction *in situ* positioning technology based on the combination of optics and electricity, such as optical tweezers, can enable the disclosure of multidimensional molecular information and the essence of quantum conduction influences under the precise control of a single molecule. Further investment in this research area is crucial in advancing the progress of physical chemistry understanding of photoswitching phenomena and moving forward for further innovative applications at the single-molecule level.

CRediT authorship contribution statement

Song Han: Writing – original draft, Investigation, Formal analysis, Data curation. **Xiu Liang:** Writing – original draft, Investigation, Formal analysis, Data curation. **Ilya Razdolski:** Writing – original draft, Investigation, Formal analysis, Data curation. **Yu Bai:** Writing – original draft, Investigation, Formal analysis, Data curation. **Haixing Li:** Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization. **Dangyuan Lei:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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