Photochromic bisthienylethene as multi-function switches

He Tian* and Sheng Wang

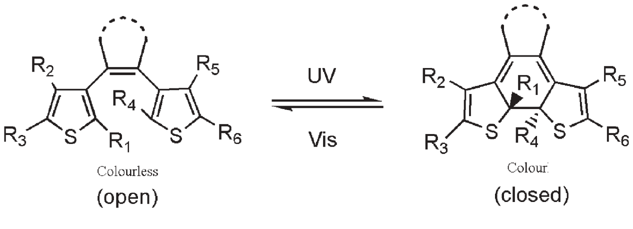
Received (in Cambridge, UK) 13th July 2006, Accepted 6th September 2006
First published as an Advance Article on the web 26th September 2006
DOI: 10.1039/b610004j

Bisthienylethenes (BTEs) are one of the most promising families of photochromic compounds because of their fatigue resistance and thermally irreversible properties for use in optoelectronic devices such as ultrahigh-density optical data storage, molecular switches, logic gates, molecular wires, sensors, and so on. This article describes recent development of switchable photochromic bisthienylethene materials, especially multi-switchable bisthienylethene materials including multi-color photochromic materials, multi-switchable organogelators and liquid crystals. We also highlight our recent contributions in this field.

Introduction

In recent years, molecular switches have attracted considerable interest of researchers because they hold great promise as molecular electronic and photonic devices. In contrast to commonplace switches that turn electric appliances on and off, some molecular switches enable the storage of information at the molecular level, which has the potential to significantly influence the development of optoelectronic materials science and information technologies.[1] Usually, molecular switches act as switching units in various optoelectronic devices and functional materials are addressed by stimulating it with light, electricity or chemical reagents to specifically switch the physical properties between two states. Alternatively, a photo-switch exhibits two stable and selectively addressable states. Especially, photoinduced alteration of chemical and physical properties of photochromic molecules is of great interest because of its potential applications for ultrahigh-density optical data storage and photoregulated molecular switches.[2] Among various types of photochromic molecules, recent considerable interest has been focused on bisthienylethenes which have excellent fatigue resistance and thermal stability in both isomeric forms, high cyclization and cycloreversion quantum yields, rapid response time, and reactivity in the solid state.[3,4] Photochromic bisthienylethene (BTE) derivatives undergo reversible photocyclization reactions between colourless ring-open and coloured ring-closed isomers when irradiated with the appropriate wavelengths of light (Scheme 1).

The thermal stability of the diarylethene in both the open-ring and closed-ring isomers makes it possible to demonstrate novel photo-switching effects, such as changes in fluorescent intensity and absorption spectra, electrochemical properties, optical rotation, magnetic properties, electron-transfer interaction, refractive index, dielectric constant, geometrical structure, and so on.[3–6] These molecular property changes can be applied to design multi-stable switching materials including photo-switching copolymers, fluorescent molecular switches, photochromic chiral switches, photo-controlled conductivity switches and liquid-crystal switches. In this article, we describe recent development of switchable photochromic bisthienylethene molecular materials, especially multi-switchable bisthienylethene materials including multi-colour copolymers, multi-switchable organogelators and photochromic liquid crystals. We also present specific examples from our own research and highlight our contributions in this field.



Scheme 1 Photochromism of bisthienylethene (BTE).

Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai, 200237, P. R. China. E-mail: tianhe@ecust.edu.cn; Fax: +86-21-64252288; Tel: +86-21-64252756

Prof. He Tian received his PhD degree in 1989 from East China University of Science & Technology (ECUST) (Shanghai, China). From 1991 to 1993 and in 2000, Dr Tian did research on organic functional materials twice in Germany, both supported by the Alexander von Humboldt Foundation. Dr Tian became a full professor at ECUST in 1994. In 1999, he was appointed Cheung Kong Distinguished Professor by the Education Ministry of China. His current research interests include the syntheses of novel functional organic dyes or co-polymers and the development of interdisciplinary material science that determines the electronic and optical properties of the materials. Prof. Tian has published over 180 papers in international journals and four academic books (in Chinese). He has also been awarded 28 Chinese patents.

Sheng Wang was born in 1974 and received his PhD degree in Applied Chemistry (June 2006) from the East China University of Science & Technology (ECUST) supervised by Prof. Tian. Presently he works in Zhanjiang Normal University, Zhanjiang, China. His research interests are mainly focused on the development of photochromic materials and molecular switches.

Molecular switch with high fluorescent contrast

Fluorescent photochromic materials attract strong interest for their possible application in optical memory as well as in fluorescent probes. In particular, fluorescent diarylethenes, which show reversible change in fluorescent intensity along with the photochromic reaction, are useful non-destructive optical readout systems.[7–9] Understanding the fluorescent diarylethene photochromic reactions at single-molecule level will help to ultimately realize ultrahigh-density single molecule optical memory.[9] Irie and co-workers[10] synthesized a photochromic diarylethene and fluorescent bis(phenylethynyl)anthracene units are linked through an adamantyl spacer (Fig. 1) and investigated the fluorescent photochromic reaction of the diarylethene derivatives. They observed digital fluorescence on/off switching between two discrete states at the single-molecule level upon irradiation with UV and visible light and the "on"- and "off"-times were dependent on the power of the UV and visible light. The fluorescent contrast in the single molecular level was controlled by the background noise.

Neckers and co-workers[11] reported a photochromic bisthienylethene moiety attached to fluorescent 4,4-difluoro-8-(4′-iodophenyl)-1,3,5,7-tetramethyl-4-bora-3*a*,4*a*-diaza-*s*-indacene (iodo-BODIPY) *via* a phenylacetylene linker. UV-light induced isomerization of the photochromic BTE unit results in a significant decrease in fluorescence intensity while the fluorescence can be also recovered with visible light irradiation. Fluorescence quenching in the photochromic isomerization process is caused generally by an intramolecular energy transfer mechanism. Switching of fluorescence is reversible and can be repeated many times without significant loss of its intensity. Regretfully, the highly fluorescent contrast signal was only observed in solution.

Based on our previous work on photochromic BTEs, some new fluorescent switches with high contrast containing BTEs were developed, in which the absorption of the BTE unit should have large overlap with the emission of fluorescent chromophore. This would increase the energy transfer (FRET) efficiency, and consequently increase the fluorescent contrast of the binary states. We designed and synthesized a highly fluorescent contrast photochromic bisthienylethene-bridged naphthalimide (NA) dimer (abbreviated as BTE-NA shown in Scheme 2).[12] Scheme 2 presents the optical switching function of BTE-NA. The open and closed isomers of BTE-NA represent "1" and "0" binary digital codes. It exhibits good photo-regulating luminescence with very high contrast (85 : 1) in poly(methyl methacrylate) (PMMA) doped films. The strong fluorescence emission with high-contrast switching in the solid film could increase the density of the stored information. We also demonstrated its use in rewritable optical two-dimensional recording (Fig. 2). Reversible, high-degree fluorescence modulation of a naphthalimide (NA) chromophore was realized by photoisomerization of the BTE subunit in polymer matrices. Considering its high-contrast photoswitchable fluorescence feature and the inherent characteristics of pristine bisthienylethene, BTE-NA can be suggested as a promising candidate for erasable optical data storage.[12]

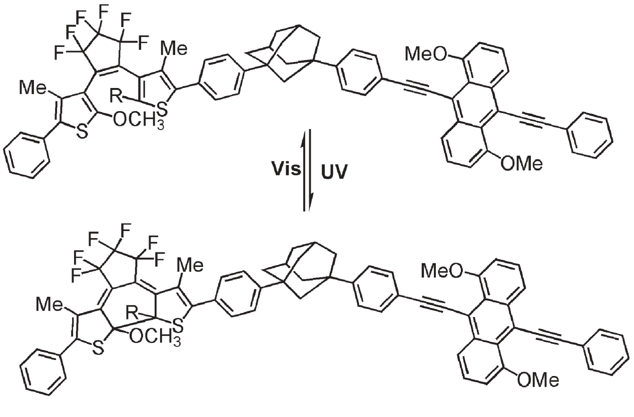
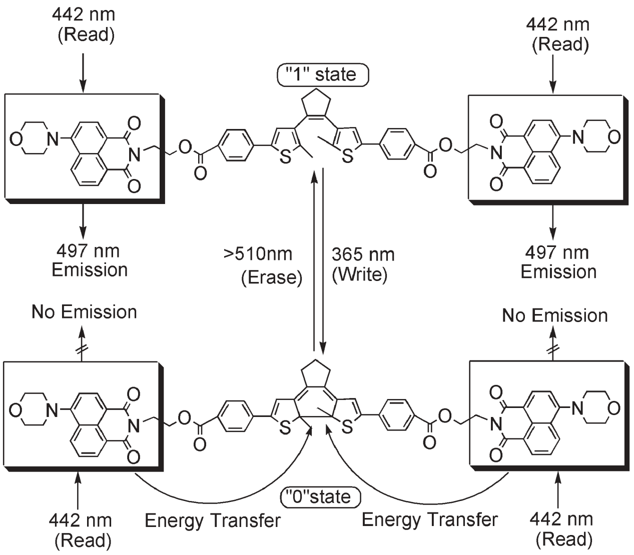


Fig. 1 The single molecular level fluorescent switch prepared by Irie and co-workers.[10]



Scheme 2 Structures and photo-switching behaviour of BTE-NA.

Another approach to develop fluorescent photochromic switches is to shift the luminescent wavelength into the near-IR region. For example, a new coplanar binuclear porphyrazine bearing six bis(trimethylthiophenyl) photochromic functionalities at the periphery was synthesized in our lab recently,[13] shown in Scheme 3, which undergoes open-to-closed ring or closed-to-open ring photoisomerization in different quantum yields by irradiation with 365 or 730 nm light. The photocyclization of any BTE unit on this macrocycle would quench

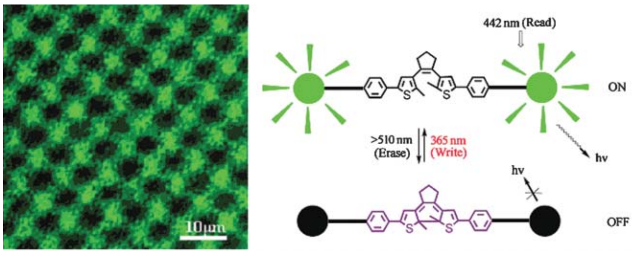
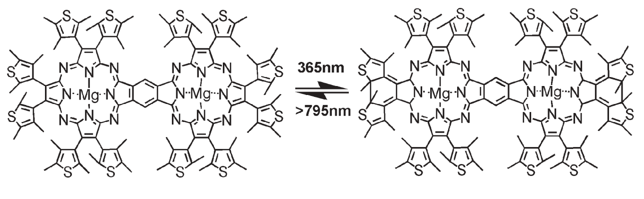
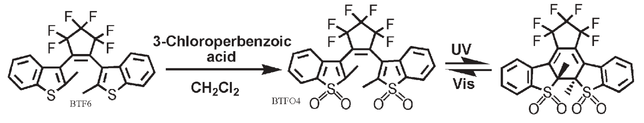


Fig. 2 Fluorescence image generated from 365-nm irradiation (5 min) of the BTE-NA doped PMMA film through a dot-patterned contact mask. The light regions indicate luminescence, and the dark regions are non-luminescent (λ_{ex}: 442 nm).



Scheme 3 The photochromic process of a new binuclearporphyrazinato magnesium(II) complex.



Scheme 4 Molecular structures of BTF6 and BTFO4 as reported by Kim and co-workers.[14]

effectively the luminescence of the system. The compound also showed high extinction coefficients, which should be improved for BTE unit inherent characteristics, and near-IR luminescence regulation with photochromic reaction in a reversible manner by the photoisomerization of the BTE moiety, which would also be useful for fluorescent probes and optical readouts for erasable memory media.

Some scientists have made an effort on increasing of fluorescence efficiency of BTEs. Kim and co-workers[14] synthesized a new fluorescent photochromic diarylethene system by the oxidation of 1,2-bis(2-methyl-1-benzothiophene-3-yl) perfluorocyclopentene (BTF6) and the fluorescence quantum yield of its sulfonyl derivative 1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-3-yl)perfluorocyclopentene (BTFO4) increased following photo-cyclization, opposite to that found for BTF6 (Scheme 4). The oxidation of the sulfide groups of the benzothiophene rings of BTF6 transformed the c-isomer from a very weak emitter to a highly fluorescent chromophore. Overall, the results of this study provide a new design synthetic strategy for the design of highly fluorescent materials with potential applications in non-destructive photochromic read-outs.

Photochromic polymeric switches

In usual one-component photochromic systems, they interconvert between only two states: the "colourless" and "coloured". On the other hand, in multi-component systems comprised of different kinds of photochromic units, reversible multi-state switching between several states can be realized by combination of the binary states of each component. In a two-component system, for example, four states could be produced, and eight states could be induced in a three-component system. Multi-component or multi-coloured systems of diarylethenes were reported for the first time by Fernandez-Acebes and Lehn.[15] They demonstrated that the absorption properties of multi-component diarylethene mixtures in solution as well as on silica-gel plates can be modulated by controlling different wavelength light. Irie and co-workers also reported a multi-component single crystal, which contains two or three types of compound that exhibit yellow, red, and blue colours; the crystal was expected to show a full range of colours upon photo-irradiation.[16,17] Another ideal approach to practical optical-electronic devices is the preparation of multi-component photochromic copolymers. Photochromic copolymers are the most promising solid materials in practical application because of their excellent rotating spread film property and photochromism in solid films.[18] Various types of one-component photochromic copolymers have been synthesized by radical polymerization,[19] oxidation polymerization,[20] Wittig polycondensation[21] and ring-opening metathesis polymerization.[22,23] These photochromic copolymers show excellent photochromic properties in solution. We synthesized a two-component photochromic copolymer P(two-BTE-MMA) by radical polymerization (Fig. 3).[24]

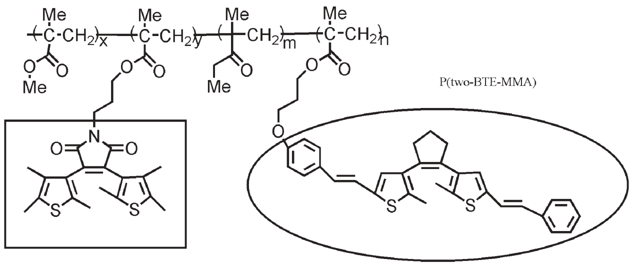


Fig. 3 Two-component photochromic copolymer P(two-BTE-MMA).

We investigated multi-colour properties of P(two-BTE-MMA) in solution and in solid films, which exhibit multi-switchable photochromic behaviour with four states. This copolymer turned from colourless to a brick-brown colour upon irradiation with 402 nm light. Then it turned back to its initial state upon irradiation with 521 nm light. Upon further irradiation on colourless copolymer with 342 nm light, it turned blue. When P(two-BTE-MMA) film was exposed simultaneously to 342 and 402 nm light, it turned bluish violet. Fig. 4 shows the multi-colour photochromic absorption changes upon irradiation with different light sources. Based on the experiments on P(two-BTE-MMA) it is inferred that the above colour changes originates from the photoreaction of the copolymer as shown in Scheme 5.

When the two types of BTE units in P(two-BTE-MMA) were open-ring states (**a(OO)**), P(two-BTE-MMA) shows a

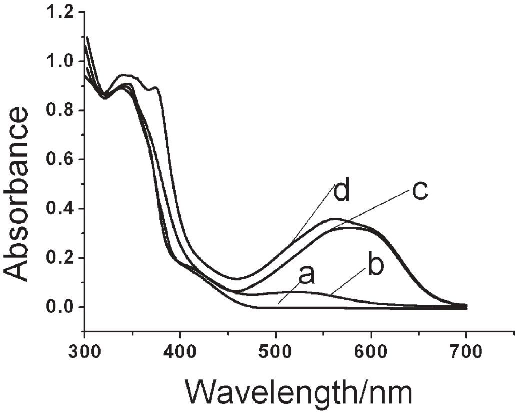
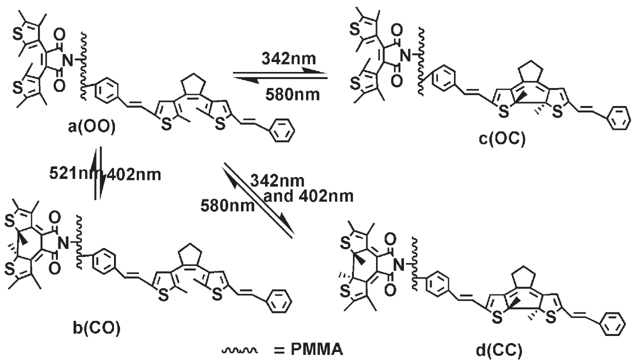


Fig. 4 Absorption changes of photochromic copolymer P(two-BTE-MMA) in a solid film upon irradiation with different wavelength light: (a) initial state, (b) 402 nm, (c) 342 nm, (d) 342 nm and 402 nm.



Scheme 5 Photoreactions of copolymer P(two-BTE-MMA).

colourless initial state. Upon irradiation with 402 nm light, the 2,3-bis(2,4,5-trimethyl-3-thienyl)-*N*-hydroxylpropylmaleiimide unit **A** in P(two-BTE-MMA) converts to its closed-ring form while the 1-(5-benzovinyl-2-methyl-3-thienyl)-2-(5-benzovinyl-(4′-methacrylate propyl ether)-2-methyl-3-thienyl)cyclopentene unit **B** still remains in its open-ring state (**b(CO)**); thus P(two-BTE-MMA) shows the colour of the closed isomers of **A**. Upon irradiation with 342 nm light, the **B** unit in P(two-BTE-MMA) converts to its closed-ring isomer but the **A** unit is inactive to this irradiation wavelength; the state **c(OC)** thus shows the colour of the closed isomers of **B**. When the copolymer P(two-BTE-MMA) was exposed simultaneously to 342 and 402 nm light, it shows the colour of both closed-ring isomers **A** and **B** (**d(CC)**) shown in Scheme 5.

While the copolymer P(two-BTE-MMA) has still low photochromic content this copolymer provides a molecular design method for multi-switchable photochromic copolymers. This approach is more practical than doping several photoactive components in polymer matrices, or relying on the challenge of obtaining multi-component single crystals. Recently, Wigglesworth and Branda[25] reported a family of multi-addressable, multi-coloured photo-responsible copolymers prepared by ring-opening metathesis polymerization (ROMP) (Fig. 5), which could be interconverted between the several unique states.

A three-component copolymer, for example, could be switched between the eight possible states. Because each photochromic diarylethene structure has unique absorption characteristics in both its ring-open and ring-closed states, the copolymers made up of them are multi-addressable. Copolymers CP_1, CP_2 and CP_3 (shown in Fig. 5) contain two BTE units and can display four unique states. Copolymer CP_4 contains three BTE units and can exhibit up to eight possible states in a single polymer. This type of material has potential application in multi-frequency optical data storage and display technologies.

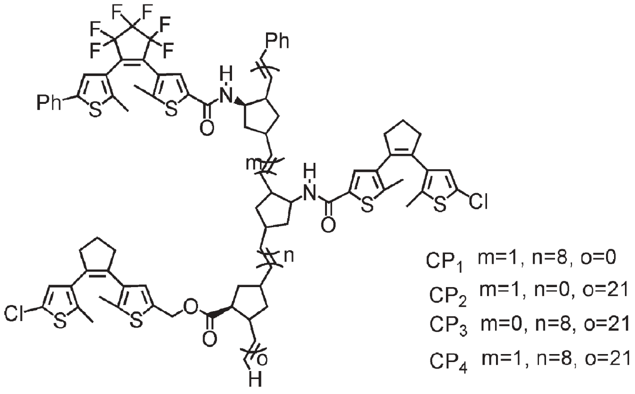


Fig. 5 Structure of photochromic copolymers CP_1–CP_4 prepared by Wigglesworth and Branda.[25]

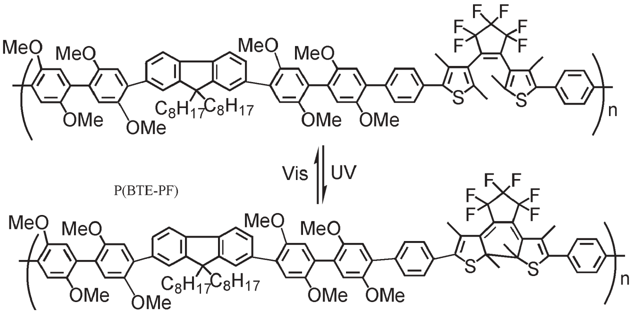


Fig. 6 Photoswitch conductivity of photochromic copolymer P(BTE-PF) reported by Irie and co-workers.[26]

The photochromic conductivity of polymeric switching materials has also attracted considerable attention because of promising application in photovoltaic effects, non-linear-optical response, and photoconductivity. Recently, Irie and co-workers[26] reported a novel photochromic conductivity switching copolymer (P(BTE-PF) shown in Fig. 6) based on BTE and its photon-mode modulation in electric conductivity. Large and twisted oligophenylene–fluorene (PF) units were introduced between diarylethene sites, and the separations on this copolymer main chain were as large as *ca.* 4 nm. The resulting co-polymer exhibits a high conductivity modulation, whose photochromic conversion ratio was as small as 35% in the solid film. The electrical conductivity can be switched quasi-reversibly many times by alternating irradiation with UV and visible light, so leading to potential as active materials in future photo-mode molecular memory and switching devices such as ‘‘photon mode’’ RAM (random access memory).

Kim and Lee synthesized[27] a photochromic copolymer based on BTE and trimethylsilyl-substituted *p*-phenylene vinylene (TPV) (P(BTE-TPV) shown in Fig. 7). The photoisomerization of this copolymer was induced by incorporating a 2,3-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene unit, while TPV units directly connected to the diarylethene unit allowed the extension of π-electron delocalization. The conductivity of P(BTE-TPV) was significantly increased when the BTE unit was converted to a closed form (coloured) by irradiation with UV light. The conductivity switching was reversible by alternative irradiation of UV and

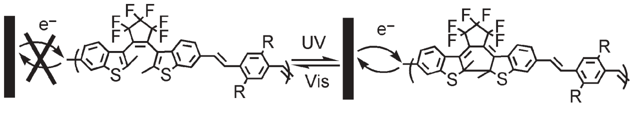


Fig. 7 The photochromic-conductivity process of polymer P(BTE-TPV) prepared by Kim and Lee.[27]

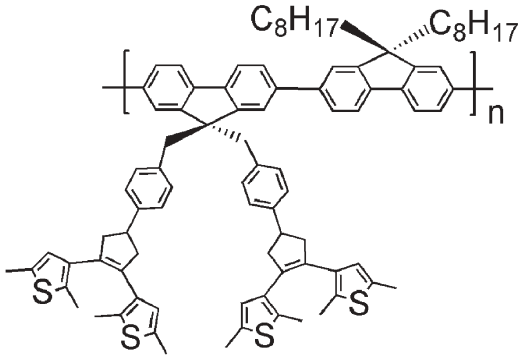


Fig. 8 A high-content pendant photochromic copolymer P(2-BTE-PF).

visible light. In fact, in order to characterize clearly the photocontrolling conductivity of nanowires based on photochromic BTE, the photomodulating conductivity of a single BTE molecule attached on the surface of a gold electrode had been investigated by Feringa's group more recently.[28] Since photochromic BTE units have a limited photocyclization quantum yield,[3] it is hard to obtain excellent electron and energy transfer properties through the π-conjugation based on those photochromic polymeric or oligomeric nanowires. It is still a challenge to improve the on/off ratio for the photo-switchable polymers. Specifically, how to optically control such molecular wires (single molecule, oligomers and copolymers) by external stimuli becomes an important theme.

Recently, our group[29] synthesized a high-content pendant photochromic copolymer P(2-BTE-PF) with a BTE : fluorene mole ratio of 2 : 1 (Fig. 8) by typical palladium-catalyzed Suzuki coupling reaction, whose photochromic content was as high as 53 wt%. P(2-BTE-PF) exhibits excellent photochromism both in solution and in solid films. Good-quality films of bulky material were obtained by spin-casting without a supporting polymer matrix.

To further increase the number density of fluorescent BTE molecules in the polymer film and to also impart self processability, Park and co-workers[30] designed and synthesized a novel class of "aggregation-induced enhanced emission" (AIEE)-based fluorescent photochromic poly(DCS-BTE) (shown in Fig. 9) by Knoevenagel condensation, whose strong fluorescence in the neat polymer film could be photoswitched through highly efficient bistable photochromism (fluorescence switching ratio >10 : 1). Such a strongly enhanced fluorescence emission coupled with high-contrast photochromic switching in poly(DCS-BTE) film suggests their viable application to an erasable optical memory. Erasable fluorescence photo-imaging on the spin-coated poly(DCS-BTE) film was successfully demonstrated.

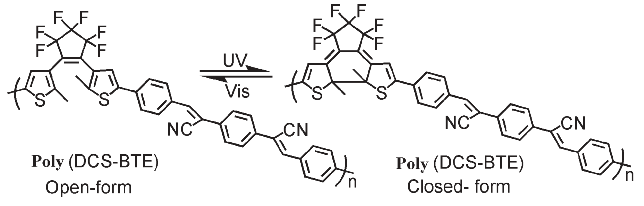


Fig. 9 Photochromic reactions of poly(DCS-BTE) reported by Park and co-workers.[30]

Photochromic chiral switches

Molecules responsive to external stimuli are the basis for the studies of molecular switches and are the key elements in molecular level devices. If the output signals of molecular switches are chiral properties of molecular systems, they are regarded as chiral molecular switches. In fact, to understand, establish, and ultimately control chirality at the molecular and supramolecular level is one of the frontiers of molecular science.[1,2] The photo-regulation of chirality is fundamentally significant because it has the potential to influence novel liquid crystalline materials, non-destructive data storage, and catalytic asymmetric synthesis. In all cases, the combination of a high-performance photo-responsive molecular backbone and a chiral architecture that has an inherently large ability to interact and transfer its chirality to the environment is increasingly important to develop.

Photochromic BTEs appropriately satisfy the demand because they undergo thermally irreversible photocyclization reactions with excellent photo-fatigue. They have been used with varying success in chiroptic applications.[31–33] Recently, Branda and co-workers[34] reported a photo-responsive BTE derivative bearing chiral pinene-based arms (Fig. 10), which underwent a stereo-selective photoinduced cyclization reaction to produce >98% of a single diastereomer. This system satisfies the requirements of a successful chiroptical photoswitch. It was thermally stable in both its states. It displays high stereo-selectivity in its photocyclization reactions, and it exhibits large changes in circular dichroism (CD) and ORD spectral properties.

Feringa and co-workers[35,36] reported the co-assembly of achiral with chiral diarylethene photochromic switches, accompanied by a dynamic selection and amplification in a supramolecular system (Fig. 11). It exhibited the highly specific self-assembly features of low molecular weight gelators (LMWG) bearing multiple hydrogen bonding groups, which can be addressed and controlled by incorporation of a diarylethene photo-responsive unit. The co-assembly enables the transfer and propagation of chirality in the co-aggregate's supramolecular structure. Photochemical ring-closure can lock this chiral information at the molecular level. Diarylethene switches are presented in two, rapidly exchanging conformations (*P* and *M* helicity). The photochemical ring-closure leads to the *RR* or *SS* enantiomers in equal amounts. It was possible

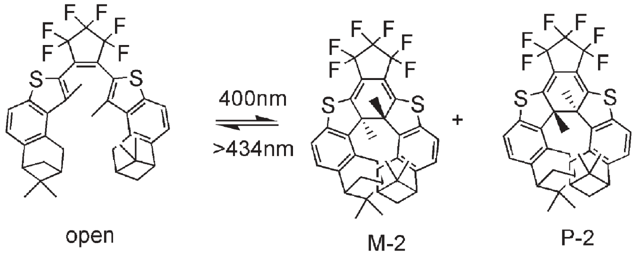


Fig. 10 Photochromic process of chiral switches prepared by Branda and co-workers.[34]

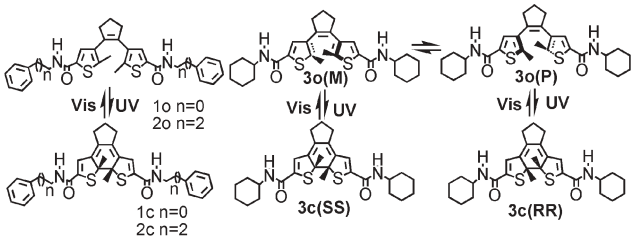
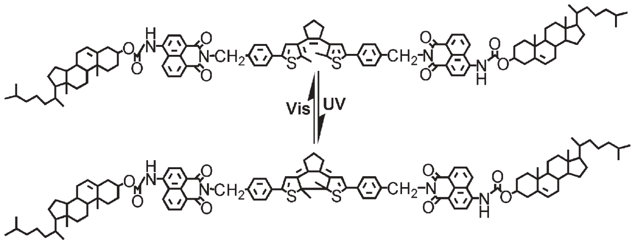


Fig. 11 The chiral diarylethene switches reported by Feringa and co-workers[35,36] used for selection and amplification upon aggregation by hydrogen-bond formation; **o** = open form, **c** = closed form, UV: λ = 313 nm, VIS: λ > 420 nm.



Scheme 6 The structure and photochromic process of BTE-NA-(chol)$_2$.

to assemble cooperatively these chiral and achiral amide substituted perhydrodithienyl switches into supramolecular assemblies. The selection of only one of photoactive conformers of the chiral switches **1o** (and **2o**) during aggregation controls the stereochemistry of achiral switch **3o**, resulting in chiral induction with up to eight-fold chiral amplification.

Recently, we[37] have synthesized a photochromic fluorescent organogel based on BTE bridged naphthalimides (abbreviated as BTE-NA-(chol)$_2$, Scheme 6) and succeeded in constructing a multiple switching system responding to light, thermal stimuli, fluoride anions and proton stimuli. It exhibits excellent photochromic properties and defined thermoreversible properties in an organogel system. The visual images of the BTE-NA-(chol)$_2$ gel with a network structure composed of fibrous aggregates were observed with a scanning electronic microscope (SEM) (Fig. 12). At the same time, by taking advantage of the ability of F$^-$ and protons to induce obviously different absorption and fluorescence spectra of BTE-NA-(chol)$_2$ in solution under sequential alternating UV/Vis light irradiation, a multiple switch was realized, which makes it promising for application in the fields of opto- and electronic smart materials, logic gates, fluorescence sensors and other molecular photonic devices.

Interestingly, BTE-NA-(chol)$_2$ shows reversible chiral changes in the gel phase and in solution by light, F$^-$ and proton stimulation. Fig. 13 shows the CD spectra changes of the BTE-NA-(chol)$_2$ gels with 365 nm irradiation. The open form of BTE-NA-(chol)$_2$ gels has a weak negative Cotton effect at 410 nm, Upon irradiation with 365 nm light for 10 min, a typically strong positive Cotton effect at 415 nm was observed. It is inferred that the cholesterol chiral unit induced diarylethene chirality changes by irradiation with 365 nm light.

Fig. 14 shows the CD spectra changes of BTE-NA-(chol)$_2$ in THF solution (2.0 × 10^{-4} mol L^{-1}) with 365 nm irradiation,

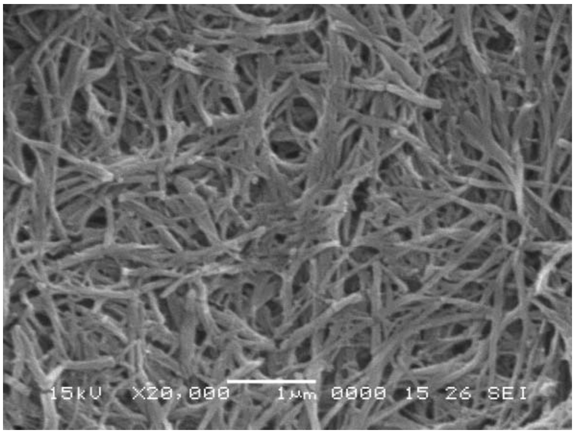


Fig. 12 SEM images of BTE-NA-(chol)$_2$ gel (the gel was prepared from the toluene–ethanol (1 : 3 v/v), [BTE-NA-(chol)$_2$] = 0.5 wt%).

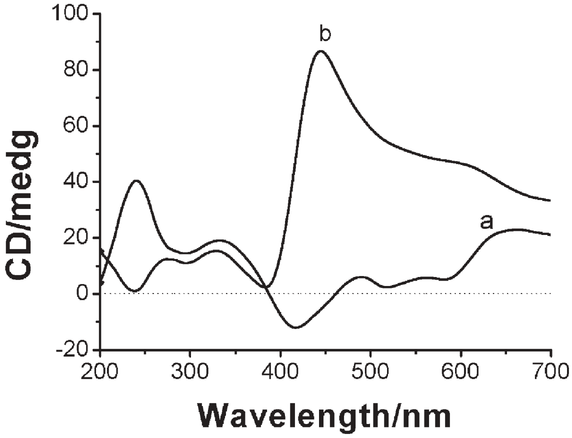


Fig. 13 The CD spectra changes of BTE-NA-(chol)$_2$ gel with 365 nm irradiation: (a) the open form of BTE-NA-(chol)$_2$ gel; (b) the closed form of BTE-NA-(chol)$_2$ gel.

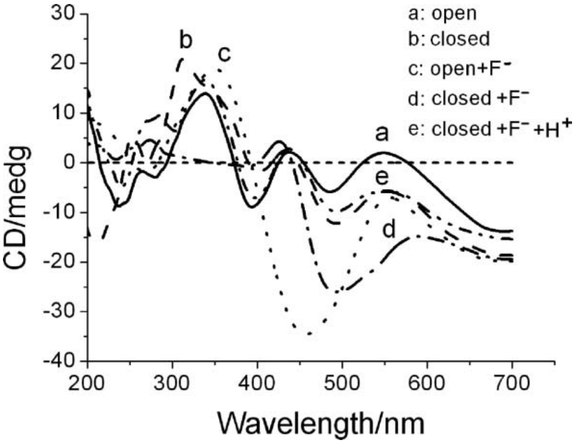


Fig. 14 The CD spectra changes of the BTE-NA-(chol)$_2$ in THF solution (2.0 × 10^{-4} mol L^{-1}) with 365 nm irradiation. (a) The open form of BTE-NA-(chol)$_2$; (b) the closed form of BTE-NA-(chol)$_2$; (c) the open form of BTE-NA-(chol)$_2$ upon titration with F$^-$; (d) BTE-NA-(chol)$_2$ upon titration with F$^-$ followed by irradiation at 365 nm; (e): BTE-NA-(chol)$_2$ upon titration with F$^-$, irradiation at 365 nm, followed by titration with protons.

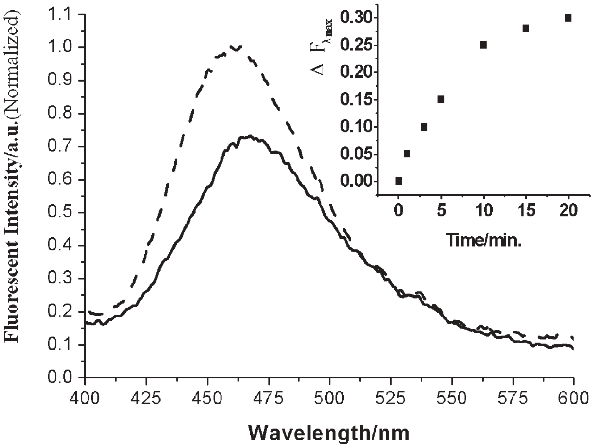


Fig. 15 Fluorescent spectra (excited at 355 nm) of the BTE-NA-(chol)$_2$ gel: the open-ring isomer (—) and the photostationary state (---) (0.5 wt/v%) upon irradiation by 365 nm light at room temperature. Inset curves show the fluorescent change value at maximum emission wavelength with irradiation times.

F$^-$ and proton stimulation. Two evident Cotton effects at 400 nm and around 480 nm were observed in the open form of BTE-NA-(chol)$_2$ in solution (Fig. 14, curve (a)). Upon irradiation with 365 nm light, the CD spectra changed (Fig. 14, curve (b)). Upon titration with F$^-$ of the open form of BTE-NA-(chol)$_2$, the CD spectra changed again (Fig. 14, curve (c)); then upon irradiation with 365 nm light, the CD spectra changed from curve (c) to curve (d); upon titration with protons the CD spectra changed to (e). From Fig. 14, we can see that the CD spectra of BTE-NA-(chol)$_2$ shows sharp changes upon titration with F$^-$. There are two Cotton effects, one is a positive Cotton effect at 353 nm (19 M^{-1} cm^{-1}), the other is a negative Cotton effect at 450 nm (-34 M^{-1} cm^{-1}).

In addition, BTE-NA-(chol)$_2$ shows a reversible fluorescent organogelator molecular switch. Fig. 15 shows the fluorescent emission spectral changes of BTE-NA-(chol)$_2$ in a gel phase in which a weak fluorescence emission peak around 470 nm is observed. Upon irradiation with 313 nm light, the fluorescence intensity is gradually increased. The obvious fluorescence changes were observed by the naked eye (Fig. 16).

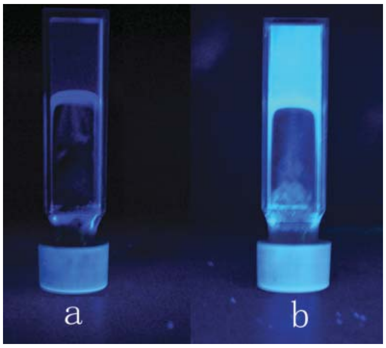


Fig. 16 Fluorescent images of the BTE-NA-(chol)$_2$ gel: the open-ring isomer (a) and in the photostationary state (b) upon irradiation by 313 nm light at room temperature.

Table 1 The truth table

Entry	I1	I2	I3	I4	O1	O2	O3	O4
1	0	0	0	0	0	0	0	0
2	1	0	0	0	1	1	0	0
Memory 2′	0	0	0	0	1	1	0	0
4	0	1	0	0	0	0	0	0
5	0	0	1	0	0	0	1	1
6	0	0	0	1	0	0	0	0
7	1	0	1	0	1	1	1	1
Memory 7′	0	0	1	0	1	1	1	1
9	0	1	1	0	0	0	1	1
10	0	1	0	1	0	0	0	0
11	1	0	0	1	1	1	0	0
Memory 11′	0	0	0	1	1	1	0	0

Molecular logic gates are increasingly important in attributing chemical reactivity to molecular devices. Specific input signals of basic logic gates can be programmed into single molecules that generate readable output signals, such as fluorescence or UV/Vis light.[38–41] By taking advantage of BTE-NA-(chol)$_2$ multi-mode switching processes, a complicated molecular logic gate with four optical outputs responding to four-inputs based on the truth table shown in Table 1 is constructed, in which BTE-NA-(chol)$_2$ starts its switching characteristics with the initial state in the dark, *i.e.*, all inputs does not stimulate the system at initial step. The inputs **I1**, **I2**, **I3** and **I4** are UV light (365 nm), visible light (⩾510 nm), fluoride ion and proton, respectively. The four optical outputs **O1**, **O2**, **O3** and **O4** are the absorption at 550 nm, the fluorescence emission at 450 nm, the absorption at 500 nm and the fluorescence emission at 570 nm, respectively. This first entry with an inputs string is 0000 and the outputs string is 0000. Then the second entry starts with UV irradiation (**I1** on), which induces BTE-NA-(chol)$_2$ changing colour to red with strong fluorescence, *i.e.* **O1** and **O2** are both on, and this entry is with the input string of 1000 and the output string of 1100. Then if **I1** (UV) is switched back to *off* in this case, the input string 0000 is restored. However, the corresponding output string should remain as 1100, because that the molecular switch has memorized the influence of the input in the previous step (referred to "Memory 2′ entry" in the truth Table). As mentioned above the memory state could be erased by the irradiation of visible light and BTE-NA-(chol)$_2$ returns its initial state, which is indicated by the fourth entry in the truth Table with the inputs string of 0100 and outputs string of 0000. The molecular switch BTE-NA-(chol)$_2$ underwent a whole cycle responding to UV/visible irradiation, which are referred by the four entries in the truth Table.

Besides UV/visible irradiation, this particular molecular switch has also "memory" effect between solution and gel phases, if temperature acts as a thermal input (not shown in the truth Table). In addition, the four entries with **I1** (UV) and **I2** (Visible) both "on" at the same time are meaningless for the photochromic system, these states are undefined on the output and therefore they are not listed in the truth Table.

Two-photon absorption (TPA) is a nonlinear optical process in which a chromophore that would normally be excited by a single-photon of shorter wavelength is excited by two photons of longer wavelengths. Two-photon absorption (TPA) photochromic materials are one class of attractive TPA materials,

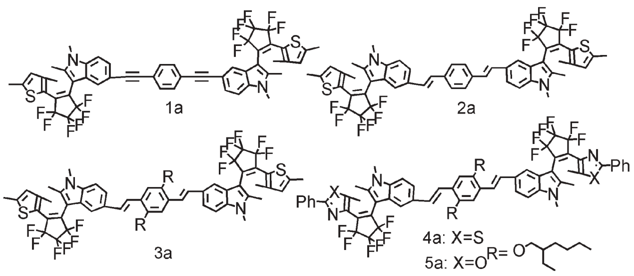


Fig. 17 Chemical structures of the diarylethene dimers (BTE-dimer) prepared by Irie and co-workers.[42]

since they have potential application in three-dimensional optical data storage media. Irie and co-workers[42] designed and synthesized a series of TPA photochromic diarylethene compounds (Fig. 17), which show excellent two-photon absorption (TPA) properties. Among the diarylethene derivatives, compound **5a** having oxazolyl rings, showed the most favourable photochromic performance as a TPA photochromic molecule. Compound **5a** has a TPA cross-section of 23 GM at 820 nm and shows a photochromic colour change based on two-photon absorption of 820 nm light.

We also investigated the two-photon absorption properties of BTE-NA-(chol)$_2$ in the gel phase and in solution stimulated by light and fluoride ion. We found that BTE-NA-(chol)$_2$ in the gel showed different two photon absorption and emission properties before and after photochromic reaction (Fig. 18(a) and (b)). A fluorescent dot was observed at the cross-focus point of the two laser beams. The beam of 800 nm laser can transmit through the semi-transparent gel phase. In addition, we found that two beams of the laser (800 nm) in parallel transmitted through the gel can induce the BTE-NA-(chol)$_2$ gel to undergo photochromic reaction (shown in Fig. 18(d)) while a single photon laser at longer wavelengths (*e.g.* 800 nm) did not induce any photochromism (Fig. 18(c)). We also observed that BTE-NA-(chol)$_2$ in solution shows different two-photon absorption and two-photon excited emission properties with light and fluoride ion stimulation (Fig. 18(e), (f) and (g)); when a two-photon beam passes through the solution, they show different two-photon fluorescent emission.

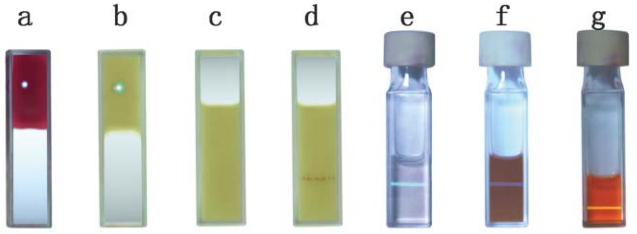
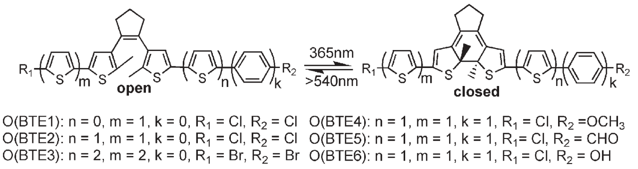


Fig. 18 The TPA image of the BTE-NA-(chol)$_2$ in the gel phase and in THF solution (2.0×10^{-4} mol L^{-1}); (a) and (b) obtained with the cross focus; (d), (e), (f) and (g) obtained by the parallel configuration. (a) The closed form of BTE-NA-(chol)$_2$ in gel; (b) the open form of BTE-NA-(chol)$_2$ in gel; (d) the TPA photochromic of BTE-NA-(chol)$_2$ in gel; (e): the open form of BTE-NA-(chol)$_2$ in solution; (f) the closed form of BTE-NA-(chol)$_2$ in solution; (g) the open form of BTE-NA-(chol)$_2$ titration with F$^-$ in solution. (c) The open form of BTE-NA-(chol)$_2$ with one-photon irradiation in gel.



Scheme 7 Photochromic bisthienylethene–thiophene oligomers O(BTEs).

A series of novel photochromic thiophene oligomers with BTE units were successfully synthesized *via* a Suzuki coupling method in our laboratory more recently (abbreviated as O(BTEs) shown in Scheme 7).[43] These structurally symmetric or unsymmetric bisthienylethene derivatives could be obtained by controlling the ratio of the starting materials and reagents. All the thiophene oligomers O(BTEs) show good photochromic properties, fatigue resistance and excellent solubility in the pristine state. Some of the compounds have switchable electrochemical and two-photon properties. As a case, the TPA cross section of O(BTE3) was determined by femtosecond open-aperture Z-scan technique according to a previously described method.[44] The experiments show the open-aperture Z-scan data of O(BTE3) and a TPA coefficient β of 9.23×10^{-11} cm W^{-1} was obtained by data fitting. The value of the TPA cross section for O(BTE3) at 800 nm is 181 GM.

Photochromic liquid crystals

The control of the structure and optical properties of liquid-crystalline (LC) phases by means of light is a major challenge in the development of molecular devices and optical data storage systems. So far various types of photo-responsive liquid crystals have been reported.[45–47] The combination of liquid-crystalline and photochromic behaviour in molecular systems promises to be very useful in optical technological devices. Frigoli and Mehl[48] synthesized a class of room-temperature nematic photo-switchable liquid crystals shown in Fig. 19.

Recently, Mehl and co-workers synthesized mesogenic LC photochromic diarylethenes without linking to mesogens *via* alkyl spacers (Scheme 8).[49] Small variations in molecular structure affect the LC properties dramatically as well as the

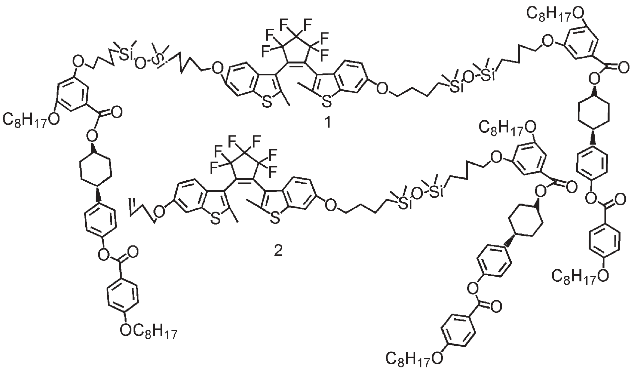
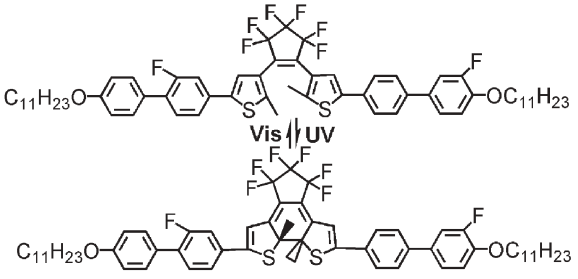
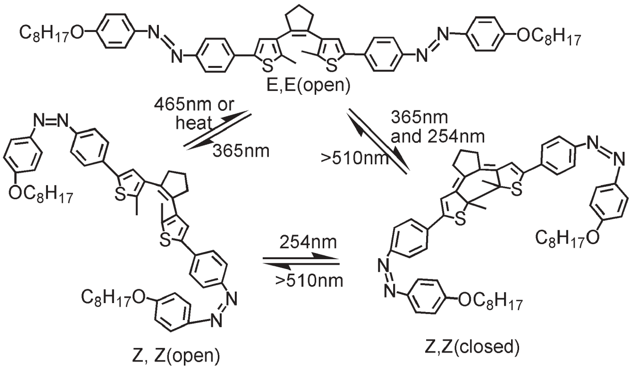


Fig. 19 Molecular structures of photochromic liquid crystals reported by Frigoli and Mehl.[48]



Scheme 8 Photochromic liquid crystals prepared by Mehl and co-workers.[49]



Scheme 9 The structure and photochromic processes of BTE-AZO.

photo-switching, the absorption, and the fluorescence behaviour of these systems.

The attractive properties of LC photochromic diarylethenes encouraged us to design and synthesize a novel LC biphotochromic compound (BTE-AZO, Scheme 9) based on BTE and azo units, which might realize multi-state photochromic reaction with four different wavelengths (254, 365, 460 and 510 nm) of irradiation.

We investigated the photochromic properties of BTE-AZO. Fig. 20 shows absorption spectral changes of BTE-AZO in THF solution. The absorption peak of the open-ring form was observed at 285 and 400 nm. Upon irradiation with UV light (365 nm), the absorption peak intensity at 285 nm gradually increased while it gradually decreased at 400 nm. We inferred that the BTE-AZO molecule only undergoes *ZZ–EE* photoisomerization reaction in the azo unit due to its high extinction coefficient, until the photostationary state of the azo unit is reached. After a long-term irradiation with UV light (254 nm), a weak absorption appeared around 590 nm (inset in Fig. 20), which means that only at that time the bisthienylethene unit undergoes photocyclization. Upon visible light (>510 nm) irradiation, the original absorption spectrum was converted back to that of the initial open-ring isomer of BTE-AZO (*E*,*E*). Only upon irradiation with UV light (254 nm), a very weak absorption at 590 nm was also observed.

In addition, we have investigated this BTE-AZO liquid crystal by crossed optical polarizing microscopy equipped with a temperature controller. When cooling from the isotropic phase, the mesophase with typical nematic Schlieren texture began to appear at about 156.5 °C. Some crystalline-like phase began to appear at 122 °C upon cooling to 80 °C. The typical nematic Schlieren texture appeared over the temperature range 156.50–80 °C (Fig. 21). The mesophase becomes clear at 162 °C and shows a nematic phase just below this clearing temperature. The further characterization of such interesting mesophases and investigation of their liquid-crystal application properties are in progress.

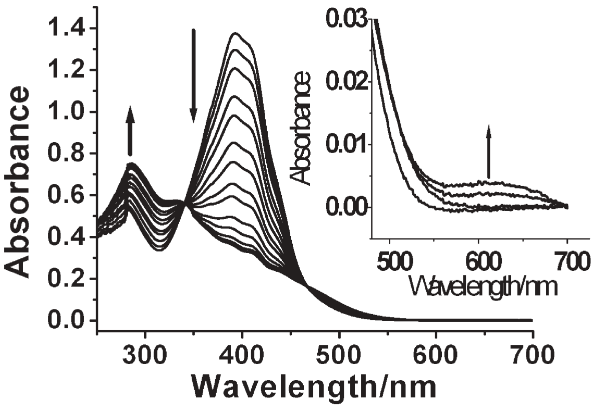


Fig. 20 Absorption changes of BTE-AZO in THF (1.0×10^{-5} mol L^{-1}) upon irradiation at 365 nm.

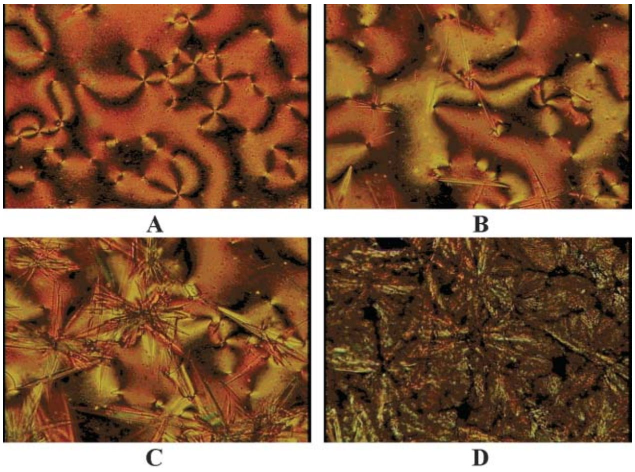
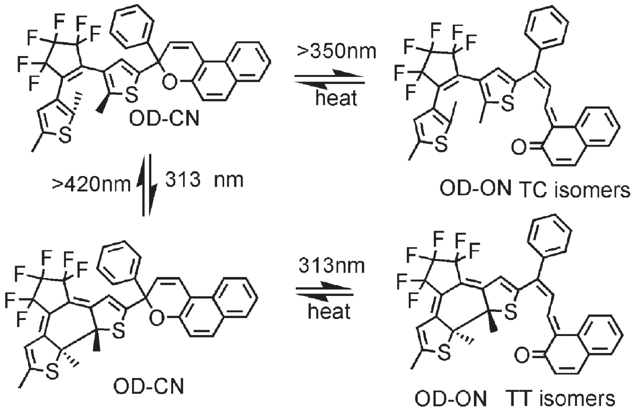


Fig. 21 Crossed polarized optical texture micrograph of BTE-AZO (A, B, C and D on second cooling at 157.8, 122, 109 and 80 °C, respectively).

Multi-addressable photochromic switches

Multi-addressable organic materials stimulated by light is currently a very active research topic and such systems are expected to be of great importance for optical computing as logic gates, field-effect transistors and high density data storage systems. The goal is a miniaturization of functional elements down to the molecular level, which could result in a markedly increased performance as a consequence of ultrahigh density of the functional elements compared to that of current devices. A large number of multi-addressable photochromic switches have been reported.[4]

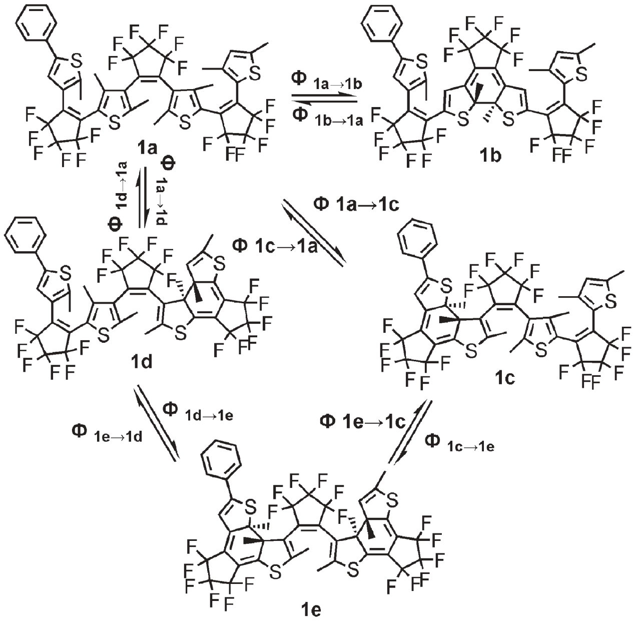
Frigoli and Mehl[50] reported a multiple addressing in a hybrid biphotochromic system (OD-CN) consisting of a naphthopyran unit and a diarylethene group as shown in



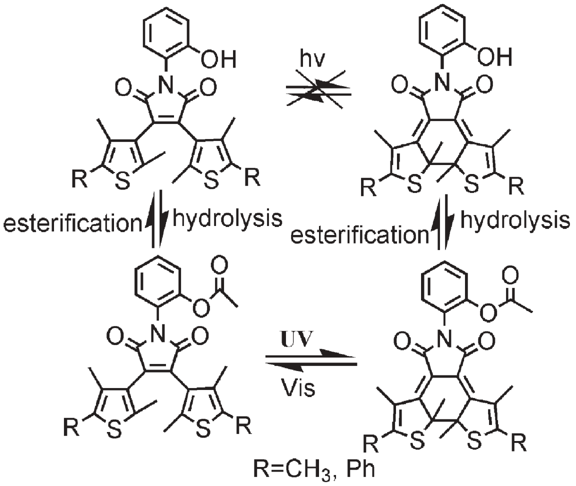
Scheme 10 Photochemical reactions of the hybrid OD-CN showing four photochromic states reported by Frigoli and Mehl.[50]

Scheme 10. An important feature in the design of this system is the different absorption behaviours of the naphthopyran and the BTE groups which are connected through a carbon–carbon single bond. The different behaviour of this two-component photochromic system is essentially bistable. The naphthopyran units open to a number of isomers upon irradiation, most of which revert back thermally to the closed forms in the dark, which results in a multi-addressable hybrid photochromic system. Four different states were observed in this system, which are characterized by very different absorption properties and can be addressed in the photon mode.

Irie and co-workers[51] synthesized a fused bisthienylethene full-colour photochromic trimer (Scheme 11), which has three bisthienylethene moieties: bis(2-thienyl)ethene, (2-thienyl)(3-thienyl)ethene and bis(3-thienyl)ethene, with two thiophene rings in common. There are three possible designs for the fused trimers that have three colour components. The yellow, red or blue components can be located in the central unit. However, the trimer showed full-colour photochromic performance by choosing appropriate wavelengths of light. The advantage of a one-molecule system over mixed systems is high image resolution, constant colour balance in a large area, and possible application to a multifrequency single-molecule memory.



Scheme 11 Photochromic reactions of the full colour BTE trimer reported by Irie and co-workers.[51]



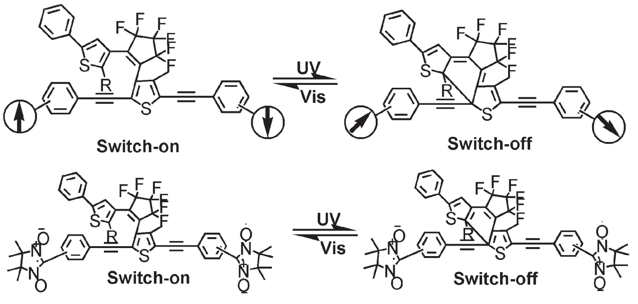
Scheme 12 Chemically gated diarylethene derivatives reported by Irie and co-workers.[51]

In addition, Irie and co-workers[52] reported on the synthesis of chemically gated diarylethene derivatives containing hydroxyphenyl groups (Scheme 12). The excited states of the molecule are efficiently quenched by intramolecular proton transfer. Therefore, they are not photochromic. On the other hand, when the hydroxyl group is protected by esterification, the esterified diarylethenes are expected to undergo typical photochromic reactions. Such chemically gated systems can be applied to display materials, memory media as well as molecular logic gates.

Photochromic magnetic switches

Molecular magnetism can be photo-controlled by using spin crossover phenomena, such as light-induced excited spin state trapping, light-induced thermal hysteresis and ligand-driven light-induced spin change. Several systems using photochromic units are also reported. Among them, the most effective photo-switching of intramolecular magnetic interaction has been observed by using diarylethene derivatives as photo-switching units. The switching of molecular magnetism is based on the molecular structure change of the diarylethene unit; the open ring isomer of the biradical has a disjoint configuration while the closed-ring isomer has a resonant quinoid structure. This difference in the electronic structure brought about the change in the exchange interaction.

Recently, Tanifuji, Irie and Matsuda[53] proposed a new diarylethene with a 2,5-bis(arylethynyl)-3-thienyl switching unit, in which two nitroxide radicals are placed in the same aryl unit and the π-conjugated chain is extended from the 2- and 5-positions of the thiophene ring in one aryl unit of the diarylethene (Scheme 13). Three types of aryl groups, 2,5-thienylene, *p*-phenylene and *m*-phenylene, were used in the arylethynyl moiety. The diarylethene photo-switching units



Scheme 13 Photo-switching of the intramolecular magnetic interaction.

have an extended π-conjugated chain on one side of the diarylethene. The photochromic reactivity was dependent on the arylethynyl group. Diarylethenes with an *m*-phenylene group showed efficient photochromic reactivity. Along with the photochromic reaction the diarylethenes showed photo-switching of an ESR spectrum originating from the change in the magnetic interaction between two unpaired electrons. The open-ring isomer showed stronger exchange interaction than the photo-generated closed-ring isomer. The magnetic interaction between the two radicals *via* the π-conjugated chain was altered by photocyclization.

Conclusions

In this article we present and report on new photochromic molecular switches based on bisthienylethene units. The new photochromic fluorescent switches show fast and promising behavior, especially at the single molecule level. Fluorescent switches with high contrast and near-IR fluorescent switches are most promising to realize non-destructive readouts in high density data storage and fluorescent probes. There are two types of photochromic bisthienylethene polymer switches: main-chain polymer and pendent polymer. The most attractive photochromic polymeric switches are multi-addressable or multi-colour photochromic copolymers which show multi-state photochromic reactions, which can be useful for solid photochromic materials employed for high density data storage. Photochromic chiral switches can be observed in a supramolecular system by self-assembly in for instance low molecular weight photochromic organogels. In addition, two-photon absorption (TPA) photochromic materials have possible application in three-dimensional optical data storage media.[54] The molecular design of photochromic liquid-crystal switches is hopeful to combine liquid-crystalline and photochromic units in molecular systems, which promises to be very useful in optical technological devices. Multi-addressable switches fused in a photochromic molecular system can realize full-colour photochromism, which will minimize a record dot in high density optical storage. In recent years, photochromic molecular assemblies have been extensively studied as information storage systems and have become known as chemical computers. Willner′s group and we[55] realised the integration of a BTE photochromic unit with transducers that allow the electronic readout of the logic operation is essential if any practical use of these systems is going to be achieved.[56] This new technique couples electrochemical and photochemical stimuli, which generates a write–read–erase information processing system with a set/reset option. This breakthrough has the potential to enhance the complexity of information that can be processed by molecular units.[56] Obviously, for long-term stability and environmental durability, developing new photochromic materials that can be processed into large-area solid films that display excellent photochromic properties remains the ultimate goal.

Acknowledgements

The authors thank the National Natural Science Foundation of China (90401026 and 20476027), National Basic Research 973 Program (2006CB806205) and the Scientific Committee of Shanghai for financial support. We thank Dr Quan Li (Kent University, USA) for his assistance to measure the liquid-crystal properties of BTE-AZO and Prof. S. X. Qian (Fudan University, Shanghai) for their measurements of two-photon properties of photochromic compounds. H. T. thanks all the students who have worked on photochromic materials in his group.

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