

Chapter 2

Novel Ethene-Bridged Diarylethene Photochromic Systems: Self-Assembly, Photoswitcher, and Molecular Logic Gates

Shangjun Chen, Wenlong Li and Wei-Hong Zhu

Abstract The last decade has witnessed the great expansion of the photochromic family, especially the most promising representative, diarylethene, owing to the excellent thermal stability and outstanding fatigue resistance. Till now, (perfluoro/hydro)cyclopentene bridge has been proved to be the best choice for diarylethenes. However, cyclopentene bridge also limits the molecular modification within the side aryl groups. In fact, other novel ethene bridges would enlarge the versatility of diarylethene architectures, enhance the photochromic performance, and finally endow other photo-modulated properties. This chapter summarizes the recent development in the diarylethenes with novel ethene bridge and their applications on self-assembly, photoswitcher, and molecular logic gates.

Keywords Ethene bridge • Self-assembly • Photoswitcher • Molecular logic gates

2.1 Introduction

Photochromic materials have attracted considerable attention due to their potential application in photo-responsive materials and devices [1–13]. Among various organic photochromes, diarylethenes (DAEs) are one of the most promising families owing to their excellent thermal stability and outstanding fatigue resistance [14]. Particularly, DAEs with perfluorocyclopentene as ethene bridge have been extensively studied [15–18]. To date, the rational design of DAEs has been mainly focused on the variation of substituents in side aryl moieties of DAEs. In contrast,

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the central ethene bridges for the versatility of DAE architectures reported so far have been mostly limited to cyclopentene or perfluorocyclopentene units [19–25]. The modification on the central ethene bridge can provide several distinct advantages: (i) remarkably expanding the versatility of photochromic DAEs, (ii) conveniently improving the photochromic properties including thermal stability, fatigue resistance, as well as quantum yields, and (iii) widely exploring the applications of DAEs in self-assembly, photoswitcher, and molecular logic gates [26–30]. Indeed, chemical tailoring of the central ethene bridges to append novel switchable functions has been well demonstrated. This chapter summarizes those novel photochromic DAEs on the basis of the categories of ethene bridges.

2.2 Four-Membered Ring-Based Ethene Bridges

DAEs with four-membered ring chromophore at the center were relatively rare. As an interesting four-membered ring diketone, Krayushkin et al. [31] utilized cyclobutene-1,2-dione as the ethene bridge for the development of photochromic DAE derivatives. However, 2,5-dimethylthiophene-substituted cyclobutene-1,2-diones (**1**) exhibit no photochromism in solution or in crystalline state, which is attributed to its rigidity. In order to develop photochromic cyclobutenedione derivatives, the thiophene rings were replaced by thieno[3,2-*b*]thiophene residues, bringing forth a new DAE with typical photochromic properties. Here, in the case of **2**, the retained aromaticity of the substituent and a long conjugation chain in the closed isomer were considered to guarantee the photocyclization of **2** (Chart 2.1).

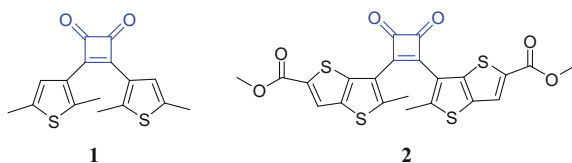
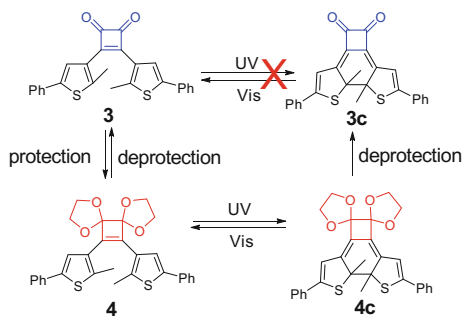


Chart 2.1 Cyclobutene-1,2-dione based DAE compounds **1** and **2**

Chart 2.2 Photochromism of cyclobutene-1,2-dione based DAE compound **3** and 1,2-bis ketene based DAE compound **4**



As shown in Chart 2.2, Belser et al. [32] developed an interesting chemically gated dithienylethene switch based on the same ethene bridge. Similar to **1**, compound **3** does not undergo any photochromic reaction upon UV irradiation. Given that the excited state of **3** is efficiently quenched, the formation of a thermally very unstable intermediate rather than a normal closed-form isomer leads to the non-photochromism. In contrast, upon protecting both ketone functionalities of **3**, the typical photocyclization upon irradiation at 365 nm can be observed, which was evidenced by UV–visible and NMR spectra. Although the ring-closing and ring-opening reactions for **4** could be performed only several times as a result of the formation of side products, the protection and deprotection reactions of ketone groups did not show any undesired side reactions.

2.3 Five-Membered Ring-Based Ethene Bridges

As well demonstrated, the absorption band in the ring-closed isomers of DAEs was dependent upon the ring size, which controls the molecular planarity, thus affecting the π -conjugation extent in the closed-ring isomers [26, 33]. Moreover, the cyclization quantum yield is also relying on the ring size, and the highest value was observed for the five-membered ring derivatives. As a consequence, the five-membered ring is the most studied cycloalkene structure for the ethene bridge in DAEs. However, up to now structurally less versatile hexafluorocyclopentene is usually employed as the central ethene moiety, and in these cases, the chemical modifications are limited only to the side aromatic rings. Therefore, tailoring the ethene moiety with other functional five-membered aromatic ring in place of the traditional hexafluorocyclopentene bridge has become attractive, especially for improvement in photo-switching characteristics of photochromic molecules. Many commercially available functional groups such as thiophene, benzothiophene, benzothiophene dioxide, thiazole, imidazole, imidazoline, and their derivatives were widely exploited as the central ethene moiety. When a π -conjugating aryl group is placed as the ethene bridge, the relative photochromic properties such as absorbance, fluorescence, thermal stability, and quantum yield can be modulated. Upon changing the π -conjugation in easily accessible ways, the molecularly rational design can then construct photo-triggered molecular switches.

As an easy structural modulation and low aromatic stabilization energy, the five-membered aromatic thiophene has been widely exploited as the ethene bridge to modulate the absorption and fluorescence of the DAEs. This aryl group was first employed as the ethene bridge by Kawai and Irie et al. [34] for the purpose of re-routing the connection mode of the π -conjugation system with the photochromic reaction. Three triangle terthiophene derivatives (**5**, **6**, and **7**) with different substituents were developed by conventional cross-coupling of thiophene derivatives (Chart 2.3). As demonstrated, substitution with a phenyl unit on the 5-position of thiophene ethene bridge could induce a red shift in the absorption band of the closed form.

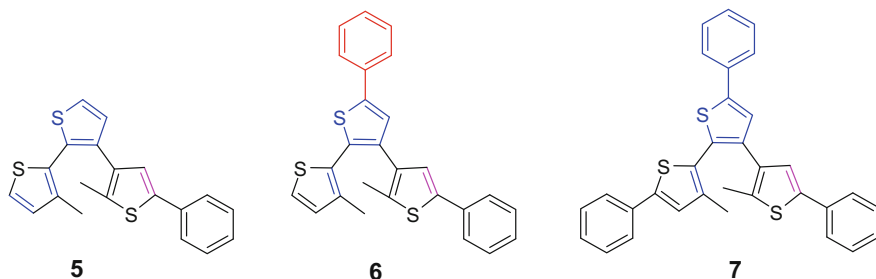
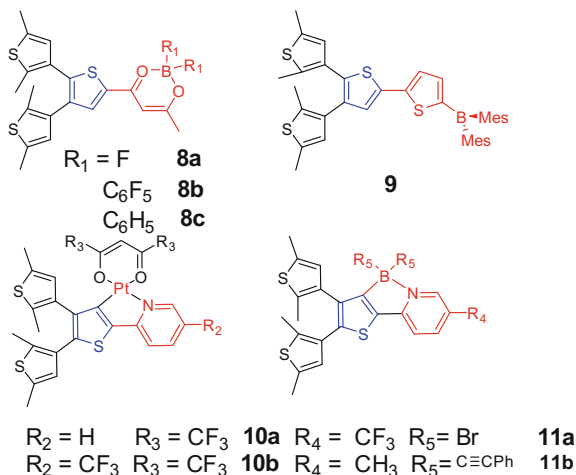


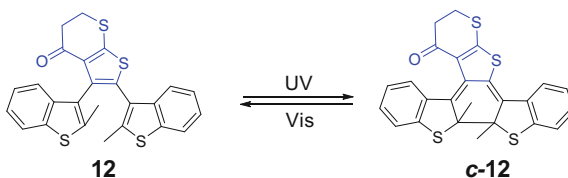
Chart 2.3 Thiophene-based triangle terthiophene derivatives **5**, **6**, and **7**

Chart 2.4 Chemical structures of photochromic borane and Pt complexes



More recently, Yam et al. prepared several versatile DAE ligands upon incorporation of different functionalized units at 5-position in the central thiophene bridge (Chart 2.4). As a good ligand for boron or transition metal centers, β -diketonate unit was introduced into the thiophene ring. Near-infrared (NIR) photochromic behavior and photo-switchable luminescence were observed upon coordination of boron (III) sources ($\text{BF}_3 \cdot \text{OEt}_2$, $\text{B}(\text{C}_6\text{F}_5)_2\text{F} \cdot \text{OEt}_2$, and BPh_3) with the β -diketonate photochromic ligand (**8**) [35]. Interestingly, the maximum absorption band was red-shifted from *ca.* 630 nm (free ligand) to 758 and 810 nm for **8a** and **8b**, respectively. Upon transferring from their ring-open into closed form, the distinct decrease by 90% in luminescence quantum yields was accompanied. Density functional theory (DFT) and time-dependent DFT (TDDFT) calculations indicate that the observed NIR luminescence is originated from $\pi \rightarrow \pi^*$ transition from the π orbital localized on the condensed cyclohexadiene unit to the π^* orbital delocalized over the whole boron (III) moiety. In contrast, when 5-dimesitylboryl-thiophene unit was grafted onto the ethene bridge, the resulting three-coordinated boron (III) derivative (**9**) is photochromically inactive [36]. Here,

Fig. 2.5 Chemical structures and photochromism of DAE compound **12**



the highly suppressed photochromic reactivity might be resulted from the presence of the highly emissive $\pi \rightarrow \pi^*/P\pi(B)$ excited state. Indeed, the photochromic reactivity can be restored upon F^- ion binding to the boron center. They further developed cyclometalated platinum(II) complexes (**10**) and bis(alkynyl)borane complexes (**11**) by introducing a pyridine unit into the central ethene bridge [37, 38], along with interesting red or NIR phosphorescence.

As shown in Chart 2.5, Ahn et al. [39] modified the thiophene ring and achieved an interesting turn-on fluorescence from ring-open to ring-closed isomer. Generally, many ring-open DAEs exhibit fluorescence, while the corresponding ring-closed forms exhibit weak or quenched fluorescence. However, upon exposure to UV light at 312 nm, compound **12** is converted to the ring-closed form (**c-12**), exhibiting a remarkable increase in reddish fluorescence at 580 nm with a fluorescence quantum yield of 0.11. The fluorescence of **c-12** was stable enough for several days at room temperature in the dark, but quenched rapidly upon irradiation with visible light. Importantly, the fluorescence on–off cycle could be repeated at least 10 times without any decrease in the fluorescence intensity of **c-12**, highly desirable for live cell imaging.

Chen et al. [40, 41] also reported DAE derivatives with a 2,5-dihydrothiophene bridging unit that provide a facile synthetic route to construct symmetric and nonsymmetric photochromic derivatives. As well known, a photochromic DAE possesses two conformations with two heterocyclic rings in mirror symmetry (parallel conformation) or C_2 symmetry (antiparallel conformation). In general, the population of the two conformations bestows the equivalent ratio (1:1) in solution. Since the photocyclization proceeds only from the antiparallel conformation, the cyclization quantum yield cannot exceed 0.5. There exists one approach to increase the quantum yield, that is, changing the ratio of two conformers. Kawai et al. [42] has unprecedentedly achieved a quantitative photocyclization quantum yield in hexane by using benzothiophene as the ethene bridge. Impressively, the photocyclization quantum yield of **13** in hexane reached $98 \pm 2\%$, one of the largest values for known photochromic systems. The combination of X-ray crystallography, NMR spectroscopy, and DFT calculations clearly indicated that the multiple intramolecular noncovalent interactions including weak CH–N hydrogen bonds as well as S–N and CH– π interactions take place between benzothiophene unit and side chain thiazole units, allowing to fasten the geometry of **13** in the photo-reactive antiparallel conformation (Chart 2.6). Very recently, the same group has also developed several similar DAE analogues based on the same ethene bridge, in which substituent effects on the photochromic properties as well as photoacid release induced by photocyclization were carefully studied [43, 44].

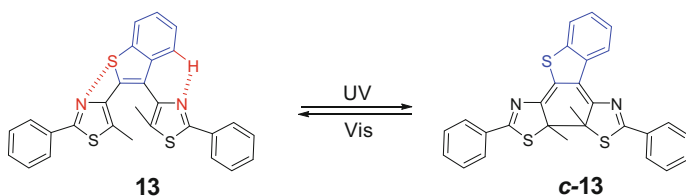


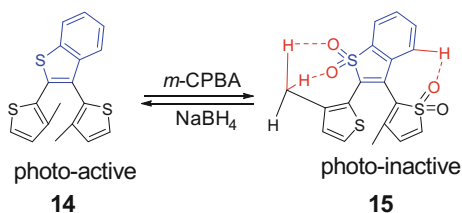
Chart 2.6 Photochromism of benzothiophene based DAE compound **13** with the predominant photoactive antiparallel conformation via the molecular rigidity with the multiple intramolecular noncovalent interactions

The benzothiophene unit could be further oxidized into benzothiophene dioxide, which can also be exploited as ethene bridge (**14**) [45]. Li et al. reported an interesting photo-responsive molecular switch, in which the photochromic activity can be reversibly locked and unlocked via controlling the oxidation/reduction state of benzothiophene unit. X-ray crystallography and NMR measurements revealed that there exists the intramolecular hydrogen bonding interaction between S=O group and hydrogen (Chart 2.7), and thus prohibiting the rotation of photochromic unit by steric hindrance (**15**). Obviously, the suppressed photoactivity of the oxidized state is resulted from the stronger intramolecular interactions, which can efficiently stabilize and enrich the photo-inactive parallel conformation.

In spite of the gated photochromism, the greatly improved thermal stability can also be achieved by oxidizing the benzothiophene unit into benzothiophene dioxide [46]. For instance, compound **17** with benzothiophene dioxide as the ethene bridge showed much better thermal stability than compound **16** based on benzothiophene (Chart 2.8). As calculated, the energy difference between ring-open and ring-closed isomers in the oxidized DAE **17** (11.55 kcal mol⁻¹) is similar to that of the perfluorocyclopentene analogues (11.64 kcal mol⁻¹), indicative of the excellent thermal stability for **17**.

Zhu et al. also reported an interesting gated photochromic reactivity controlled by complexation/dissociation with BF₃ based on a benzothiophene dioxide ethene bridge [47]. Photochromic **18** possesses two phenylthiazole units and exhibits typical photochromic reaction in solution with excellent fatigue resistance. It also undergoes color change from colorless to violet in crystalline state, along with a typical antiparallel conformation and a short distance (3.700 Å) between the two photo-active carbon atoms. Interestingly, the photochromism of **18** in solution was prevented to a great extent upon the addition of BF₃•Et₂O, showing a specific

Chart 2.7 Mechanism of the “lock and key” process between **14** and **15**



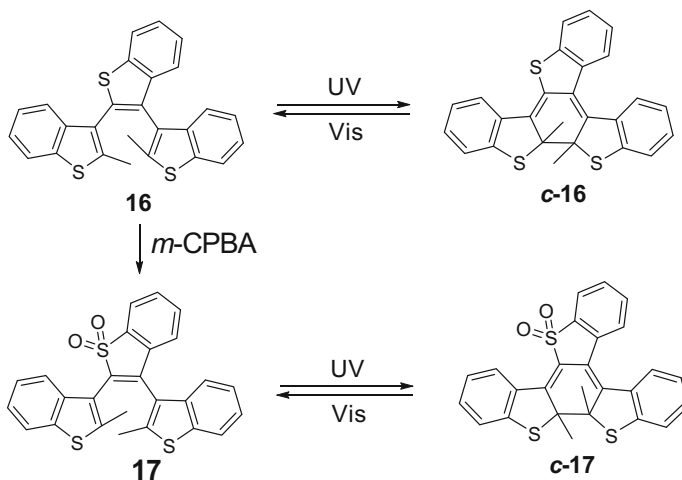


Chart 2.8 Photochromism of benzothiophene based compound **16** and benzothiophene-dioxide based compound **17**

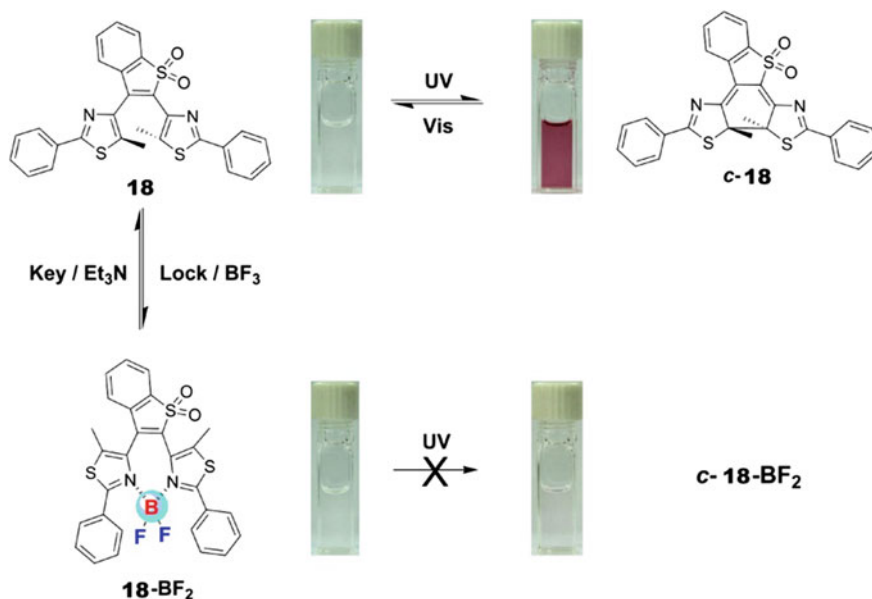


Fig. 2.1 Proposed mechanism of “Lock and Key” gated process of **18**

“Lock” gate. And the gate behavior is reversibly controllable. By the addition of Et_3N , the photochromic property could be recovered. This phenomenon did not occur for H^+ and metal ions, such as Zn^{2+} , Mn^{2+} , Mg^{2+} , Ca^{2+} , and Ba^{2+} . A proposed mechanism of the “Lock and Key” gated process is shown in Fig. 2.1.

A rigid seven-membered ring is formed with thiazole rings when coordinating with BF_3 , resulting in a longer distance between two active carbon atoms, by which the initial photochromic reaction is completely blocked. The addition of Et_3N can destroy the coordination between **18** with BF_3 , thus recovering the original characteristic photochromicity. This proposed mechanism was further evidenced by the ^1H NMR titration and theoretical simulation. Before adding BF_3 , the two signals corresponding to the photo-active methyl protons appeared at 2.10 and 2.03 ppm with the integration ratio of 1:0.06, while the integration ratio changed to 1:1 upon adding BF_3 , possibly arisen from the change of the ratio of the parallel and antiparallel conformations during the coordination to BF_3 (Fig. 2.2). Additionally, the electrospray ionization mass spectrum (ESI MS) at m/z of 541.1 $[\text{M}-\text{HF}]^+$ also provides strong evidence for the existence of **18**- BF_2 . Theoretical calculations also indicate that the gated photochromism of **18** in response to BF_3 is reasonable to ascribe the formation of the rigid photochromically deactivated boron-coordination conformation.

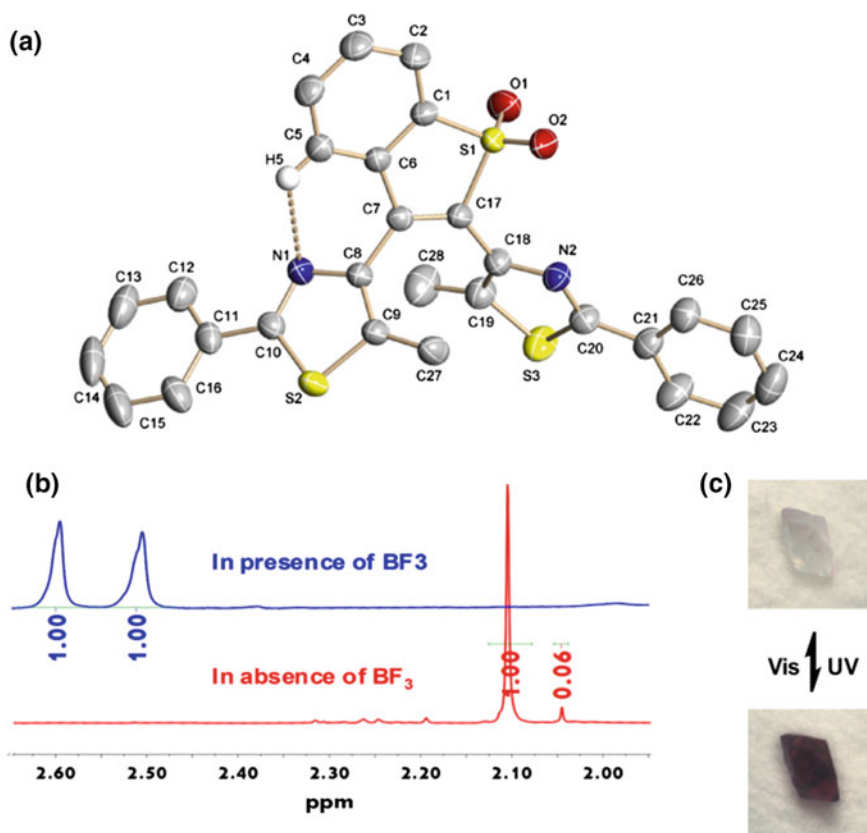


Fig. 2.2 **a** Single crystal structure of **18** with displacement ellipsoids shown at the 50% probability level, **b** changes in ^1H NMR spectra of **18** with or without BF_3 , **c** color changes of **18** in the crystalline state

Quantitative photo-switchable DAEs with excellent fatigue resistance and high thermal stability are highly desirable for photo-optical modulation, especially in the field of exploiting one ray of light to encode another ray of light, in which information in optical format can be directly transferred from one beam to another without converting back to the electronic format. Based on above-mentioned same ethene bridge, Zhu et al. also developed a DAE derivative (**19**) containing two thiazole units on each side chain, which impressively exhibited several advantages such as fast quantitative cyclization, excellent fatigue resistance, and high thermal stability both in solution and in the crystal state (Fig. 2.3). All those photochromic properties guarantee **19** as a promising candidate for photo-optical modulation. To demonstrate the possibility of photo-optical modulation, the photo-switchable thin film containing **19** in polylactide was fabricated. Upon alternative irradiation with laser light of 375 and 561 nm, the specific photochemical conversions between the bistable states were carried out reversibly and quantitatively. In such process, the binary digital information was firstly encoded into the photo-switchable thin film by the two lasers. The reversibly photochromic reactions in the thin film in turn encode orthogonal nonmodulated beams into digitally encoded modulation [48].

Zhu et al. [49–51] further widely explored the benzothiophene dioxide unit as the ethene bridge, especially for logic gates and photo-responsive self-assembly

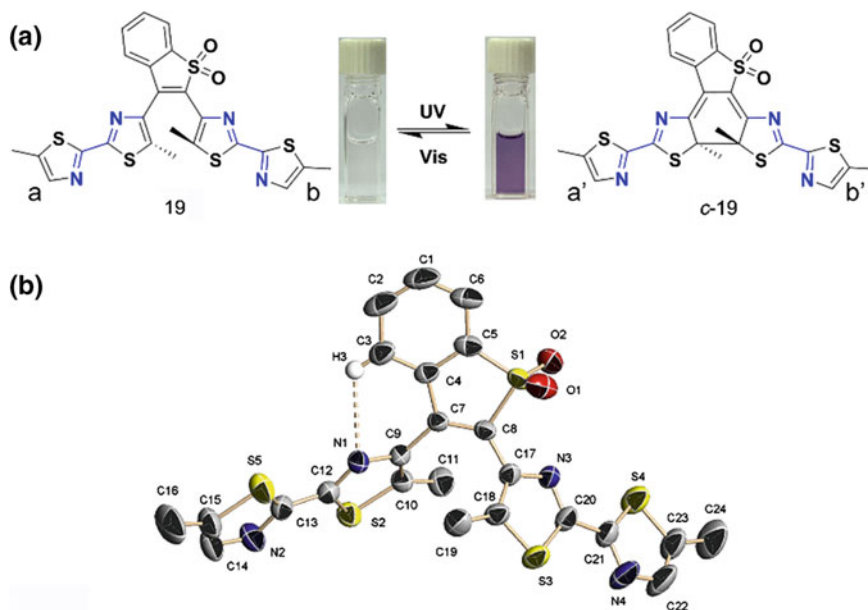


Fig. 2.3 **a** Photochromic reaction of **19** with desirable properties of excellent fatigue resistance, high thermal stability, and quantitative photoswitching. **b** Single crystal structure of **19** in the open-isomer state

systems. Molecular logic gates are capable of processing information, and the output signals in the keypad lock are critically dependent upon the proper combination and sequence of input signals. For practical application, complicated keypad lock with three or more inputs is becoming interesting. Recently, an interesting sequence-dependent responses have been realized on the basis of multi-responsive photochromic switcher (**20**) containing benzothiophene dioxide unit as the ethene bridge (Chart 2.9) [49]. Due to the specific basicity and coordination capability of imidazole unit, **20** shows distinct multiple photochromic properties in the presence of protons and Ag^+ . The absorption spectra of **20** display reversible changes under different pH values as a result of the protonation–deprotonation process of the imidazole unit (**20-H**). In particular, the photocyclization reaction of **20** is perturbed by the efficient coordination of **20** with Ag^+ , which is demonstrated by UV/Vis and NMR spectra. Upon the addition of Ag^+ , the two signals of the imidazole hydrogens (N–H) became broadened and shifted from 12.85 to 13.05 ppm to the downfield

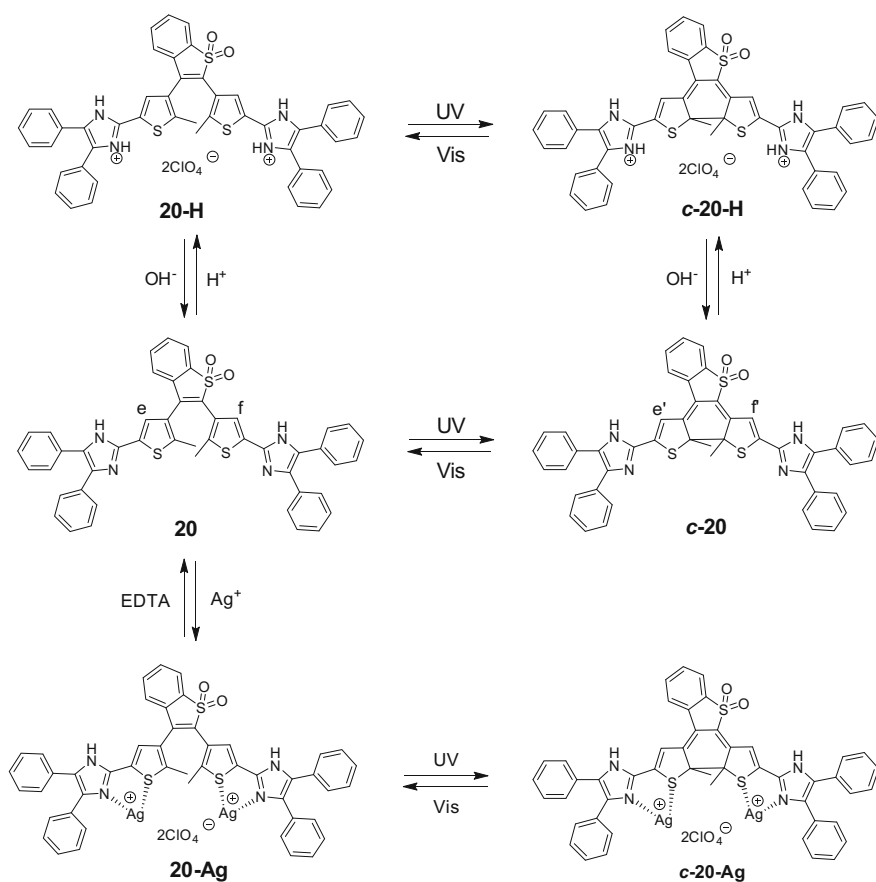


Chart 2.9 Photochromic responses of **20** to light, H^+ and Ag^+

around 13.45 and 13.67 ppm, respectively. The observed deshielding effect of the imidazole hydrogens confirmed the coordination of Ag^+ with the imidazole nitrogen. In this way, an INHIBIT logic gate was constructed by using the absorbance at 610 nm as output signals, and using UV irradiation (365 nm) and Ag^+ as inputs. When Ag^+ is present, the photocyclization of **20** was prohibited to some extent, and the absorbance at 610 nm was below the threshold (0.45), while only the single input of UV irradiation can induce the absorbance value of **20** at 610 nm higher than the defined threshold. Taken together, the absorbance behavior at 610 nm was coincided with the Boolean logic INHIBIT. Moreover, **20** exhibited an interesting sequence-dependent behavior upon the addition of combinational inputs of protons (P), Ag^+ (A), and UV irradiation (U). Interestingly, only the combination inputs AUP with exact input sequence of Ag^+ (first), UV irradiation (second), and protons (third) can suppress the photocyclization reaction of **20**, giving a low absorbance value at 610 nm among the six possible sequential input combinations (i.e., PAU, PUA, UPA, UAP, APU, and AUP). Consequently, a specific keypad lock with three inputs of protons (P), Ag^+ (A), and UV irradiation (U) can be developed.

DAEs with multi-addressable states are desirable to create complex circuits. Compound **21** can behave as a multi-addressable absorbance and fluorescence switch triggered by protons, chemical ions, and light (Fig. 2.4), in which the pyridine unit is utilized as an efficient ligand and a proton acceptor [50]. Addition of

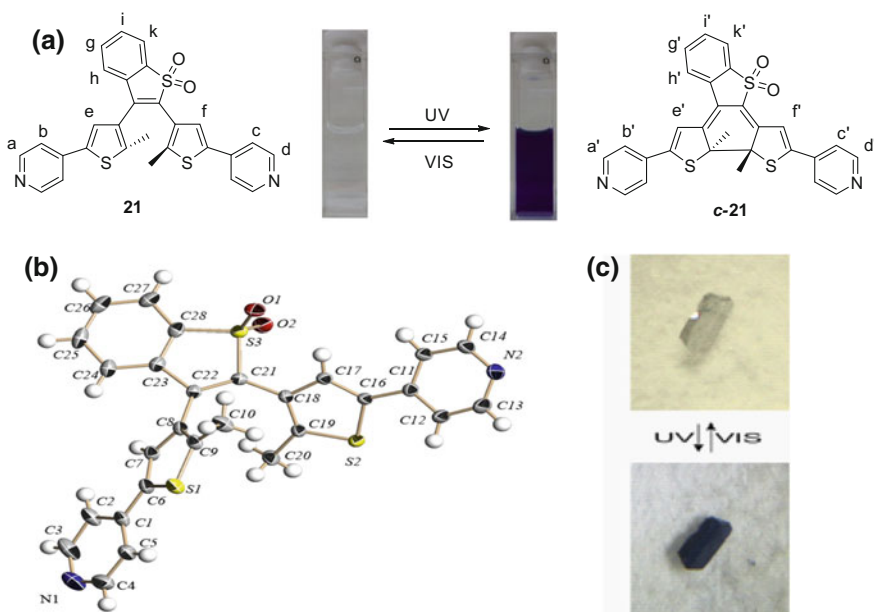


Fig. 2.4 a Photochromic reaction and photographic images of **21**, b ORTEP representation of the crystal structure of **21** with displacement ellipsoids shown at the 50% probability level, c color changes of **21** in the crystal state

2.0 equiv. HClO_4 protonated **21** into **21-H⁺** accompanied with a bathochromic shift by 40 nm in the absorption band originally at 345 nm, and an increase in fluorescence intensity at 467 nm upon excitation at the isosbestic point of 318 nm with respect to the initial **21**. Upon UV irradiation at 365 nm, two new absorption bands appeared at 431 and 638 nm due to the resulting closed form of **21-H⁺**, and the fluorescence was also quenched completely. When titrated with different metal ions such as Cd^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Zn^{2+} , and Ba^{2+} , there induced only Hg^{2+} and Cu^{2+} ions obvious changes in absorption and fluorescence of **21**. Compared with free PSS of **21**, Hg^{2+} and Cu^{2+} caused different bathochromic shift in the absorption (65 and 34 nm, respectively) accompanying with naked eye observable color changes. Moreover, the fluorescence of **21** was increased to twice of the initial upon adding 2.0 equiv. of Hg^{2+} , while it was almost completely quenched upon adding 1.0 equiv. of Cu^{2+} . Alternatively, the quenched fluorescence due to the addition of Cu^{2+} can be restored when further addition of Hg^{2+} . However, the fluorescence cannot be quenched by adding Cu^{2+} when Hg^{2+} was already present. The color and fluorescence changes are resulted from the difference in relative binding stoichiometry and association affinities. The titration of Job's plot indicates that **21** forms a 1:1 complex with Hg^{2+} while a 2:1 complex with Cu^{2+} . By fully taking advantage of multiple optical states with **21** induced by protons, ions, and light, a variety of molecular logic gates such as half adder, half subtractor, 4-to-2 encoder, 2-to-4 decoder, and 1:2 demultiplexer were constructed with the unimolecular platform by employing absorption and emission properties at different wavelengths as outputs with the appropriate combination of chemical and photonic stimuli.

The construction of artificial supramolecules capable of achieving a variety of biological functions through conformational changes triggered by external stimuli is of particular interest. Inspired by the successful examples of the nanoscale multi-functionalized supramolecular metallacycles, Zhu and Yang et al. [51] constructed a family of multi-diarylthene hexagons with precise control of the shape and size as well as the specific number of photochromic units via the coordination-driven self-assembly (Fig. 2.5). The photochromic dipyrindyl compound **21** discussed above was further employed as a 120° DAE-based donor. According to the “directional bonding” model and the “symmetry interaction” model, combination of **21** with 120° and 180° diplatinum(II) acceptors Pt-1 and Pt-2 in 1:1 molar ratios generated [3+3] hexagon **BPt-1** and [6+6] hexagon **BPt-2**, respectively (Fig. 2.5). Multi-nuclear NMR (^1H and ^{31}P) and electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) analysis clearly revealed the formation of multi-DAE hexagons. Moreover, the hexagons are highly sensitive and responsive to photostimuli due to the existence of photochromic unit **21**. The colorless solution of hexagon **BPt-1** changed into dark cyan upon UV irradiation at 365 nm. And two new absorption bands at ca. 420 and 622 nm were observed in the visible region. Those typical changes could be ascribed to the corresponding ring-closed state of **BPt-1** (*c*-**BPt**) via the typical photocyclization. More importantly, the hexagons can reversibly interconvert between the ring-open and ring-closed conformations via alternative irradiation with the UV (365 nm) and visible light (>510 nm), resulting in the unprecedented quantitative ring closure for all photochromic units in the hexagons.

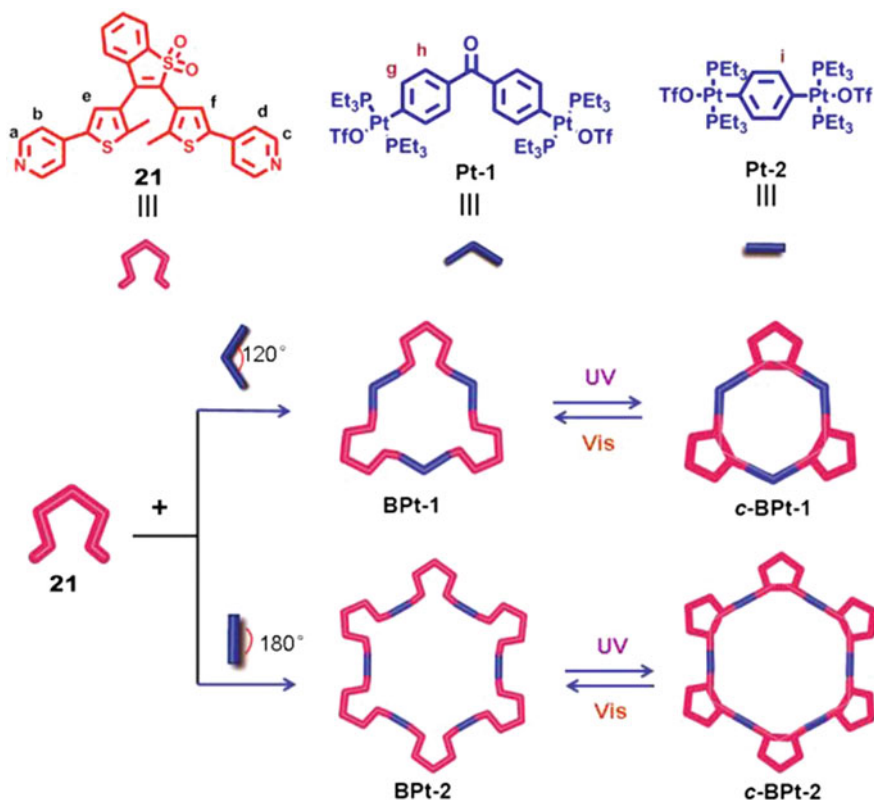


Fig. 2.5 Graphical representation of the self-assembly of the photochromic hexagons and their structural transformations

Theoretical calculations through PM6 semiempirical molecular orbital method revealed that hexagons **BPt-1** and **BPt-2** with antiparallel configurations are somewhat more stable than their analogues with parallel conformations (e.g., in the case of **BPt-1**, $E_{\text{parallel}} - E_{\text{antiparallel}} = 7.67 \text{ kcal mol}^{-1}$). Accordingly, **21** is more likely to have the antiparallel configuration rather than the parallel one because of the steric interactions during the self-assembly, leading to a high conversion yield from the ring-open form to the ring-closed form in the established multi-bisthiénylene hexagons. To the best of our knowledge, this is the first example of well-controlled reversible structural transformations in the discrete self-assembled metallacycles triggered by light irradiation, which may provide a novel approach to realization of the highly efficient supramolecule-to-supramolecule conversions.

Up to date, DAEs based on the thiazole unit as the ethene bridge have been intensively studied (Chart 2.10). Since the aromatic stabilization energy of thiazole is smaller than that of thiophene, here the low aromaticity of thiazole is expected to decrease the energy difference between the ring-open and ring-closed isomers of

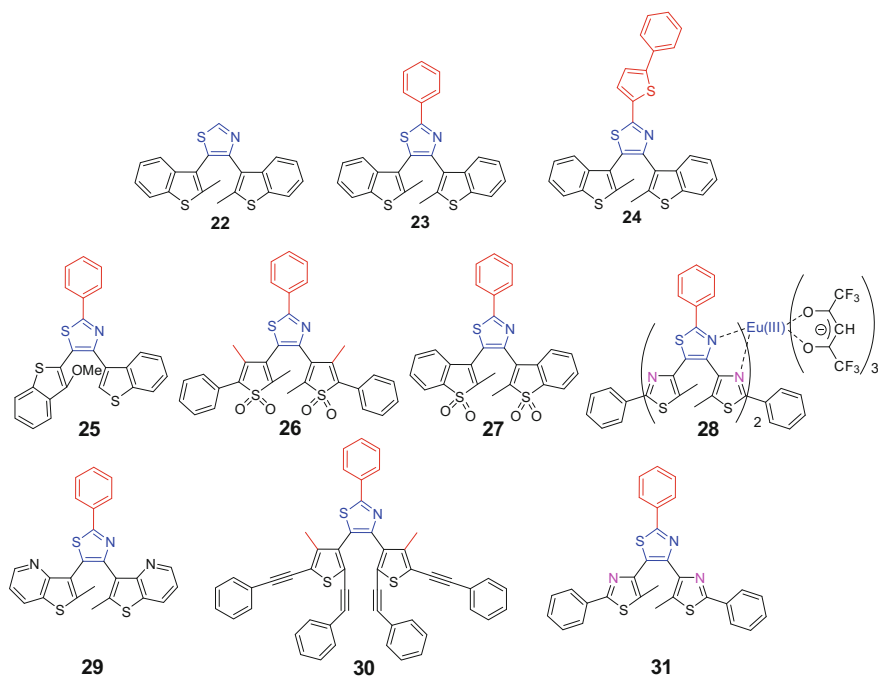


Chart 2.10 Chemical structures of thiazole based DAE compounds **22–31**

DAEs, highly preferable for constructing thermally bistable isomers. A series of 2-substituted-4,5-bisbenzothienylthiazoles (compounds **22–24**) were constructed for insight into the substituent effect at the central thiazole unit of DAEs on their absorption [52]. Their absorption bands in the ring-open and ring-closed isomers were 295, 534 nm (compound **22**), 329, 539 nm (compound **23**), and 370, 550 nm (compound **24**) in hexane, respectively. Obviously, their optical absorption bands become red-shifted when introducing the π -conjugation unit. This study provides a new way to expand π -electron systems for DAE systems.

Except this way, other strategies to modulate fluorescence were also achieved [53]. Photochromic DAE having a methoxy group and hydrogen as the leaving units at the photochemical reaction carbon atoms has been developed (**25**). Upon UV light irradiation at 365 nm, compound **25** was converted into its closed form, along with the elimination of CH_3OH , resulting in highly fluorescent condensed aromatic molecule with a characteristic emission peak at 420 nm. However, the closed form is photo-inactive. It did not return to the original **25** either by light irradiation or by heating. The turn-on fluorescence model DAE compounds in their closed form were also reported (**26** and **27**) [54, 55]. Oxidation of the thiophene unit by 3-chloroperbenzoic acid (*m*-CPBA) gave the *S,S*-dioxide derivatives, whose colored isomers exhibited green (577 nm) or orange (543 nm) fluorescence with relatively high fluorescence quantum yields of 0.35 and 0.37, respectively. Both

X-ray crystal structural analysis and DFT calculation for the closed form of **26** revealed that the weak CH/N, CH/S, and CH/OS hydrogen bonding interactions seem to make the molecule rather rigid, partly contributing to the improved emission nature of oxidized ring-closed forms. Moreover, the reversible luminescence modulation in photochromic Eu(III) complex was successfully demonstrated. Indeed, Eu(III) complex **28** (Chart 2.10) exhibited emission at 579, 592, and 614 nm under excitation at 465 nm, along with quantum yield and emission lifetime of 3.6% and 0.4 ms, respectively. These emissions are attributed to the f - f transitions of 5D_0 - 7F_0 , 5D_0 - 7F_1 , and 5D_0 - 7F_2 , respectively. The emission of the Eu(III) complex at the photo-stationary state (614 nm) was about 30% with respect to the original open isomer. In this regard, the reversible modulation of emission can be achieved upon alternative irradiation of UV (365 nm) and visible light ($\lambda > 440$ nm) [56].

A DAE derivative containing two thienopyridyl units bestowed solvent-dependent photochromic reactivity [57]. As a result of host-guest interaction, compound **29** showed the photocyclization quantum yield as high as 88% in methanol, whereas that value was only 24% in hexane. A temperature-dependent 1H NMR and X-ray crystallographic studies revealed that the intermolecular interaction with a methanol molecule together with the intramolecular interactions in solution and in crystals kept the molecular folding into the photo-reactive conformation. Compounds with fast thermal cycloreversion rate (**30**) or highly efficient oxidative cycloreversion reaction (**31**) were also reported [58, 59]. The first-order cycloreversion reaction rate constant k of **30** and the half lifetime of the closed form were evaluated to be 0.14 s^{-1} and 5.4 s at 293 K, respectively. The rapid thermal bleaching rate under dark condition might be resulted from the four rigid phenylethynyl groups. Compound **31** was found to show electrochemical oxidative ring cycloreversion with the net current efficiency as high as 90%. Interestingly, two radical cation intermediates were involved in the oxidative cycloreversion processes, and the highly stable radical cation of the ring-open and ring-closed isomers was considered to be responsible for such a high current efficiency.

Five-membered ring imidazole is an important class of aromatic heterocycles due to its attractive chemical properties. DAEs based on the imidazole ethene bridge could be conveniently synthesized [60, 61]. For instance, treatment of diketone with salicylaldehyde in the presence of NH_4Ac afforded the target compound **32** (Chart 2.11). Due to the specific coordination capability of imidazole unit, it can be even utilized as a wonderful sensor for the detection of Cu^{2+} by fluorescence mode or for the detection of Na^+ and K^+ by colorimetric mode. The spectral changes may be also induced by ligand-to-metal charge transfer (LMCT), in which the electronic charge is transferred from the ligand toward the coordinating metal. Yam et al. [62] reported a NIR photochromic rhenium (I) complexes (**33**) using a DAE unit as N,N -donor ligand (Chart 2.11). The pyridyl and imidazolyl rings in the free DAE ligand are not coplanar, and twisted around each other. However, upon coordination with Re(I), those two rings in complex **33** were fixed into a coplanar conformation. Upon photocyclization, the 2,2-linked pyridyl and imidazolyl rings became coplanar with two thiophene groups from their twisted

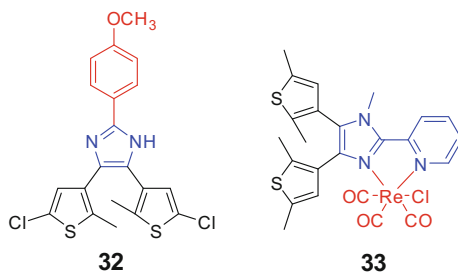


Chart 2.11 Chemical structures of imidazole based DAE compounds **32** and **33**

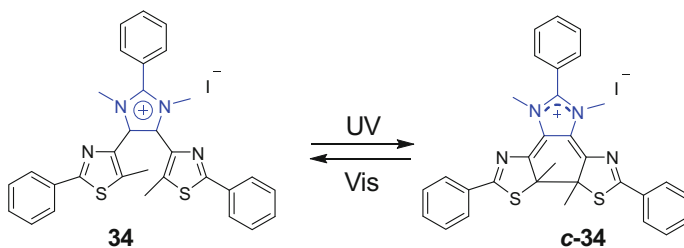


Chart 2.12 Photochromic reaction of imidazolium based DAE compound **34**

conformation before photocyclization, bringing forth a distinct increase in the π -conjugation extent, along with a large red shift in absorption to the NIR region. This conformational switching via metal coordination may open up a novel efficient strategy for constructing NIR photochromic materials.

A reversible photoconversion system between imidazolium and imidazolinium has been proposed by Kawai et al. [63] for the first time. The ring-open form **34** bestows a chemically stable imidazolium ring with the delocalized cationic charge, while ring-closed photoisomer **c-34** possesses the reactive nonaromatic imidazolinium unit (Chart 2.12). Owing to their great difference in the aromaticity and charge localization, **c-34** exhibited the characteristic solvato- and iono-chromisms, resulting in a large absorption shift by 80 nm with the different solvent polarity and counter anions.

Bielawski et al. [64] have firstly reported DAEs based on five-membered ring *N*-heterocyclic carbene (NHC) unit (**35**). They incorporated a photochromic DAE unit into the backbone of an NHC scaffold for photochemically controlling the electronic structure and donating properties (Chart 2.13). As found, the donation of electron density from nitrogen atoms to carbonyl moiety in NHC scaffold became decreased upon changing **35a** into its closed form. The Tolman electronic parameters (TEPs) revealed that the photocyclization of **35c** to its closed form significantly decreased the ability of NHC to donate electron density to the metal center. Based on the context, they made a light-activating photochromic NHC-based organocatalyst [65]. The amidation rate between ethyl acetate and 2-aminoethanol

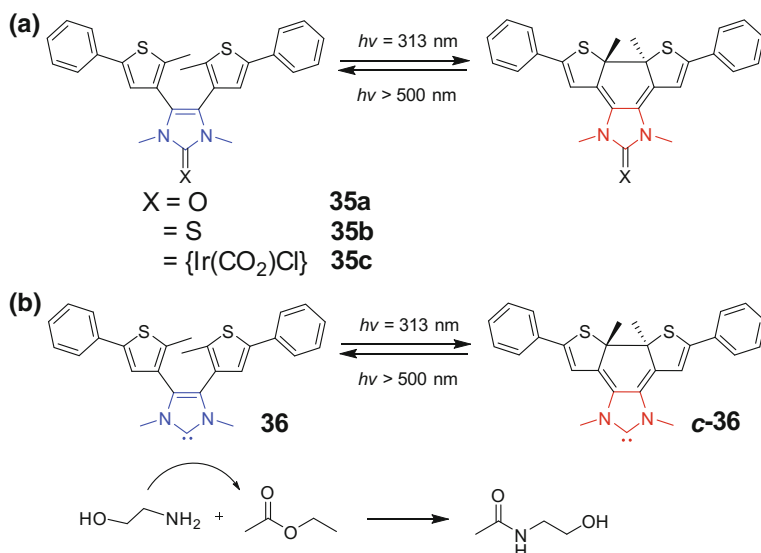


Chart 2.13 **a** Photochromism of NHC based DAE compound **35**, **b** Proposed mechanism of photoswitchable NHC **36** catalyzed condensation reaction

was found to be attenuated by two orders of magnitude in the presence of the closed form of **36** (**c-36**), while it was restored upon further visible light irradiation. ¹³C NMR analysis suggested that **c-36** was easily converted into an NHC-alcohol adduct. This imidazolium species effectively suspended the catalytic ability of the DAE organocatalysis. Moreover, its catalytic activity could be reversibly modulated by alternative UV and visible irradiation, although the photochromic NHCs undergo destruction after several cycles.

Yokoyama et al. [66] also exploited five-membered ring indenones and their acetal derivatives as ethene bridges. As a novel thermally irreversible photochromic system, bisarylindenone **37** showed photochromic back-and-forth reactions with two different visible lights (Chart 2.14). Moreover, the photocyclization quantum yield was increased to 0.81 in hexane when the central indenone unit was protected as its acetal derivative by acetalization of the carbonyl group. The increased quantum yield was possibly due to the two sets of intramolecular nitrogen–hydrogen interactions, thus constraining the conformation of **38** in favor of photocyclization. Besides the acetal derivative, bisthiazolyindenol **39** was also prepared by nucleophilic addition of the corresponding alkylolithium reagents to **37** [67]. More impressively, **39** shows both perfect diastereoselectivity (**c-39-1**) and an extremely high ring-closed quantum yield with a high conversion ratio to the closed form in hexane, which also benefits from the efficient collaborative interaction between two sets of intramolecular hydrogen bonds and the steric restriction of a *tert*-butyl group.

Shirinian et al. [68] have also developed new family of DAEs based on five-membered ring cyclopent-2-en-1-one. The typical representative **40** was prepared by several steps of acylation, alcoholysis, alkylation, and cyclization from

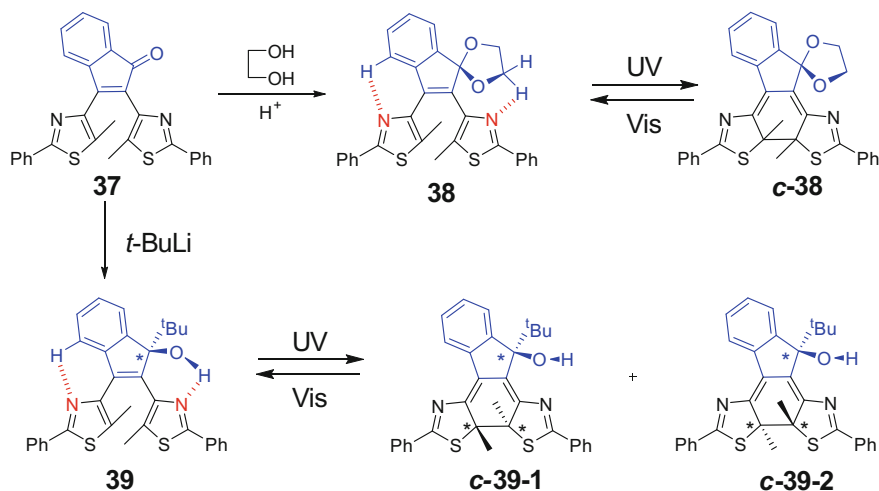


Chart 2.14 Photochromism of indenone based DAE compound **37** and indenol based DAE compound **39**

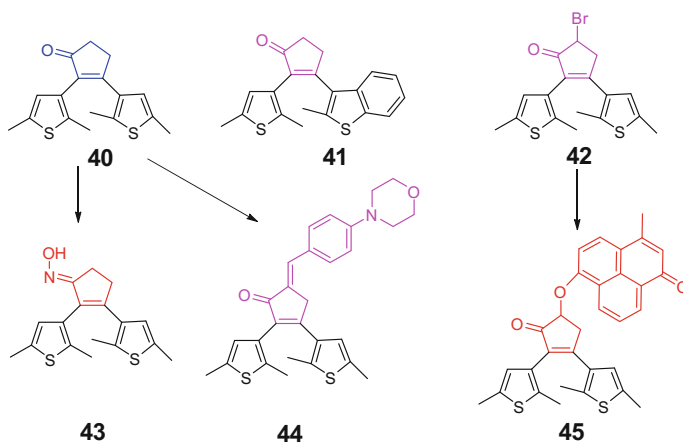


Chart 2.15 Chemical structures of photochromic DAE compounds **40–45** based on cyclopent-2-en-1-one

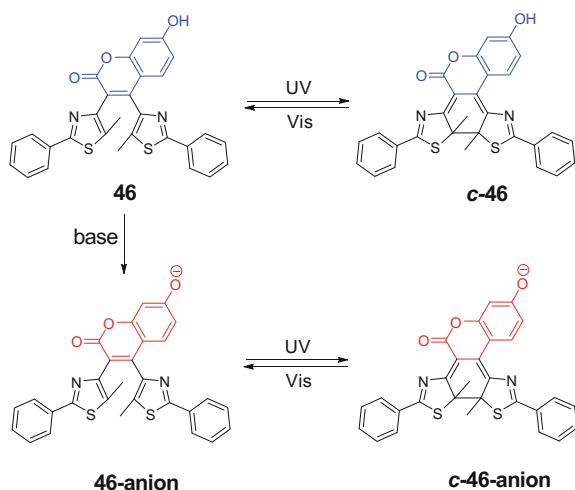
commercially available and inexpensive acetophenones (Chart 2.15). In this way, a large series of diarylcyclopentenones bearing different aryl substituents (**41–45**) can be conveniently synthesized with moderate yields. The main advantage of this class of photochromic DAEs is to lead to simple and various ethene “bridge” transformations (for instance, **42** and **43**). As a result, DAEs with different functional groups can be easily constructed for various applications such as tunable π -conjugation (**44**) and fluorescence modulation (**45**) [69].

2.4 Six-Membered Ring-Based Ethene Bridges

Six-membered aromatic groups are not commonly chosen for the ethene bridges in DAEs owing to their high stabilization energies, which significantly decrease the thermal stability of ring-closed isomers. However, the six-membered ring ethene bridge has its own advantages in closed isomers with higher ring-opening quantum yield. Besides, the aromaticity of six-membered ring can be precisely controlled by tailoring their chemical structures, allowing to widely extend the diversity in the thermally irreversible photochromic systems [70]. For instance, six-membered ring chromophores with remarkable electron-withdrawing properties and excellent fluorescence quantum yields, such as *naphthalimide*, *benzothiadiazole*, *benzo-bisthiadiazole*, and *coumarin*, are considered as favorable building blocks for ethene bridges. Indeed, such strong electron-withdrawing chromophore-based aryl bridge can not only be expected to assure considerable bistability and good fatigue resistance of DAEs, but also can bring forth interesting fluorescent on–off switcher. Exactly, the specific chromophore as an ethene bridge offers the fluorescence as one of the most attractive output modes with its easiness in detection and high signal/noise ratio, which might be reversibly modulated by typical photoisomerization. In combination of chemical processes such as intramolecular charge transfer (ICT), photo-induced electron transfer (PET), and pH, multi-addressable fluorescent photochromic systems can be established, especially for practical applications in the data storage, molecular switch, and biological images.

Yokoyama et al. [71] have recently presented a DAE derivative **46** (Chart 2.16) containing a coumarin chromophore as the central ethene bridge, resulting in an amazing dual mode for fluorescence photoswitching. DAE **46** provided high fluorescence quantum yields arising from the coumarin chromophore, which can be well modulated by the photochromic reaction as well as pH.

Chart 2.16 Photochromism of coumarin-based DAE compound **46** with a dual mode of fluorescence photoswitching



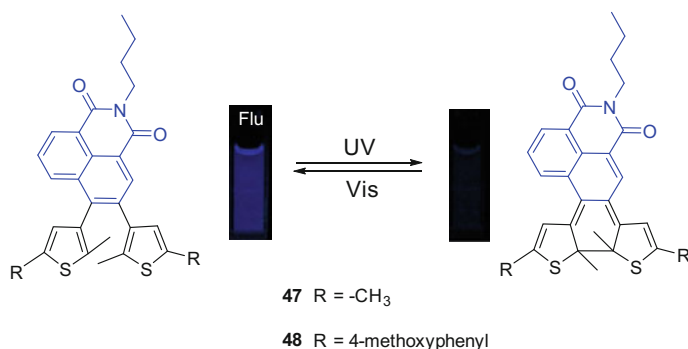


Fig. 2.6 Photochromism of naphthalimide-based DAE compounds **47** and **48**

As a typical fluorescent moiety, naphthalimide is widely used in molecular fluorescent sensors [72]. Since the remarkably electron-withdrawing imide group of naphthalimide unit when incorporated in a six-membered aryl bridge, naphthalimide might be expected to assure considerable bistability and good fatigue resistance. Zhu et al. [73] have developed two novel photochromic DAE derivatives **47** and **48** with such fluorescent moiety as the central ethene bridging unit (Fig. 2.6). Interestingly, they exhibited moderate thermal stability and good fatigue resistance. The first-order cycloreversion rate constant (k_T) for **c-48** was evaluated to be $7.4 \times 10^{-4} \text{ s}^{-1}$ in cyclohexane at 293 K. In contrast, **c-47** exhibited significantly long lifetime ($k_T 7.9 \times 10^{-6} \text{ s}^{-1}$), two order of magnitude longer than that of **c-48** under the dark thermal relaxation. Both **47** and **48** could reversibly perform the photochromism with the thermal back reaction in the dark without any obvious degradation over 5 cycles. More interestingly, the fluorescence of **47** arising from the ethene bridging naphthalimide unit was well modulated by both photochromism and solvatochromism. Upon irradiation at 365 nm, the fluorescence of **47** was distinctly quenched by 80% when reaching the photostationary state. On the other hand, solvent polarity also plays a significant role in the luminescent wavelength of **47**, red-shifted by 130 nm from about 420 nm in nonpolar cyclohexane to around 550 nm in polar acetonitrile. Here, the distinct solvent effects upon fluorescence wavelength can be attributed to the ICT effect and solvent relaxation of the incorporated naphthalimide unit. This was also further supported by a Lippert–Mataga plot, essentially a linear response of fluorescent Stokes shift vs. solvent polarity. Since the fluorescence wavelength and intensity were well tuned with the light irradiation and solvents to such a great extent, two logic gates, NOR and INHIBIT, were further constructed with **47**, utilizing light irradiation and polar solvent as input signals, and fluorescence as output.

In order to further modulate the fluorescence of DAEs, the excellent reversible redox unit of ferrocene (**Fc**) was further incorporated into naphthalimide chromophore for developing DAE **49** (Fig. 2.7) [74]. As demonstrated, the incorporated **Fc** unit in the system of **49** plays a great role in the fluorescence quenching,

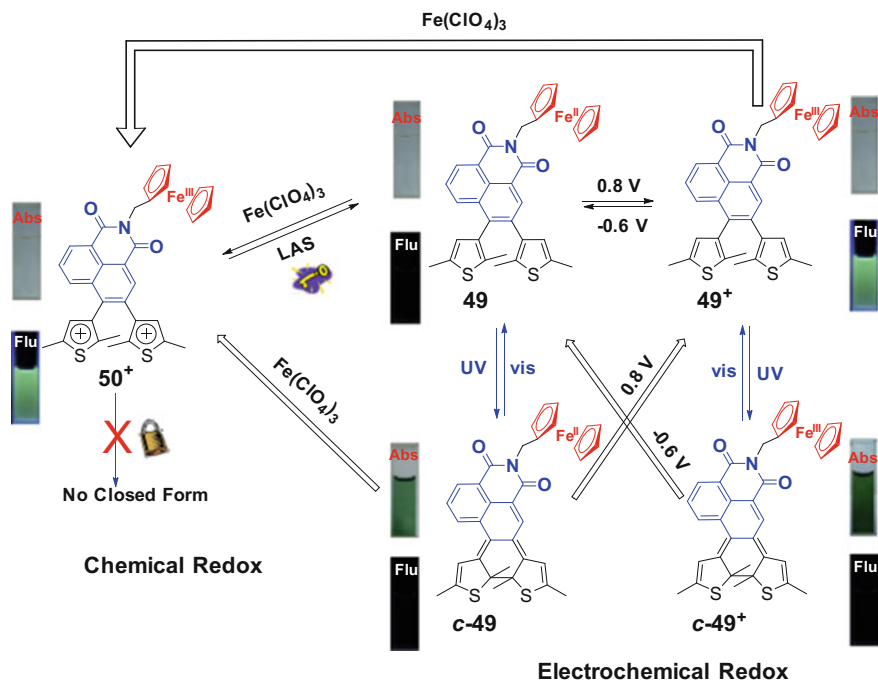


Fig. 2.7 Photochromism of ferrocene (Fc) incorporated naphthalimide-based DAE compound **49**: gated photochromism and multi-addressable states

possibly due to the specific PET process from the imide **Fc** unit to naphthalimide moiety. Indeed, the fluorescence of **49** can be easily tuned with chemical and/or electrochemical redox processes via blocking or recovering the PET effect. Consequently, a photo- and redox multi-addressable molecular fluorescent switch was achieved.

2,1,3-Benzothiadiazoles are well-known fluorescent building blocks with strong electron-withdrawing ability in the design of functional materials, such as organic light-emitting diodes (OLEDs), nonlinear optical (NLO) materials, and solar cells. Zhu et al. [75] incorporated this six-membered ring chromophore as the central ethene bridging unit to develop the photochromic DAE derivative **51** (Fig. 2.8), possessing good photochromic performance with moderate thermal stability and fatigue resistance in solution. Compound **51** still keeps considerable bistability when replacing the five-membered cyclopentene ring with a six-membered fluorescent moiety of benzothiadiazole unit as the central ethene bridge. The fatigue-resistant characteristics of **51** in solution indicated that about 35% of performance were lost after 10 repeated cycles. Similar to **49**, the fluorescence of **51** can also be well modulated by solvatochromism and photochromism. Upon excitation at the isosbestic point of 340 nm, compound **51** exhibits intense luminescence at 470 nm with an efficiency of 7.7% in cyclohexane. When irradiated at

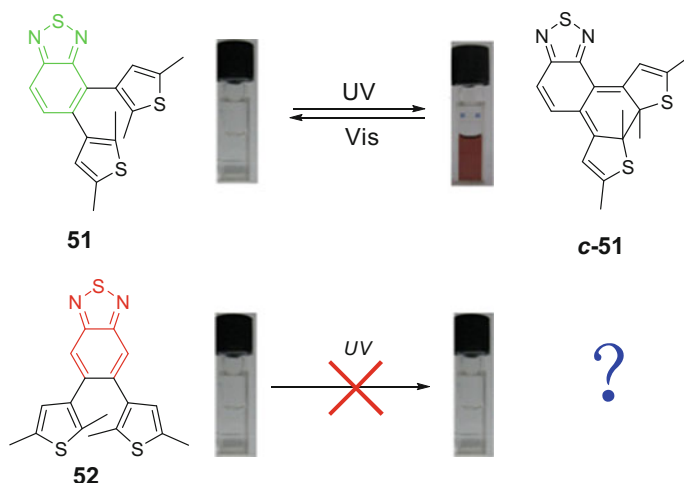


Fig. 2.8 Photochromism of 2,1,3-benzothiadiazole-based DAE compounds **51** and **52**. Insert: the corresponding photographic changes under UV irradiation at 310 nm in cyclohexane

310 nm, **51** underwent photocyclization with a distinct fluorescence quenching by 70% when reaching the photo-stationary state. For the solvatochromism, a shift by 65 nm was observed from 470 nm containing two components of 2.1 ns (52%) and 7.0 ns (48%) with $\chi^2 = 1.3$ in cyclohexane to 535 nm containing those of 5.3 ns (87%) and 5.8 ns (13%) with $\chi^2 = 1.2$ in acetonitrile for **51**, which is attributed to the ICT effect similar to **47** and **48** due to the large difference in dipole moments between the excited and ground states.

More interestingly, the photochromic nature of these compounds is found to be critically dependent upon the substitution position of 2,1,3-benzothiadiazole. In unexpected contrast with the good photochromic performance of **51** in solution, there is no obvious color change for **52** upon UV light irradiation (Fig. 2.8), in which the two dimethylthiophene groups are located on 5,6-position of benzothiadiazole. The great difference between the photochromic performances of **51** and **52** can be well explained by Woodward–Hoffmann rules [75]. As calculated, **51** and **52** have the same number of π -electrons, and the π -electrons on the benzothiadiazole unit delocalize in the plane of hexatriene framework. However, the LUMO symmetries of the simplified hexatriene framework in **51** is C_2 symmetry, while the mirror symmetry was found in **52**. Accordingly, photocyclization of **52** could only follow the disrotatory cyclization in accordance with the orbital symmetry conservation theory. The resulting closed form in such way is certainly unstable due to the large steric hindrance, which is consistent with the ground-state potential-energy surfaces (PESs). There are two minima on the PES of **51** corresponding to the ring-open and ring-closed isomers, in which the high energy barrier of about 52 kcal mol⁻¹ allows the reaction only to proceed by photoexcitation. However, on the PES of **52**, no stable isomer is located when the reaction coordinate goes from

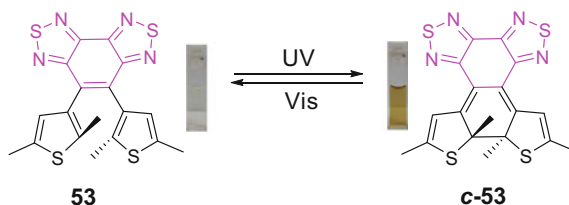


Fig. 2.9 Photochromism of benzobisthiadiazole-based DAE compound **53**. Insert: the corresponding photographic changes upon alternating illumination between UV (310 nm) and visible (575 nm) light

3.47 to 1.4 Å. As a matter of fact, from the single crystal data, **52** is not really a typical 1,3,5-hexatriene unit since the bond length connecting two thiophene units is 1.451(2) Å, a typical single bond rather than a double bond.

As demonstrated above, DAEs containing highly polar and electron-withdrawing chromophores (2,1,3-benzothiadiazole and naphthalimide units) exhibit good photochromic performance with moderate fatigue resistance. However, those building blocks bear aromaticity to great extent, which facilitates the undesirable thermal back reaction due to the large loss of aromatic stabilization energy upon photocyclization from the ring-open to the ring-closed form. A less aromatic ethene moiety is expected to give higher thermal stability to the closed form of the DAEs. With this in mind, Zhu et al. developed a highly bistable DAE (**53**, Fig. 2.9) by introducing benzo[1,2-*c*:3,4-*c'*]bis [1,2,5] thiadiazole (abbreviated as benzobisthiadiazole) with low aromaticity as a new six-membered ring central ethene bridge [70]. As demonstrated, the thermal stability of the closed isomer is comparable to the widely known five-membered hexafluorocyclopentene-based counterpart.

Generally in DAE derivatives, the six-membered ring ethene bridge with large aromaticity always brings forth the undesirable thermal back reaction even at room temperature due to the large loss of aromatic stabilization energy upon photocyclization. However, **53** preserves very amazing thermal stability with almost flat decays in various solvents such as cyclohexane, THF, and even ethanol in the dark at room temperature. As found with very nice fatigue resistance, it is capable of keeping intact without any obvious degradation upon alternating UV (365 nm) and visible light (575 nm) irradiation in degassed THF when repeatedly toggled between the open form and closed form. Moreover, even at high temperature (80 °C) in toluene, **53** shows only 5.4% decrease in its absorbance at 457 nm after 800 min. In addition, according to the DFT simulation, the ring-open isomer is more stable only by $-4.607 \text{ kcal mol}^{-1}$ with respect to the ring-closed isomer in THF. As a result, the destabilization energy of **53** caused by the loss of aromaticity is very small during the course of photocyclization.

In order to get a better understanding of the relationship between the aromaticity of six-membered ring ethene bridges and thermal stability, three similar photochromic compounds **54**, **55**, and **56** (Fig. 2.10) containing *naphthalimide*,

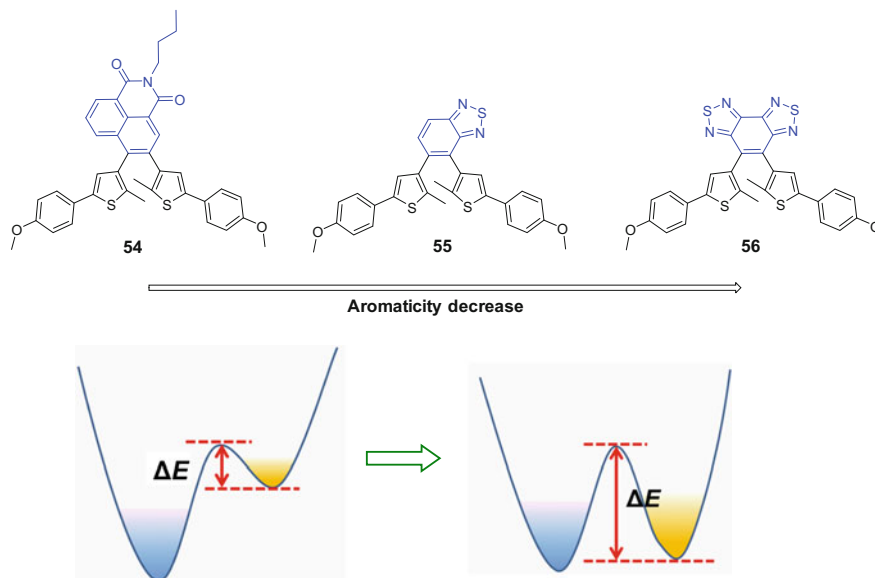


Fig. 2.10 Chemical structures of DAEs containing *naphthalimide*, *benzothiadiazole*, and *benzobisthiadiazole* as different six-membered ring ethene bridges for taking insight into the relationship between the aromaticity of six-membered ring ethene bridges and thermal stability

benzothiadiazole, and *benzobisthiadiazole* were systematically compared [76]. X-ray single crystal analyses revealed that in all these open-ring form crystals, only the parallel conformation was observed, indicating that all these three systems cannot undergo photocyclization in the single crystalline state. Furthermore, the length of the double bonds for central ethene bridges within *naphthalimide*, *benzothiadiazole*, and *benzobisthiadiazole* is 1.398(2), 1.383(4), and 1.371(5) Å, respectively, which is well consistent with the aromaticity tendency: *benzobisthiadiazole* < *benzothiadiazole* < *naphthalimide*. Exactly, among three compounds, the relatively short bond length in **56** (1.37 Å) is the nearest to typical double bond (1.33 Å).

The three ethene bridges with different degree in aromaticity gave a systematic comparison in the thermal stability evolution for their corresponding closed forms (**c-54**, **c-55** and **c-56**). As expected, **c-54** is the most unstable even at 293 K due to the large difference in ground-state energy before and after irradiation. The thermal back reaction rates for **c-54** are 1.01×10^{-3} , 1.27×10^{-3} , 3.10×10^{-3} , and $3.71 \times 10^{-3} \text{ s}^{-1}$ in cyclohexane, toluene, THF, and acetonitrile, respectively. More impressively, the decay becomes much faster in chloroform ($1.80 \times 10^{-1} \text{ s}^{-1}$). Due to the decrease of aromaticity, **c-55** shows no obvious thermal back reaction in nonpolar solvents like toluene even at 328 K. However, **c-55** is not stable in polar solvents such as chloroform, which was found to follow the similar first-order decay with a constant of $1.52 \times 10^{-5} \text{ s}^{-1}$, four magnitudes slower than that of **54** ($1.80 \times 10^{-1} \text{ s}^{-1}$). In distinct contrast, no obvious thermal back reaction could be

observed for **56** in the dark at 273 K for a prolonged time. As a matter of fact, **56** preserves very unprecedented thermal stability with almost flat decays and does not show any thermal back reaction in various solvents such as cyclohexane, toluene, chloroform, and even in acetonitrile in the dark at 293 K. Even more, when the pure closed form of **56**, successfully separated on aluminum oxide eluted with CCl_4 and dichloromethane, was placed at the elevated temperature (328 K) in toluene, it did not show any obvious decrease in its absorbance at 655 nm after 800 min. Generally, in DAE derivatives, the destabilization from the destruction of the aromatic thiophene rings and central ethene bridges during the course of photocyclization can increase the ground-state energy of the closed-ring isomer, and the cycloreversion reaction in the ground states has to overcome the energy barriers correlating with the ground-state energy differences. When the ground-state energy difference is large, the energy barrier becomes small and the cycloreversion reaction readily takes place. Here, the calculated values of ground-state energy difference between the open and closed isomers for **54**, **55**, and **56** are -4.93 , -10.16 , and $-20.44 \text{ kcal mol}^{-1}$ in vacuum, respectively. Accordingly, the thermal cycloreversion reaction could not occur easily in the case of *c*-**56** with respect to *c*-**54** and *c*-**55**, resulting in the excellent thermal stability of *c*-**56** in a variety of solvents.

Based on the above benzobisthiadiazole ethene bridge, DAEs with extremely high photocyclization quantum yield were realized by introducing a large bulky terminal benzothiophene unit into the side chains [77]. Amazingly, the rotation of benzothiophene unit was completely suppressed due to the large steric strain between benzobisthiadiazole and benzothiophene (Fig. 2.11). Consequently, the interconversion between the parallel conformation (**57p**) and antiparallel conformation (**57a**) was blocked (Fig. 2.11B). Actually, as two stable isomers **57p** and **57a** can be easily separated by a common silica gel chromatography, both of them exhibit excellent thermal stability even at 343 K. The isolated pure antiparallel conformer **57a** shows photocyclization quantum yield as high as 72.9% in THF, which is twice as large as that of **53** and **BTF6**. However, due to the ICT deleterious to the photocyclization, the photocyclization quantum yield can be further improved with grafting the strong electron-withdrawing units such as acetyl or nitro groups onto benzothiophene. Indeed, the fluorescence quantum yield of **60a** was very low (0.01%), meaning that the ICT channel was efficiently blocked. As a whole, the photocyclization quantum yield of **60a** was increased to 90.6% with two strategies including separating the pure antiparallel conformer and suppressing the unfavorable ICT.

2.5 Metal Coordination Ligand-Based Ethene Bridges

The development of photochromic ligands for coordination to different metal complex systems has received increasing attention, opening up new avenues and dimensions in research of photochromism. The rational design of photochromic ligands and judicious choice of the transition-metal complex systems allow to tailor

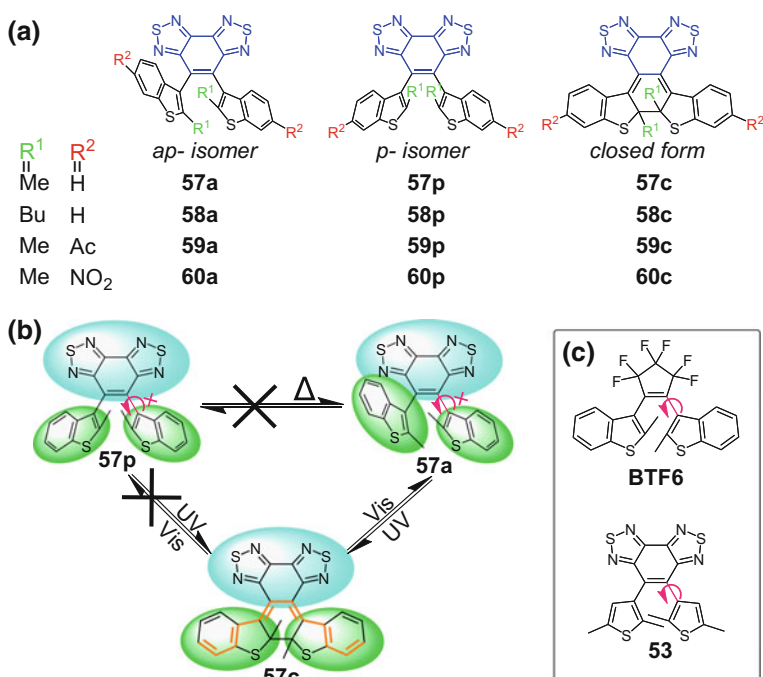


Fig. 2.11 **a** Chemical structures of benzobisthiadiazole-based DAE compounds **57–60** with complete separation of parallel conformation, and antiparallel conformation and the closed isomers, **b** conversion relationship of parallel conformation, antiparallel conformation and closed isomer for **57**, **c** reference compounds **BTF6** and **53**

the photo-switching capability of metal complex functionality and the perturbation to photochromic moiety. Without the necessity to vary the organic framework by tedious synthetic approaches, the convenient coordination of DAE ligands to metal ions could give rise to interesting photo-switching properties, such as fluorescence modulation, electron transfer, and nondestructive data processing.

In order to construct fluorescence nondestructive readout systems, Tian et al. [78, 79] made full use of NIR fluorescent chromophores such as *phthalocyanine* and *tetraazaporphyrin* as ethene bridges for DAEs (**61** and **62**, Chart 2.17). Interestingly, the corresponding metal (Mg^{2+} , Zn^{2+} , Pd^{2+} , and Pt^{2+}) phthalocyanine and tetraazaporphyrin complexes undergo typical photochromic reactions with nice fatigue resistance both in solution and in solid film. The essential NIR fluorescence from the chromophore is far away from the sensitive region of photocyclization and cycloreversion, thus guaranteeing their potential applications in nondestructive readout system.

Zhang et al. [80] reported similar DAE-phthalocyanine hybrid (**63**, Chart 2.17) with photo-controllable *J*-aggregation. As found, *J*-aggregation became even stronger when the hybrid was transferred into its closed form possibly due to better molecular planarity. In return, the *J*-aggregation state could improve the thermal

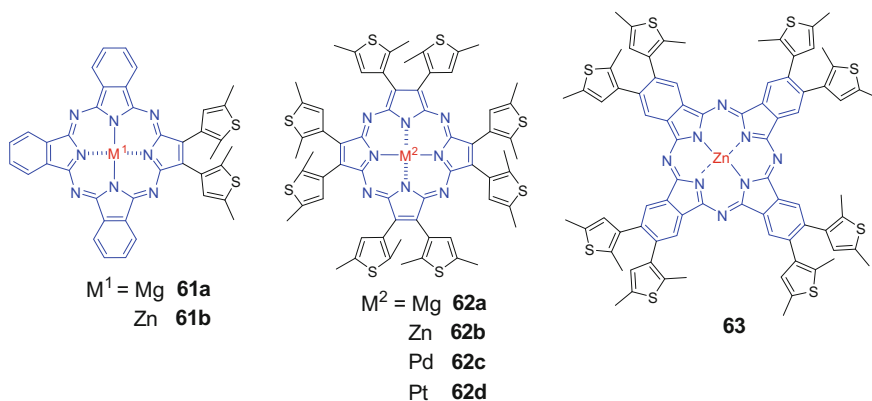


Chart 2.17 Chemical structures of photochromic metal DAE complexes (61–63) containing phthalocyanine and tetraazaporphyrin

stability of ring-closed form, which was converted to the open form instantly when the aggregation was broken. This phenomenon may explain why the photochromic reaction of similar derivatives was not observable in some solvents.

Yam et al. [81–83] have developed photochromic DAE ligands using 1,10-phenanthroline as the ethene bridge (64 and 65, Chart 2.18). Photochromic ligand, 5,6-dithienyl-1,10-phenanthroline, and related transition-metal complexes with Re(I) and Zn(II) were conveniently prepared. The interesting MLCT (metal-to-ligand charge transfer) sensitized photochromism as well as intramolecular energy-transfer process from the $^3\text{MLCT}$ to the ^3IL (intraligand) state were both investigated in details by ultrafast transient absorption and time-resolved emission spectra. On coordination to Re(I) tricarbonyl system (64), the photocyclization could be induced by extending the excitation wavelength from UV region at 340 nm in the free ligand to the MLCT excitation at 480 nm in the complex. All complexes exhibit strong $^3\text{MLCT}$ phosphorescence. The benzene solution of Re complex produced luminescence at 595 nm upon excitation onto the MLCT

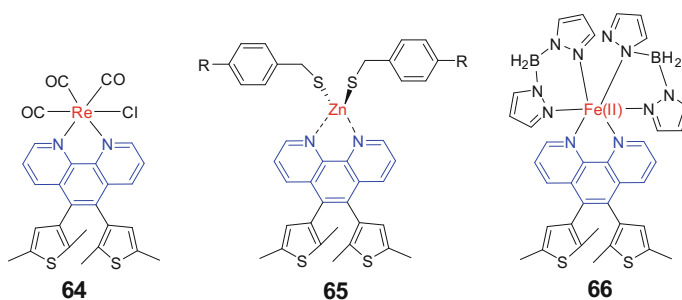


Chart 2.18 Chemical structures of photochromic metal DAE complexes 64–66 containing 1,10-phenanthroline

absorption band at >400 nm, while this value red-shifted to 644 nm in the closed form due to the increase in the extended π -conjugation upon photo-induced ring-closing reaction. Also, **65** showed photoluminescence, which was critically sensitive to the nature of thiolate ligand, ranging from 510 to 620 nm in the solid state at 77 and 298 K.

More recently, this photochromic DAE ligand was also utilized by Oshio et al. [84] to prepare Fe(II) spin-crossover (SCO) complex for the purpose of magnetic switching (**66**, Chart 2.18), which could be reversibly transferred between the diamagnetic low-spin (LS) state and the paramagnetic metastable high-spin (HS) state through a typical light-induced excited spin-state trapping (LIESST) effect by changing temperature and light irradiation.

2.6 Conclusion

The unique modification on the ethene bridge can effectively expand the versatility of DAEs, and brings forth rich properties to the photochromic switching molecules. Structurally, these specific DAEs can shorten synthetic routes with commercially available starting materials, which would finally benefit the industrial process and scaling-up. Meanwhile, five-/six-membered ring-based DAEs with the most excellent photochromic performances have the most appropriate backbones for the structural innovations to achieve various applications in self-assembly, photo-switcher, and molecular logic gate. However, for the real practical applications, it is still a tough task to gain the extra properties without sacrificing the original performances of DAEs, especially the thermal stability and fatigue resistance. Therefore, there still remains plenty of room to further develop novel ethene bridge-based DAEs, which is much likely to be the most promising candidates for the next generation of photochromic systems.

References

1. Hirshberg Y (1956) Reversible formation and eradication of colors by irradiation at low temperatures. A photochemical memory model. *J Am Chem Soc* 78:2304–2312
2. Bouas-Laurent H, Dürr H (2001) Organic photochromism (IUPAC Technical Report). *Pure Appl Chem* 73:639–665
3. Browne WR, Feringa BL (2009) Light switching of molecules on surfaces. *Annu Rev Phys Chem* 60:407–428
4. Zhang JJ, Zou Q, Tian H (2013) Photochromic materials: more than meets the eye. *Adv Mater* 25:378–399
5. Ratmo MF, Massimiliano T (2005) Electron and energy transfer modulation with photochromic switches. *Chem Soc Rev* 34:327–336
6. Yagai S, Kitamura A (2008) Recent advances in photoresponsive supramolecular self-assemblies. *Chem Soc Rev* 37:1520–1529

7. Yildiz I, Deniz E, Raymo FM (2009) Fluorescence modulation with photochromic switches in nanostructured constructs. *Chem Soc Rev* 38:1859–1867
8. Tsujioka T, Irie M (2010) Electrical functions of photochromic molecules. *J Photochem Photobiol, C Photochem Rev* 11:1–14
9. Rafal K, Fraser JS, Grzybowski BA (2010) Nanoparticles functionalised with reversible molecular and supramolecular switches. *Chem Soc Rev* 39:2203–2237
10. Dong H, Zhu H, Meng Q, Gong X, Hu W (2012) Organic photoresponse materials and devices. *Chem Soc Rev* 41:1754–1808
11. Fihey A, Perrier A, Browne WR, Jacquemin D (2015) Multiphotochromic molecular systems. *Chem Soc Rev* 44:3719–3759
12. Andreasson J, Pischel U (2015) Molecules with a sense of logic: a progress report. *Chem Soc Rev* 44:1053–1069
13. Qu D-H, Wang Q-C, Zhang Q-W, Ma X, Tian H (2015) Photoresponsive host-guest functional systems. *Chem Rev* 115:7543–7588
14. Irie M, Fukaminato T, Matsuda K, Kobatake S (2014) Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem Rev* 114:12174–12277
15. Muxin H, Reent M, Bice H, Yu-Sheng C, Dietmar S, Michael J, Clever HG (2013) Light-triggered guest uptake and release by a photochromic coordination cage. *Angew Chem Int Ed* 52:1319–1323
16. Berberich M, Würthner F (2012) Terrylene bisimide-diarylethene photochromic switch. *Chem Sci* 3:2771–2777
17. John-Christopher B, Carl-Johan C, Gates BD, Branda NR (2010) Two-way photoswitching using one type of near-infrared light, upconverting nanoparticles, and changing only the light intensity. *J Am Chem Soc* 132:15766–15772
18. Yan W, Quan L (2012) Light-driven chiral molecular switches or motors in liquid crystals. *Adv Mater* 24:1926–1945
19. Mallick A, Garai B, Addicoat MA, Petkov PS, Heine T, Banerjee R (2015) Solid state organic amine detection in a photochromic porous metal organic framework. *Chem Sci* 6:1420–1425
20. Lasorne B, Fihey A, Mendive-Tapia D, Jacquemin D (2015) A curve-crossing model to rationalize and optimize diarylethene dyads. *Chem Sci* 6:5695–5702
21. Herder M, Schmidt BM, Grubert L, Pätzelt M, Schwarz J, Hecht S (2015) Improving the fatigue resistance of diarylethene switches. *J Am Chem Soc* 137:2738–2747
22. Fukaminato T, Hirose T, Doi T, Hazama M, Matsuda K, Irie M (2014) Molecular design strategy toward diarylethenes that photoswitch with visible light. *J Am Chem Soc* 136:17145–17154
23. Cui X, Zhao J, Zhou Y, Ma J, Zhao Y (2014) Reversible photoswitching of triplet-triplet annihilation upconversion using dithienylethene photochromic switches. *J Am Chem Soc* 136:9256–9259
24. Robert GS, Stefan H (2014) Controlling covalent connection and disconnection with light. *Angew Chem Int Ed* 53:8784–8787
25. van der Molen SJ, Liao J, Kudernac T, Agustsson JS, Bernard L, Calame M, van Wees BJ, Feringa BL, Schönenberger C (2009) Light-controlled conductance switching of ordered metal–molecule–metal devices. *Nano Lett* 9:76–80
26. Hohlneicher G, Mueller M, Demmer M, Lex J, Penn JH, Gan LX, Loesel PD (1988) 1,2-Diphenylcycloalkenes: electronic and geometric structures in the gas phase, solution, and solid state. *J Am Chem Soc* 110:4483–4494
27. Amir Mahmoud A, Stéphanie B, Zach E, Branda NR (2014) Controlling a polymer adhesive using light and a molecular switch. *J Am Chem Soc* 136:3024–3027
28. Torben S, Alejra E, Heck J, uuml, rgen, Carmen H (2015) Photoswitching behavior of a cyclohexene-bridged versus a cyclopentene-bridged dithienylethene system. *Chem Phys Chem* 16:1491–1501
29. Yuan K, Boixel J, Chantzis A, Jacquemin D, Guerchais V, Doucet H (2014) Benzothiophene or benzofuran bridges in diaryl ethenes: two-step access by Pd-catalyzed C–H activation and theoretical/experimental studies on their photoreactivity. *Chem Eur J* 20:10073–10083

30. Chan JC-H, Lam WH, Yam VW-W (2014) A highly efficient silole-containing dithienylethene with excellent thermal stability and fatigue resistance: a promising candidate for optical memory storage materials. *J Am Chem Soc* 136:16994–16997
31. Krayushkin MM, Shirinian VZ, Belen'kii LI, Shadronov AY, Martynkin AY, Uzhinov BM (2002) Synthesis of photochromic derivatives of cyclobutene-1,2-dione. *Mendeleev Commun* 12:141–143
32. Kühni J, Belser P (2007) Gated photochromism of 1,2-diarylethenes. *Org Lett* 9:1915–1918
33. Irie M (2000) Diarylethenes for memories and switches. *Chem Rev* 100:1685–1716
34. Kawai T, Iseda T, Irie M (2004) Photochromism of triangle terthiophene derivatives as molecular re-router. *Chem Commun*: 72–73
35. Poon CT, Lam WH, Wong HL, Yam WW (2010) A versatile photochromic dithienylethene-containing beta-diketonate ligand: near-infrared photochromic behavior and photoswitchable luminescence properties upon incorporation of a boron(III) center. *J Am Chem Soc* 132:13992–13993
36. Poon CT, Lam WH, Yam VW (2011) Gated photochromism in triarylborane-containing dithienylethenes: a new approach to a “lock-unlock” system. *J Am Chem Soc* 133:19622–19625
37. Chan JC-H, Lam WH, Wong H-L, Zhu N, Wong W-T, Yam VW-W (2011) Diarylethene-containing cyclometalated platinum(ii) complexes: tunable photochromism via metal coordination and rational ligand design. *J Am Chem Soc* 133:12690–12705
38. Wong H-L, Wong W-T, Yam VW-W (2012) Photochromic thienylpyridine-bis(alkynyl) borane complexes: toward readily tunable fluorescence dyes and photoswitchable materials. *Org Lett* 14:1862–1865
39. Pang S-C, Hyun H, Lee S, Jang D, Lee MJ, Kang SH, Ahn K-H (2012) Photoswitchable fluorescent diarylethene in a turn-on mode for live cell imaging. *Chem Commun* 48: 3745–3747
40. Liu HH, Chen Y (2012) Modulation of absorption and fluorescence of photochromic diarylethene by intramolecular hydrogen bond. *J Phys Org Chem* 25:142–146
41. Chen Y, Zeng DX, Fan MG (2003) Synthesis and photochromic properties of functional diarylethene with a 2,5-dihydrothiophene bridging unit. *Org Lett* 5:1435–1437
42. Fukumoto S, Nakashima T, Kawai T (2011) Photon-quantitative reaction of a dithiazolylarylene in solution. *Angew Chem Int Ed* 50:1565–1568
43. Nakashima T, Tsuchie K, Kanazawa R, Li R, Iijima S, Galangau O, Nakagawa H, Mutoh K, Kobayashi Y, Abe J, Kawai T (2015) Self-contained photoacid generator triggered by photocyclization of triangle terarylene backbone. *J Am Chem Soc* 137:7023–7026
44. Olivier G, Takuyama N, Fran M, ccedil ois, Tsuyoshi K (2015) Substituent effects on the photochromic properties of benzothiophene-based derivatives. *Chem Eur J* 21:8471–8482
45. Xiaochuan L, Yuzhen M, Bingcai W, Gonggan L (2008) “Lock and key control” of photochromic reactivity by controlling the oxidation/reduction state. *Org Lett* 10:3639–3642
46. Jeong Y-C, Gao C, Lee IS, Yang SI, Ahn K-H (2009) The considerable photostability improvement of photochromic terarylene by sulfone group. *Tetrahedron Lett* 50:5288–5290
47. Wu Y, Chen SJ, Yang YH, Zhang Q, Xie YS, Tian H, Zhu WH (2012) A novel gated photochromic reactivity controlled by complexation/dissociation with BF₃. *Chem Commun* 48:528–530
48. Wu Y, Xie Y, Zhang Q, Tian H, Zhu W, Li ADQ (2014) Quantitative photoswitching in bis (dithiazole)ethene enables modulation of light for encoding optical signals. *Angew Chem Int Ed* 53:2090–2094
49. Chen S, Guo Z, Zhu S, Shi W, Zhu W (2013) A multiaddressable photochromic bithienylethene with sequence-dependent responses: construction of an INHIBIT logic gate and a keypad lock. *ACS Appl Mater Interfaces* 5:5623–5629
50. Chen S, Yang Y, Wu Y, Tian H, Zhu W (2012) Multi-addressable photochromic terarylene containing benzo[*b*]thiophene-1,1-dioxide unit as ethene bridge: multifunctional molecular logic gates on unimolecular platform. *J Mater Chem* 22:5486–5494

51. Chen S, Chen L-J, Yang H-B, Tian H, Zhu W (2012) Light-triggered reversible supramolecular transformations of multi-bisthiénylene hexagons. *J Am Chem Soc* 134:13596–13599
52. Kutsunugi Y, Kawai S, Nakashima T, Kawai T (2009) Photochromic properties of terarylene derivatives having a π -conjugation unit on central aromatic ring. *New J Chem* 6:1368–1373
53. Nakagawa H, Kawai S, Nakashima T, Kawai T (2009) Synthesis and photochemical reactions of photochromic terarylene having a leaving methoxy group. *Org Lett* 11:1475–1478
54. Taguchi M, Nakagawa T, Nakashima T, Kawai T (2011) Photochromic and fluorescence switching properties of oxidized triangle terarylenes in solution and in amorphous solid states. *J Mater Chem* 21:17425–17432
55. Taguchi M, Nakagawa T, Nakashima T, Adachi C, Kawai T (2013) Photo-patternable electroluminescence based on one-way photoisomerization reaction of tetraoxidized triangle terarylenes. *Chem Commun* 49:6373–6375
56. Nakagawa T, Atsumi K, Nakashima T, Hasegawa Y, Kawai T (2007) Reversible luminescence modulation in photochromic europium(III) complex having triangle terthiazole ligands. *Chem Lett* 36:372–373
57. Nakashima T, Fujii R, Kawai T (2011) Regulation of folding and photochromic reactivity of terarylenes through a host-guest interaction. *Chem -Eur J* 17:10951–10957
58. Kawai S, Nakashima T, Atsumi K, Sakai T, Harigai M, Imamoto Y, Kamikubo H, Kataoka M, Kawai T (2007) Novel photochromic molecules based on 4,5-dithienyl thiazole with fast thermal bleaching rate. *Chem Mater* 19:3479–3483
59. Nakashima T, Kajiki Y, Fukumoto S, Taguchi M, Nagao S, Hirota S, Kawai T (2012) Efficient oxidative cycloreversion reaction of photochromic dithiazolythiazole. *J Am Chem Soc* 134:19877–19883
60. H-h Liu, Chen Y (2012) Selective photoconversion of photochromic diarylethenes and their properties. *New J Chem* 36:2223–2227
61. Liu H-H, Chen Y (2013) Synthesis and photophysical properties of thiolactone derivatives. *Tetrahedron* 69:1872–1876
62. Lee PH-M, Ko C-C, Zhu N, Yam VW-W (2007) Metal coordination-assisted near-infrared photochromic behavior: a large perturbation on absorption wavelength properties of n, n-donor ligands containing diarylethene derivatives by coordination to the rhenium(I) metal center. *J Am Chem Soc* 129:6058–6059
63. Nakashima T, Goto M, Kawai S, Kawai T (2008) Photomodulation of ionic interaction and reactivity: reversible photoconversion between imidazolium and imidazolinium. *J Am Chem Soc* 130:14570–14575
64. Neilson BM, Lynch VM, Bielawski CW (2011) Photoswitchable n-heterocyclic carbenes: using light to modulate electron-donating properties. *Angew Chem Int Ed* 50:10322–10326
65. Neilson BM, Bielawski CW (2012) Photoswitchable organocatalysis: using light to modulate the catalytic activities of N-heterocyclic carbenes. *J Am Chem Soc* 134:12693–12699
66. Morinaka K, Ubukata T, Yokoyama Y (2009) Structurally versatile novel photochromic bisarylindenone and its acetal: achievement of large cyclization quantum yield. *Org Lett* 11:3890–3893
67. Ogawa H, Takagi K, Ubukata T, Okamoto A, Yonezawa N, Delbaere S, Yokoyama Y (2012) Bisarylindenols: fixation of conformation leads to exceptional properties of photochromism based on 6π -electrocyclization. *Chem Commun* 48:11838–11840
68. Shirinian VZ, Shimkin AA, Lonshakov DV, Lvov AG, Krayushkin MM (2012) Synthesis and spectral properties of a novel family of photochromic diarylethenes-2,3-diarylcyclopent-2-en-1-ones. *J Photochem Photobiol, A* 233:1–14
69. Lonshakov DV, Shirinian VZ, Lvov AG, Nabatov BV, Krayushkin MM (2013) New fluorescent switches based on photochromic 2,3-diarylcyclopent-2-en-1-ones and 6-ethoxy-3-methyl-1H-phenalen-1-one. *Dyes Pigm* 97:311–317
70. Zhu W, Yang Y, Metivier R, Zhang Q, Guillot R, Xie Y, Tian H, Nakatani K (2011) Unprecedented stability of a photochromic bisthiénylene based on benzobisthiadiazole as an ethene bridge. *Angew Chem Int Ed* 50:10986–10990

71. Suzuki K, Ubukata T, Yokoyama Y (2012) Dual-mode fluorescence switching of photochromic bisthiazolylcoumarin. *Chem Commun* 48:765–767
72. Duke RM, Veale EB, Pfeffer FM, Gunnlaugsson T (2010) Colorimetric and fluorescent anion sensors: an overview of recent developments in the use of 1,8-naphthalimide-based chemosensors. *Chem Soc Rev* 39:3936–3953
73. Meng XL, Zhu WH, Zhang Q, Feng YL, Tan WJ, Tian H (2008) Novel bisthienylethenes containing naphthalimide as the center ethene bridge: photochromism and solvatochromism for combined NOR and INHIBIT logic gates. *J Phys Chem B* 112:15636–15645
74. Zhu W, Song L, Yang Y, Tian H (2012) Novel bisthienylethene containing ferrocenyl-substituted naphthalimide: a photo- and redox multi-addressable molecular switch. *Chem -Eur J* 18:13388–13394
75. Zhu WH, Meng XL, Yang YH, Zhang Q, Xie YS, Tian H (2010) Bisthienylethenes containing a benzothiadiazole unit as a bridge: photochromic performance dependence on substitution position. *Chem Eur J* 16:899–906
76. Yang Y, Xie Y, Zhang Q, Nakatani K, Tian H, Zhu W (2012) Aromaticity-controlled thermal stability of photochromic systems based on a six-membered ring as ethene bridges: photochemical and kinetic studies. *Chem Eur J* 18:11685–11694
77. Li W, Jiao C, Li X, Xie Y, Nakatani K, Tian H, Zhu W (2014) Separation of photoactive conformers based on hindered diarylethenes: efficient modulation in photocyclization quantum yields. *Angew Chem Int Ed* 53:4603–4607
78. Tian H, Chen B, Tu HY, Müllen K (2002) Novel bisthienylethene-based photochromic tetraazaporphyrin with photoregulating luminescence. *Adv Mater* 14:918–923
79. Luo Q, Chen B, Wang M, Tian H (2003) Mono-bisthienylethene ring-fused versus multi-bisthienylethene ring-fused photochromic hybrids. *Adv Funct Mater* 13:233–239
80. Yi J, Chen Z, Xiang J, Zhang F (2011) Photocontrollable *J*-aggregation of a diarylethene-phthalocyanine hybrid and its aggregation-stabilized photochromic behavior. *Langmuir* 27:8061–8066
81. Yam VW-W, Ko C-C, Zhu N (2004) Photochromic and luminescence switching properties of a versatile diarylethene-containing 1,10-phenanthroline ligand and its rhenium(I) complex. *J Am Chem Soc* 126:12734–12735
82. Ko C-C, Kwok W-M, Yam VW-W, Phillips DL (2006) Triplet MLCT Photosensitization of the ring-closing reaction of diarylethenes by design and synthesis of a photochromic rhenium (I) complex of a diarylethene-containing 1,10-phenanthroline ligand. *Chem -Eur J* 12:5840–5848
83. Tung-Wan N, Chi-Chiu K, Nianyong Z, Vivian Wing-Wah Y (2007) Syntheses, luminescence switching, and electrochemical studies of photochromic dithienyl-1,10-phenanthroline zinc(II) bis(thiolate) complexes. *Inorg Chem* 46:1144–1152
84. Nihei M, Suzuki Y, Kimura N, Kera Y, Oshio H (2013) Bidirectional Photomagnetic conversions in a spin-crossover complex with a diarylethene moiety. *Chem -Eur J* 19: 6946–6949

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