

# Recent progresses on diarylethene based photochromic switches

He Tian\* and Songjie Yang

Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, China. E-mail: tianhe@ecust.edu.cn; Fax: +86-21-64252288

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Organic photochromic materials have received considerable attention because of their potential for photonic applications, especially for fast and high density data storage. In 2000, *Chemical Reviews* published a special issue on photochromic materials including a review about the properties and applications of diarylethene photochromic compounds. Since then much impressive progress has been made in this area. Various new diarylethene derivatives have been prepared and examined. The *tutorial review* presented herein describes developments in diarylethene-based molecular switches made in the last three years. In addition, the synthetic aspects of diarylethene photochromic compounds, which are important issues and neglected in most previous reviews, have been included.

## 1 Introduction

Concurrent with the rapid development of modern science and technology, materials for fast and high density data storage are in high demand. The information is expected to be processed at molecular or atomic-scales with response times ultimately within nanosecond or picosecond levels. Organic photochromic materials have shown to be one of the most promising of memory media that meet such demands. With organic photochromic materials, reading and writing of information are accomplished in all-photon mode. If successfully developed, these materials can provide ultra-high data storage densities and fast data-processing rates.

Photochromism is the term used for a reversible photo-induced transformation of a molecule between two isomers whose absorption spectra are distinguishably different. In general, photo-generated colored isomers return to the initial colorless isomers either photochemically or thermally. Some physical property of a

photochromic compound may be controlled by light, and the development of such molecular systems is of importance to the creation of optoelectronic and photo-optical devices which operate at both molecular and supramolecular levels. So in the past decade there has been an ever-growing interest in the synthesis, properties and applications of organic photochromic materials.<sup>1</sup>

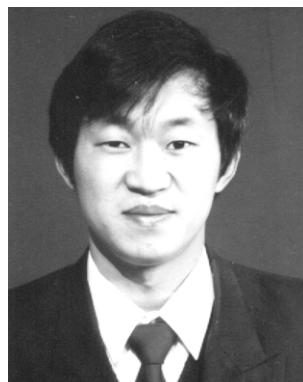
Among many known photochromic systems, diarylethenes bearing two thiophene-derived groups have received the most attention since they are particularly well suited as switching units. In 2000 the special issue on photochromic materials published in *Chemical Reviews*, Irie reviewed the properties and applications of diarylethene photochromic compounds (on page 1685).<sup>2</sup> As a new class of thermally irreversible photochromic switches, they have been found in solution as well as in the solid state to display excellent photochromic properties: excellent fatigue resistance, short response time, high quantum yields, absence of thermal isomerization, and large changes of the absorption wavelength

Professor He Tian received his B.S. degree in organic chemistry from Nanjing University of Science and Technology (Nanjing, China) in 1982. After receiving his M.S. degree in Physics from East China University of Science and Technology (ECUST) (Shanghai, China) in 1986, he studied under the direction of Professor Zhen-Hua Zhu at the Institute of Fine Chemicals late at ECUST, where he received his Ph.D. in 1989. From 1991 to 1993, Prof. Tian worked with Prof. Dr. Karl H. Drexhage (Siegen University, Germany) on organic laser dyes and in 2000 with Prof. Dr. Klaus Müllen (MPIP, Mainz, Germany) on organic photochromic copolymers, both supported by Alexander von Humboldt Foundation. During his sabbatical leave in 2001, Prof. Tian collaborated with Prof. M. G. Finn at The Scripps Research Institute in San Diego, California, USA. Prof. Tian became a full professor and director of the Institute of Fine Chemicals 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 or copolymer dyes and the development of interdisciplinary materials science that determines the electronic and optical properties of the materials. Prof. Tian has published over 110 papers in international journals and four academic books. He has also been awarded 14 Chinese patents. He is currently a member of the International Editorial Board for the *Journal of Dyes and Pigments*.

Dr. Songjie Yang was born in 1967 in Shangdong, China. He received his B.S. and M.S. degrees in applied chemistry from East China University of Science and Technology (ECUST), (Shanghai, China) in 1989 and 1992, respectively. From 1998 to 2001, Dr. Yang studied under the direction of Prof. He Tian at the Institute of Fine Chemicals at ECUST, where he received his Ph.D. in 2001 for his research on photostability organic functional dyes. His current research interests are focused on the synthesis, photochemistry and photophysics of organic functional dyes and also the development of interdisciplinary materials science.



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between the two isomers.<sup>1–4</sup> In fact, they are the most promising photochromic compounds in terms of practical applications due to their fatigue resistant and thermally irreversible properties.

## 2 Properties of diarylethene photochromic compounds

In the 1980s–1990s, Irie's group and Lehn's group synthesized a series of diarylethenes bearing two thiophene-derived groups I and II.<sup>1–3</sup> These diarylethene derivatives are promising artificial photoswitching molecules because of their outstanding fatigue-resistant photochromic performances. It should be noted that when the 4-position of the thiophene ring is not substituted by a methyl or another group, the derivatives of diarylethenes with thiophene rings are not fatigue resistant, and easily decompose upon photoirradiation.<sup>5</sup>

The molecular switches based on these diarylethene photochromic compounds can undergo reversible photocyclization between their unconjugated open-ring isomer (o) and conjugated closed-ring isomer (c) under irradiation using a light source of appropriate wavelength. Dithienylethene molecules in the open form may exist as two conformational isomers, *anti*-parallel and parallel conformations, as shown in Fig. 1. The conformers exchange even at room temperatures. The photocyclization reaction can occur only from the *anti*-parallel conformer upon irradiation with UV light, indicating that the *anti*-parallel conformation is photoactive, while the parallel conformation is photochemically inactive. Therefore, the quantum yield for the cyclization reaction is dependent on the ratio of these conformations. The population of the two conformers is usually about 1:1, so the highest cyclization quantum yield of diarylethene is about 50%.<sup>2,6</sup>

As increasing the photoactive *anti*-parallel conformation could result in an increase in quantum yield, Takeshita *et al.*<sup>7</sup> designed and synthesized thia[2.3](2,4)thiophenophan-1-ene III, in which two positions of the thiophene rings are bridged at 2- and 4-positions by a considerably long  $-\text{CH}_2\text{SCH}_2-$  linkage. They found the quantum yield of this compound for the photocyclization reaction to be 1.6 times higher than that of the corresponding non-bridged dithienylethene. This is due to the fixation of the photoactive *anti*-conformation by bridging the dithienylethene.

Up to 2001, light is the only trigger that will induce the transformation of 1,2-bis(heteroaryl) ethene systems from the open-form to the closed-form. By incorporating a quinine moiety into the molecular switch, for example, Liebeskind *et al.*<sup>8</sup> synthesized a novel class of molecular switch system based on the 2,3-bis(heteroaryl)quinines, in which a ring-closing reaction is catalyzed by strong Lewis acids such as  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ , and triflic acid to generate a switch-closed state efficiently. Their suggested mechanism for the acid-induced ring closure is shown in Fig. 2.

## 3 Development of photochromic switches

Diarylethene photochromic compounds have received increasing attention as materials of choice for designing multi-stable switch units with light controlled electrochemical and optical properties. Useful properties that may be varied include luminescence,<sup>9–14</sup> viscosity,<sup>15</sup> and optical rotation.<sup>16</sup> The remarkable light-triggered behavior of these switches relies on a photochromic dithienylethene "switch unit".

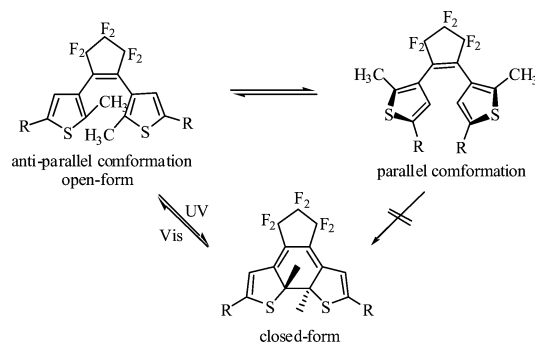


Fig. 1 Photochromic reaction of diarylethenes.

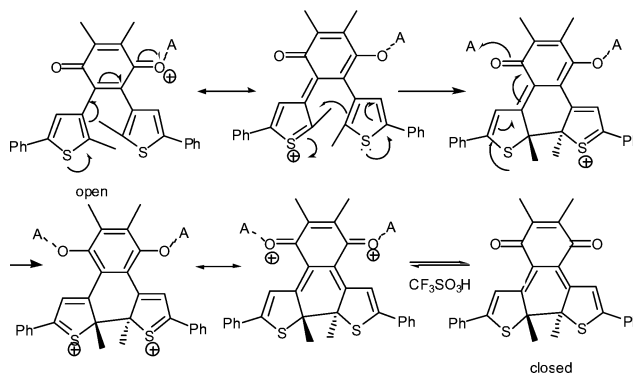
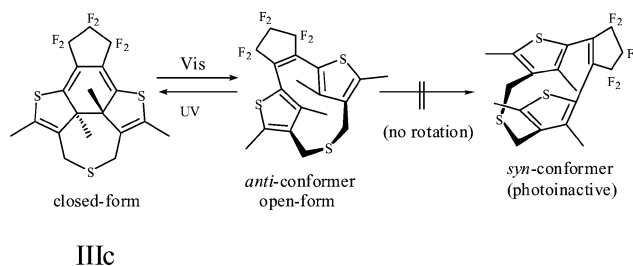
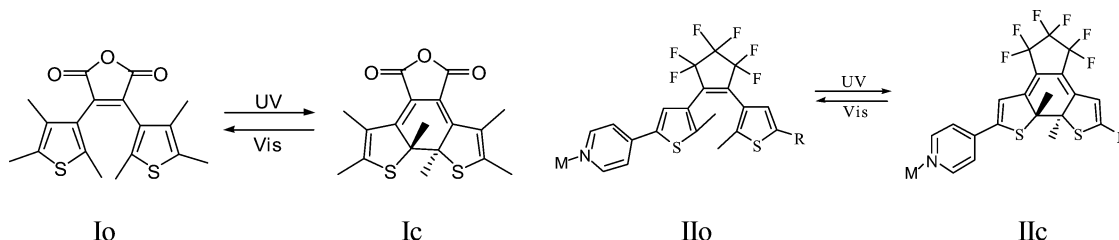


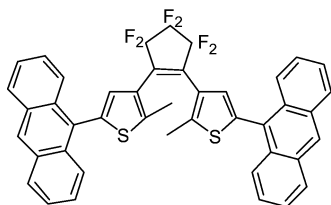
Fig. 2 Mechanism of acid-induced ring closure of 2,3-bis(thienyl)quinine

### 3.1 fluorescent photochromic switches

Fluorescent photochromic materials attract strong interest for their possible applications in optical memory as well as in fluorescent probes. In particular, fluorescent diarylethenes, which show reversible change in fluorescence intensity with photochromic reaction, are useful for the non-destructive optical read-out system. Kryschi *et al.* studied the interplay of photochromism and fluorescence in fluorescent photochromic molecule IV, where coupling of the two anthryl substituents is present across the closed isomer but absent in the open isomer. The blue fluorescence of the open isomer of the photochromic molecule IV is suppressed by the ring-closure reaction.<sup>9</sup> They thought reacting and non-reacting conformers of the open isomer for this molecule were present, which is a necessity when efficient photochromic and fluorescence properties are to be combined in a single molecule. Obviously, the coexistence of reacting non-fluorescent and fluorescent non-reacting conformers decreases the efficiency of both processes. Efficient switching of fluorescence is taking place not between *on*



and *off* states but between stronger and weaker fluorescence of a sample.



IV

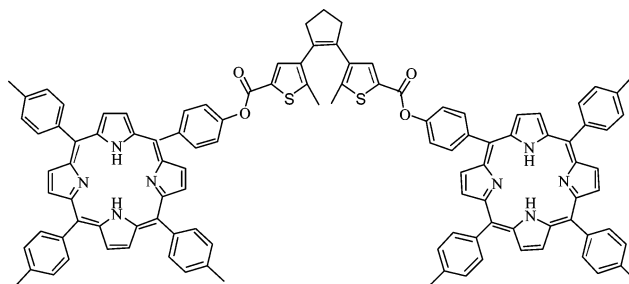
Recently, Irie *et al.*<sup>10</sup> designed and synthesized a fluorescent photoswitching molecule in which photochromic 1,2-bis(2-methoxy-4-phenyl-3-thienyl)perfluorocyclopentene and fluorescent 1,5-dimethoxy-9,10-bis(phenylethynyl)anthracene are linked through a spacer. They revealed that the fluorescence of the anthracene moiety was switched on and off with alternate ultraviolet and visible light irradiation when single photochromic molecules were embedded in a polymer film. This digital reversible switching of the fluorescence of diarylethene molecules attracted significant attention, as this compound may find applications in the design of erasable media for ultra-high density optical data storage.

Novel bis(thienyl)ethene-based tetraazaporphyrin and phthalocyanine hybrids (BTE-TAPs) synthesized in our lab,<sup>11,12</sup> shown in Fig. 3, undergo open-to-closed ring or closed-to-open ring photoisomerization in different quantum yields by irradiation with 365 nm or 730 nm light. Their maximum extinction coefficients are nearly a hundred times higher than those of ordinary bis(thienyl)ethenes. The near-IR luminescence of these compounds, excited in a region away from the one inducing photocyclization, can be regulated in a reversible manner by the photoisomerization of the bis(thienyl)ethene moiety induced by UV-light, and even two novel BTE-TAP Pt(II) complexes show phosphorescent switching property in the solid state.<sup>12</sup>

Fluorescence resonance energy transfer (FRET) is a physical process in which energy is transferred non-radiatively from an excited molecular fluorophore (donor) to a chromophore (acceptor) *via* long-range dipole-dipole coupling. Jares-Erijman and Irie *et al.*<sup>13</sup> selected Lucifer Yellow I as the donor and bis(thienyl)ethene as the acceptor to build fluorescence molecules **V**, because the

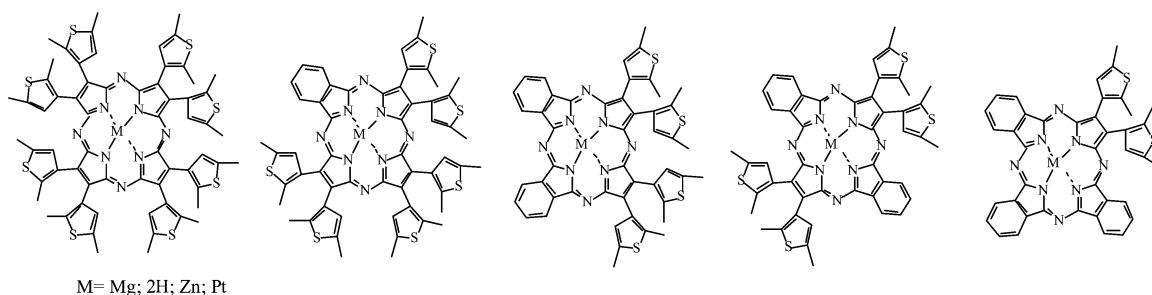
absorbance of both the closed and the open forms of the bis(thienyl)ethene are minimal within the spectral region of the donor's absorption maximum. They found that the fluorescent emission of the donor is reversibly modulated by cyclical transformations of the photochromic acceptor with irradiation of appropriate UV and visible light respectively. Only the closed form of the bis(thienyl)ethene has an absorption band overlapping the emission band of the donor, which provides the means for reversibly switching the process of FRET on and off, allowing direct and repeated evaluation of the relative changes in the donor fluorescence quantum yield.

Norsten and Branda synthesized a photochromic hybrid **VI**, where porphyrin macrocycles are attached to the ends of the 1,2-bis(3-thienyl)cyclopentene backbone.<sup>14</sup> The luminescence intensity of the porphyrin greatly depends on the state of the 1,2-(dithienyl)cyclopentene photoswitch. In the *open* form, the porphyrins display significant fluorescence intensity at 655 nm when excited at 430 nm. Irradiating the *open* form at 313 nm, the photocyclization reaction was carried out, and the non-fluorescent *closed* form was produced. Back irradiation at wavelengths greater than 480 nm regenerated the *open* form and restored the original emission spectrum. That is to say, the intensity of porphyrin fluorescence is conveniently regulated by alternate irradiation at 313 nm and at the wavelengths greater than 480 nm.



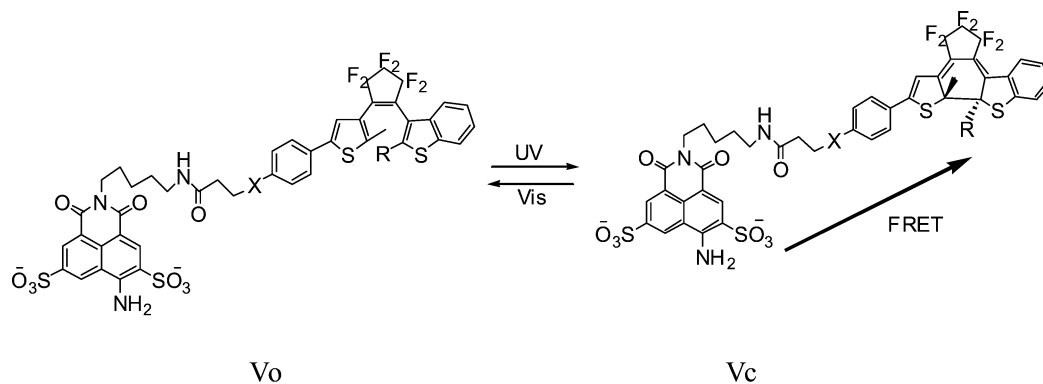
VI

In 2001, Irie's group synthesized several diarylethenes having a fluorescent 2,4,5-triphenylimidazole chromophore, for example **VII**, which underwent reversible photocyclization reactions by alternate irradiation with UV ( $\lambda = 366$  nm) and visible ( $\lambda > 480$



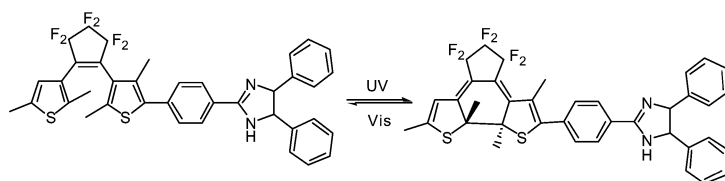
M= Mg; 2H; Zn; Pt

Fig. 3 The bis(thienyl)ethene-based tetraazaporphyrin and phthalocyanine hybrids (BTE-TAPs).



V<sub>o</sub>

V<sub>c</sub>

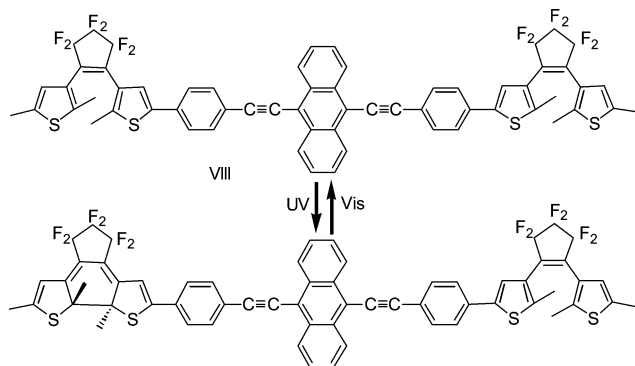


VIIo

VIIc

nm) light.<sup>15</sup> The fluorescence intensity also reversibly changed with the photochromic reactions, and the fluorescence quantum yields decreased with the increase in photocyclization quantum yields.

In photochromic dithienylethene **VIII**, containing two photochromic dithienylethene moieties linked to a fluorescent bis(phenylethynyl)anthracene residue, showed a reversible change in its fluorescence intensity by photoisomerization of the dithienylethene units (fluorescence quantum yield between 0.83 and < 0.001).<sup>16</sup> The dye also exhibited a laser emission and the emission intensity was reversibly switched by alternative irradiations with 313 nm light and  $\lambda > 500$  nm light.



Dithienylethene-bridged donor–acceptor triad **IX**, where the photoisomerizable dithienylethene (DTE) bridge, directly attached to the pyridinium acceptor, is separated from the anthracene donor by incorporation of a methylene  $\sigma$ -spacer, is capable of reversibly ON/OFF photoswitchable (photoinduced) charge separation.<sup>17</sup> In the open form **IX**, where conjugation is markedly restricted within the dithienylethene bridge, excitation of the anthracene donor leads to an intramolecular charge separation (ON state). After photocyclization to the closed isomer, where the conjugation is extended over the whole dithienylethene pyridinium subunit, the intra-

molecular charge separation is completely suppressed (OFF state).

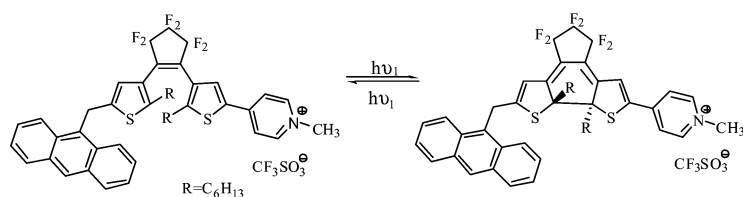
In dithienylethene-bridged diporphyrins, the close attachments of the porphyrin chromophore into the dithienylethene lead to loss of its photochromic reactivity, probably through the intramolecular energy transfer quenching but the pertinent insertion of a spacer between the dithienylethene and porphyrin ensures the photochromic reactivity of the dithienylethene moiety that can reversibly regulate the fluorescence of the porphyrin moiety.<sup>18</sup> These results encourage the extension of this strategy to the control of intramolecular electron transfer and charge separation by the reversible dithienylethene photoisomerization.

A new bis(5-pyridyl-2-methylthien-3-yl)cyclopentene **X**, as a photochromic bridging ligand, has been synthesized in our lab recently.<sup>19</sup> We observed the photochromic processes of the typical pyridine-tethered 1,2-bis(thienyl)ethene in the presence or without zinc ion. The photochromism was strongly enhanced upon the addition of  $\text{Zn}^{2+}$  and the photochromic reaction proceeded effectively from the open to the closed-ring form.

The photochromic luminescent system has limited use in data processing applications, because excitation resulted in photochemical interconversion of the photochrome, which may be a result of the emission wavelength slightly overlapping with the active absorption band associated with the ring-opening process. To circumvent this drawback, Norsten and Branda prepared the optical switch **XI** which phosphoresces at 730 nm instead of fluorescing and thus emits light energy far beyond the photochemically active absorption bands.<sup>20</sup> The excitation wavelengths exist in a narrow window of the visible spectrum between 400 and 480 nm, and the emission intensity of **XI** can be modulated by photochemically toggling between open and closed forms.

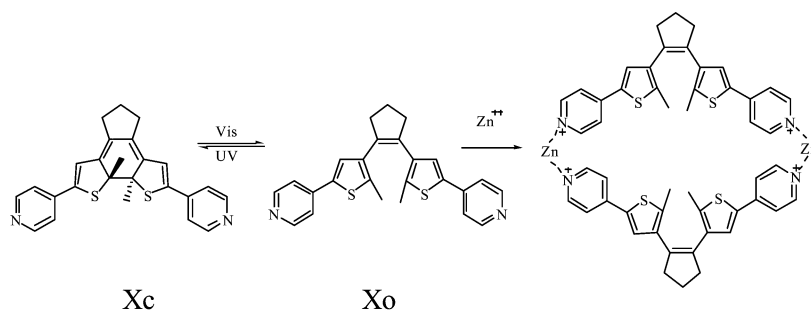
### 3.2 Supramolecular switch

The use of dithienylcyclopentenes in switchable supramolecular systems will expand the scope of available transformations and will lead to thermally stable systems. Moore's group prepared dithienyl-



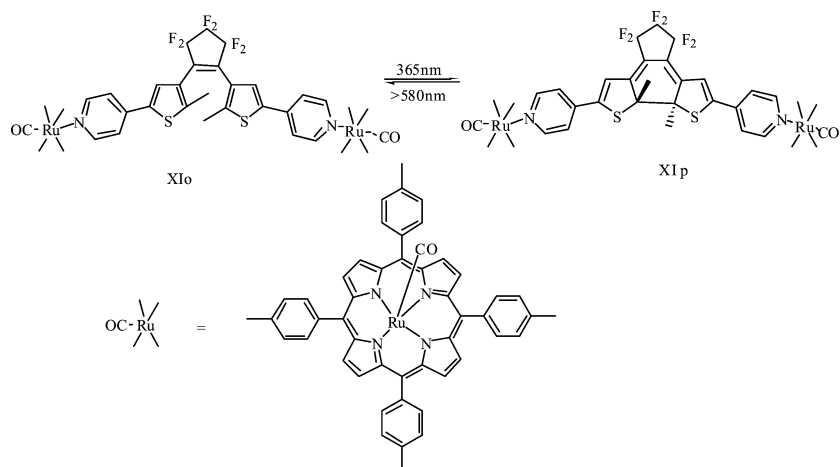
IXo

IXc



Xc

Xo



lethene(DTE)–porphyrin(P)–fullerene( $C_{60}$ ) triad **XII** as an electron-transfer switch, which showed no significant porphyrin fluorescence in either open or closed forms.<sup>21</sup> When the DTE is in the open, colorless form (DTEo), the porphyrin singlet excited state generated by visible illumination undergoes photo-induced electron transfer with a time constant of 25 ps to the  $C_{60}$  unit to give DTEo–P<sup>+</sup>– $C_{60}$ <sup>•-</sup> with a quantum yield of unity, which decays to the ground state with a time constant of 3 ns. When the DTE is in the closed colored isomer (DTEc), the porphyrin first excited singlet state generated by UV illumination is quenched by the energy transfer to DTEc in 2.3 ps, precluding significant electron transfer to the fullerene. The photonic switching of photo-induced electron transfer in **XII** can be cycled many times, and could prove useful in construction of molecular-scale optoelectronic devices for digital logic and memory applications.

In order to promote the formation of supramolecular assemblies in solution by hydrogen bonding, Feringa *et al.*<sup>22</sup> developed a new self-assembling system based on diarylethene photochromic switches with amide groups. They found that the bis-amide photochromic switch **XIII** self-assembles in apolar solvents through a cooperative association mechanism, and forms extensive aggregates resulting in highly viscous solutions. Most remarkably, the reversible photoswitching of **XIII** from the open form to the closed form causes a change in the extent of aggregation, which is accompanied by a decrease in viscosity. So the viscosity was successfully modulated by appropriate illumination, which the researchers attributed to different molecular properties like shape and conformational freedom of the open and closed form of diarylethene switch **XIII**.

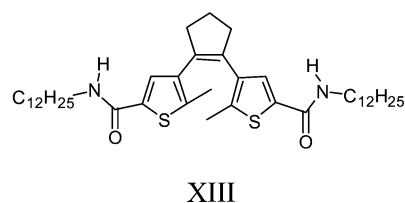
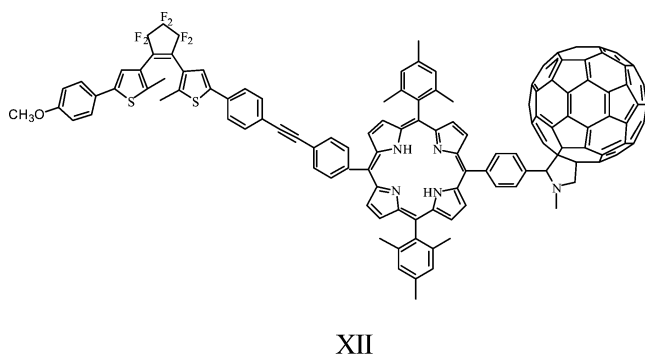
With the goal of realizing a non-destructive write–read–erase system, Branda and co-workers prepared two (*R,R*- and (*S,S*)-enantiomers of photochromic bis(oxazolines) compounds from 1,2-bis(5-chloro-2-methyl-3-thienyl)cyclopentene. By adding an equimolar amount of the two ligands in deoxygenated dichloroethane to the benzene complex of copper(I) trifluoromethane sulfonate under argon, they obtained copper(I) complexes **XIV**.<sup>23</sup> In the presence of copper(I), both the open and closed isomers strongly rotate light throughout the UV/Vis spectrum. For example,

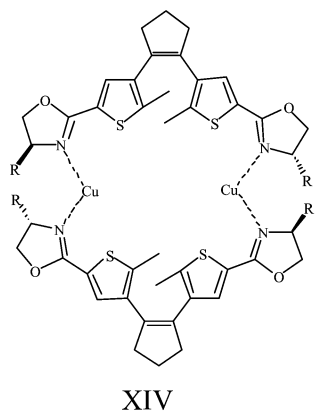
the angles of optical rotation at 450 nm and 475 nm can be regulated by toggling between the open and closed isomers by alternate irradiation at 313 nm and at wavelengths greater than 458 nm. They believed that this system could be used for reversible data processing. Although the lack of stability of the complex as well as the fact that the optical rotation signal can only be read in liquid solution will pose significant challenges for practical applications.

In 2002, Lapouyade *et al.*<sup>24</sup> prepared a new dithienylethene switch **XV**, in which a *p*-phenylaza-15-crown-5 acts as an ionophore and a formyl group acts as a strong electron-withdrawing group. They realized an efficient optical release of calcium ions in acetonitrile. Similarly, the stability and sensitivity of the supramolecular assemblies need to be improved.

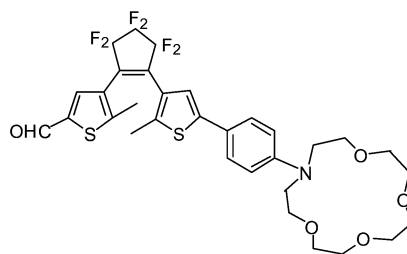
Although intermolecular magnetic interaction can be photochemically controlled by several methods, photocontrol of intramolecular magnetic interaction in a molecule had not yet been achieved until 2000. Matsuda and Irie developed a photochromic system **XVI** by incorporating two nitronyl nitroxides into a photochromic diarylethene spin coupler, and successfully realized the photoswitching of the intramolecular magnetism.<sup>25</sup> They revealed the anti-ferromagnetic interaction between two nitronyl nitroxides to be remarkably increased when the diarylethene spin coupler was switched from the open-ring isomer **XVIo** to the closed-ring isomer **XVIc**. The quantum yield of cyclization reaction of **XVIo** was about 1/8 of the value of the corresponding compound without nitronyl nitroxides. The cycloreversion reaction was also strongly suppressed. This is due to the contribution of the resonant quinoid structure **XVIc**.

One year later, they synthesized the dimer **XVII** where a diarylethene dimer was used as a photoswitching core and two nitronyl nitroxide radicals were placed at both ends of a diarylethene.<sup>26</sup> When a diarylethene dimer is used as a switching unit, there are three kinds of photochromic states; open–open (OO), closed–open (CO), and closed–closed (CC) by alternate irradiation with UV and visible light. The photochromic reaction proceeded effectively from open–open to closed–closed. Each diarylethene chromophore served as a switching unit to control the magnetic

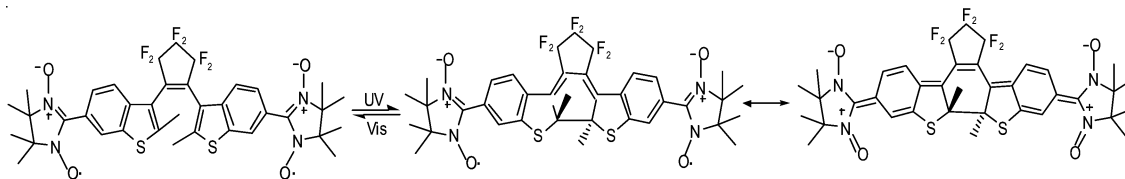




XIV



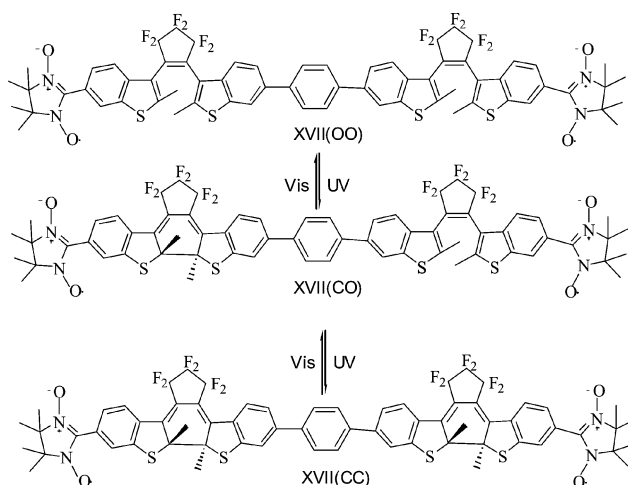
XV



XVIo

XVIc

interaction. The magnetic interaction between end nitronyl nitroxide radicals was controlled by the switching units in series. The magnetic interaction in **XVII** (OO) and **XVII** (CO) was much smaller than **XVII** (CC). While **XVII** (OO) and **XVII** (CO) were in the “OFF” state, **XVII** (CC) was in the “ON” state.

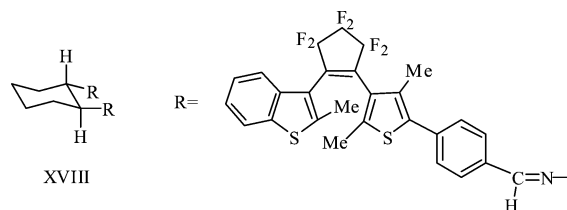


### 3.3 Liquid crystal switch

Over the past decade, considerable efforts have been made to develop light-driven ferroelectric liquid crystals (FLC) spatial light modulators (photo-switches) for potential applications in optical computing, dynamic holography, telecommunications, and optical data storage. Doping 1,2-bis[5'-(4''-heptoxyphenyl)-2'-methylthien-3'-yl]perfluorocyclopentene in the achiral SmC liquid crystal 2-(4-butyloxyphenyl)-5-octyloxy pyrimidine, where the 4-heptyloxyphenyl substituent increases the aspect ratio of the dithienylethene chromophore to make it more compatible with the lamellar structure of the SmC\* phase and shifts the absorption maximum of the ring opened form to longer wavelengths to avoid overlap with the absorption spectrum of the FLC host, Lemieux *et al.*<sup>27</sup> showed that the spontaneous polarization of a ferroelectric liquid crystal could be modulated reversibly *via* photo-isomerization of the dithienylethene dopant. The magnitude of the photo-modulation increased with dopant concentration up to 3 mol%, and the resulting photoswitch is fatigue resistant and bistable.

In 2000, Irie's group reported on the development of an efficient and robust photochromic trigger, a chiral cyclohexane **XVIII**

having two diarylethenes, for the photoinduced large pitch change in the chiral nematic phase.<sup>28</sup> The switching cycle was performed more than 50 times without deterioration of the liquid-crystalline phase.

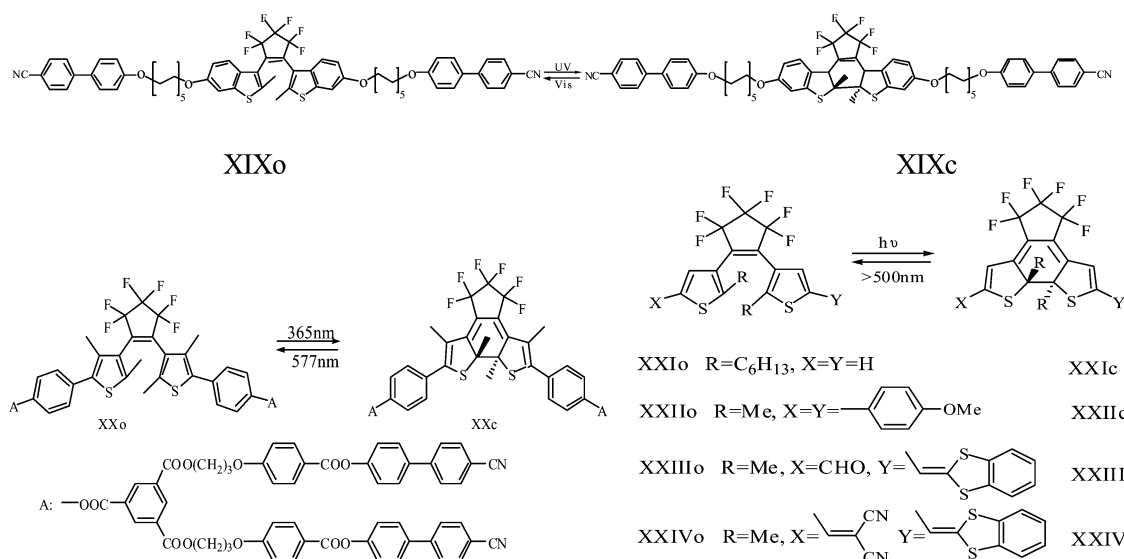


XVIII

Bobrovsky *et al.*<sup>29</sup> studied the phase behavior and optical properties of the mixture based on cholesteric copolymer with 6 wt% of a photochromic dithienylethene dopant 1,2-bis(2-ethyl-5-ethylthio-3-thienyl)hexafluorocyclopentene to find that planar-oriented films of the mixture possessed a selective light reflection in the visible region of the spectrum. UV irradiation of the mixture film led to the appearance of an intense absorbance peak in the spectral range coinciding with the selective reflection band. They associated the process with the photocyclization of the dopant and the “degeneration” of the selective light reflection.

For the photochromic liquid crystal **XIX**, a 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene system connected to two cyanobiphenyl groups (the mesogens) *via* spacers of ten methylene groups, Frigoli and Mehl investigated the influence of the photochromic group, the spacer lengths and the mesogens on the properties of such systems.<sup>30</sup> Their results indicated that in the system of separate individual functionalities of a photochromic core and mesogens linked by flexible spacers in a modular approach, the mesomorphic phase structure and range, and the absorption characteristics, can be modulated in a controlled manner by irradiation.

Similarly, Chen *et al.* successfully designed and synthesized morphologically stable photo-responsive glassy nematic liquid crystals (**XX**, for example) comprising a dithienylethene core functionalized with nematogens for processing into a mono-domain glassy nematic film in which the photo-responsive core's electronic transition moment was spontaneously aligned with the nematic director.<sup>31</sup> As a result, refractive indices and optical birefringence can be modulated to a large extent by photochemical means. They revealed that both the type and the number of nematic pendants per molecule are critical to the desired thermo tropic property and stability against thermally induced recrystallization.



### 3.4 Multi-addressable photochromic switch

Multi-component systems based on the combination of several constituents displaying different photochromic properties are of great interest since they may allow high-density storage as well as non-destructive read-out. Fernandez-Acebes and Lehn selected four different photochromic compounds **XXI–XXIV** with well-separated absorption wavelengths that the compounds displayed in their closed forms to set up multicolor systems based on multi-component mixtures of these compounds.<sup>32</sup> They demonstrated that absorption properties of the multi-component mixture in solution as well as on silica-gel plates can be modulated by controlling the wavelength, duration, and slit-width of the irradiation applied. The possibility of mixing different photochromic compounds provides a very rich, practically infinite optical diversity of combinatorial nature.

The development of more complex systems that integrate several switchable functions into a single molecule is also in progress in molecular switching technology. In 2001, Daub *et al.*<sup>33</sup> investigated photophysics and photochemistry of multi-state switching of two covalently merged biphotochromic systems 1,8-dihydro-2,3-bis(2,5-dimethyl-3-thienyl)azulene-1,1-dicarbonitrile **XXV**. The dihydroazulene (DHA)–dithienylethene (DTE) conjugate **XXVA** is photochemically converted into the dihydrothienobenzothiophene (DHB) isomer **XXVC** and the vinylheptafulvene (VHF) isomer **XXVB**, as shown in Fig. 4. That is to say, it is a multi-

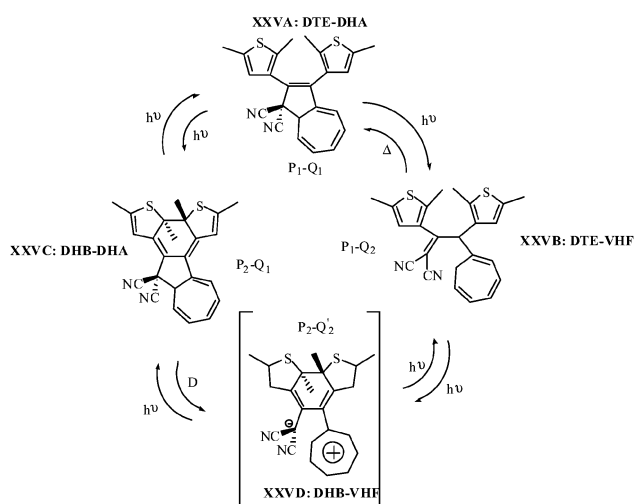


Fig. 4 Cyclic multi-state switching of system **XXV**.

addressable switching system with four addressable states co-existing within the same molecule. However, its practical applica-

tion is limited due to the thermal reversibility of all states in most cases.

A thermally stable, multi-addressable, all-photo mode system is more desirable as it will benefit from the fast response times and the ease at which monochromatic light can be tuned and focus when it is used as the switching stimulus. Branda *et al.*<sup>34</sup> presented an all-photon mode multi-addressable photochromic system **XXVI** comprised of covalently united photochromic 1,2-dithienylcyclopentene (DTE) and phenoxynaphthacenequinone (PNQ) derivatives, where all four states were accessible using light energy as the only stimulus, as illustrated in Fig. 5. Because the low-energy

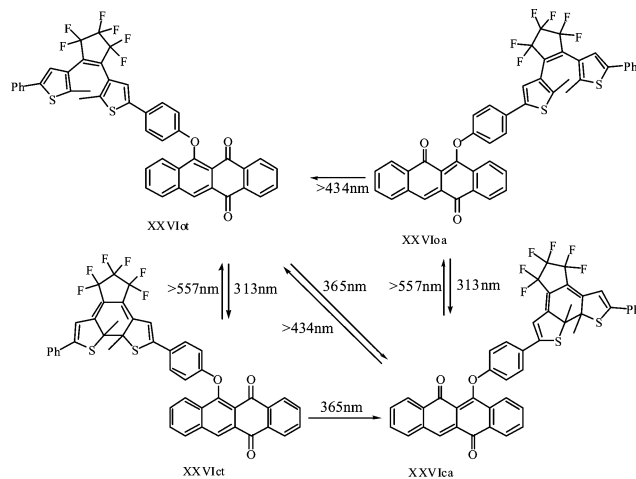
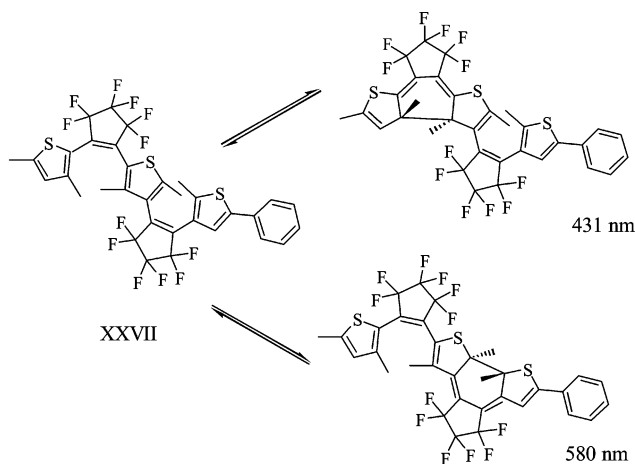


Fig. 5 The mode of action of the multi-addressable photochromic switch **XXVI**.

absorption bands of both *trans*- and *ana*-isomers of the PNQ component reside in the narrow region (400–450 nm) between where the ring-open and ring-closed isomers of the DTE component absorb, and both *trans*- and *ana*-isomers of the PNQ component are transparent in the visible spectral region where the ring-closed form of the DTE component absorbs, ring-opening can be selectively triggered without greatly affecting the amount of *trans*- and *ana*-isomer present in the hybrid (**XXVIc**–**XXVIot** and **XXVIca**–**XXVIoa**).

More recent progress on multi-color photochromism is focused on the approach to incorporate two photochromic units in one molecule. Irie *et al.*<sup>4</sup> had designed the non-symmetric molecule **XXVII** (Fig. 6), in which two types of dithienylethene moieties, bis(2-thienyl)- and bis(3-thienyl)-ethene, combined with one thiophene ring in common. The closed-ring isomer of bis(2-thienyl)ethene has the absorption maximum at shorter wavelength than that of bis(3-thienyl)ethene.



**Fig. 6** The multi-color photochromism of the fused dithienylethene **XXVII**.

### 3.5 Crystalline and amorphous photochromic switch

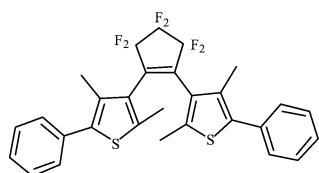
Irie *et al.*<sup>35</sup> studied the single-crystalline photochromism of the diarylethene **XXVIII**, which showed reversible surface morphological changes when alternately irradiated with ultraviolet (366 nm) and visible (>500 nm) light that drove reversible photocyclization reactions. The crystal reversibly shrinks and expands by alternate irradiation with UV and visible light. The shrinkage of the surface is digital, and each step corresponded to a thickness of 1 nm. As the authors pointed out, the crystals that the reversible light-driven shape changes have potential applications as photodriven nanometer-scale actuators.

In 2002, Irie *et al.* prepared a colorless single crystal of diarylethene mixtures by recrystallization of a mixture of **XXIX** and **XXX** (90:10).<sup>36</sup> By changing the wavelength of irradiating light (370 nm and 405 nm light), the two components selectively underwent photochromic reactions in the single crystals, which made the colorless crystals turn red, blue, or purple. The purple, red, and blue colors were completely bleached upon irradiation with visible light ( $\lambda > 450$  nm), and the crystal returned to its colorless state.

The amorphous photochromic compounds are most promising because of their optical transparency and capability to form thin films by the spin-coating method, no dilution of photochromic chromophore relative to composite polymer systems. In 2001, Irie *et al.* synthesized 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene derivatives **XXXI** having 2,4-diphenylphenyl substituents at 6 and 6' positions of the benzothiophene rings, which form a stable amorphous state, and examined their fluorescent property.<sup>37</sup>

At the same time, our group synthesized a novel photochromic amorphous molecule (spiro-BTE) **XXXII** based on bis(thienyl)ethene with a spiro-bifluorene core.<sup>38</sup> The relative high photochromic quantum yields were obtained for the spiro-BTE and the switching stability was observed for more than 200 photochromic cycles. So, the introduction of the spiro center for photochromic molecules provides a new guideline for exploring new amorphous photochromic materials with high  $T_g$ , good photostability.

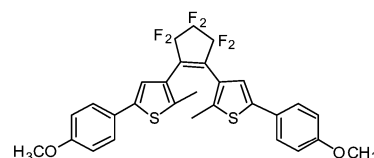
Recently, we synthesized a new amorphous material **XXXIII** based on bis(thienyl)ethene with triphenylamine core, which can form glass amorphous with the glass transition temperature  $T_g$  of 73 °C.<sup>39</sup> It is also found to exhibit photo-mode switchable property.



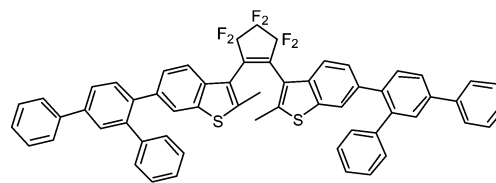
**XXVIII**



**XXIX**



**XXX**



**XXXI**

### 3.6 Polymeric photochromic switch

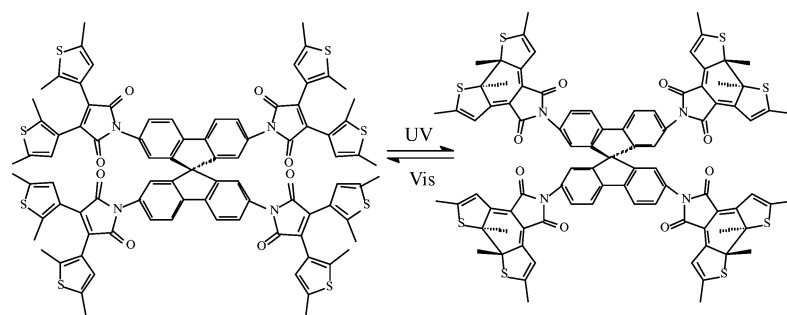
Despite the breadth of the potential applications of photochromic 1,2-dithienylethenes as functional materials, most of the published studies have focused on evaluating the utility of monomeric photochromic systems in solution. Practical application of photochromic technology requires photochromic molecules usually to be embedded in polymeric matrices. In general, precedent photochromic polymers consisted of photochromic molecules either dispersed in a matrix or covalently grafted onto the polymer main chain. The two classical methods have shown limitations: the dispersion method suffers from a concentration limit; the graft method limits the photochromic quantum yield. G. Zerbi *et al.*<sup>40</sup> synthesized a thiophene backbone photochromic polymer **XXXIV**, whose thermal stability was surprisingly higher than that of the monomer and whose cyclization quantum yield was measured as up to 86%, which was the highest in the diarylethene family. In this way they reached a maximum concentration of photochromic molecules without a reduction in the quantum yields. However, the polymer has a very small ring-opening quantum yield of 0.15%. We synthesized a novel photochromic copolymer by reacting 2,3-bis(2,5-dimethyl-3-thienyl)-*N*-allyl maleimide with methyl methacrylate (MMA).<sup>41</sup> Relatively high cyclization and ring opening quantum yields were obtained, even for the copolymers in the film. The switching stability of the photochromic copolymer was observed during over 200 optical cycles. The copolymer degraded only 4.2% under a continuous irradiation with 500–538 nm light in a period of 2 hours.

Horie *et al.*<sup>42</sup> used poly(methyl methacrylate) (PMMA) as a polymer matrix, *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethane (CMTE) as a photochromic compound, and 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a, 4a-diaza-*s*-indacene (PM546) as a fluorescent dye to prepare a polymer film where both CMTE and PM546 were molecularly dispersed. The complete on-off of fluorescence of the fluorescent dye in the polymer film was realized by photoisomerization of the photochromic compound with alternative irradiation of UV and visible light on the PMMA film. The reversible on-off cycles of the fluorescence could be repeated more than 20 times.

Cho and Kim synthesized a new type of fluorescent diarylethene oligomer **XXXV** by connecting diarylethene unit with *p*-phenylenevinylene (PPV) through Wittig polycondensation reaction to overcome the interplay between photochromism and fluorescence.<sup>43</sup> Both the photochromic response and fluorescence quantum yields of the polymer were increased by incorporating PPV unit, as compared to those of monomeric diarylethenes. Such connections of PPV with diarylethene units are an effective strategy for obtaining dual functionality of photochromism and fluorescence with high  $\Phi_f$ .

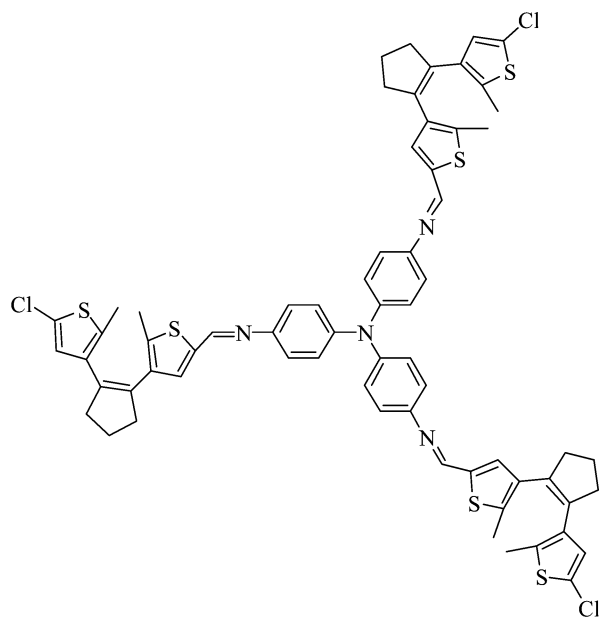
Myles and Branda prepared several novel homopolymers **XXXVI** and **XXXVII** from 1,2-bis(3-thienyl)cyclopentene deriva-



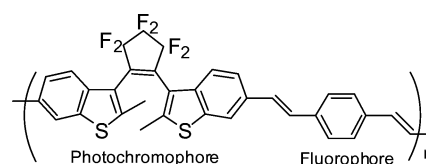


XXXIIo

XXXIIc



XXXIII



XXXV

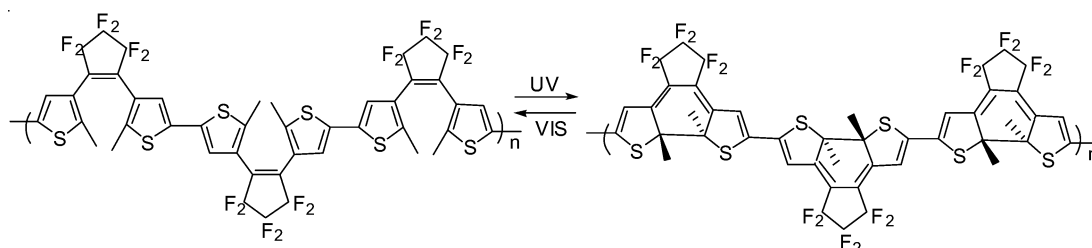
#### 4 Memory media

The photochromic switches used in erasable memory media require that both photochromic states be detectable in the read-out event in a facile and non-invasive manner. Typically, the read-out event relies on the use of UV/Vis spectroscopy to record the spectral changes near the absorption bands corresponding to the two photochromic states. However, these are the same absorptions that induce the ring-opening and ring-closing reactions. Thus, sampling near these photoactive absorption bands inevitably causes partial switching of the photochromic compound and erases the stored information. In the last few years, a strong effort has been made to discover new molecular systems with improved properties aiming at non-destructive read-out.

Recently, we designed and synthesized a novel family of photochromic bis(thiophenyl)ethene–phthalocyanine hybrids.<sup>11,12,45</sup> Among them compound **XXXVIII** proved to be a promising candidate for direct non-destructive read-out by monitoring the absorption changes of Q-band during photochromic processes. The absorption coefficient of compound **XXXVIII** at 609 nm in  $\text{CHCl}_3$  was  $5.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ , high enough for detection by absorption. Semiconductor laser source currently used in DVD-ROMs (650 nm) could be used directly as a light source for “read”. Another semiconductor laser source currently used in CD-recorders (780 nm) could be used directly as a light source for “write”. A strong UV irradiation (e.g. 405 nm blue laser) could be used as the source for “erase”, which induces the transformation between the closed form and the open form, as shown in Fig. 7.

It is well known that organic photochromic compounds allow reversible modulation of a given electronic property by an external trigger such as light. The property changes during the photochromic processes<sup>9–13,21–23</sup> might be used to realize non-destructive read-

tives using ring-opening metathesis polymerization techniques.<sup>44</sup> The novel homopolymers were soluble in common organic solvents, readily cast as thin films, had low polydispersity index, and retained their photochromic properties both in solution and in the solid state. But the photochromic properties of the cross-linked polymer **XXXVII** in solution differed from those of its monomer. They attributed this to the decrease in rotational freedom about the C–C bonds between the thiophene and cyclopentene rings due to the rigidity of each end of the photochromic skeleton joining the cross-linked polymer backbones. Free rotation about these bonds is essential to orient the orbitals for the electrocyclic ring closing reaction, and a reduced amount of ring-closure is not unexpected. The results revealed that we could develop desired polymers whose color could be predetermined by choosing the appropriate pendant functionality.



XXXIV o

XXXIV c

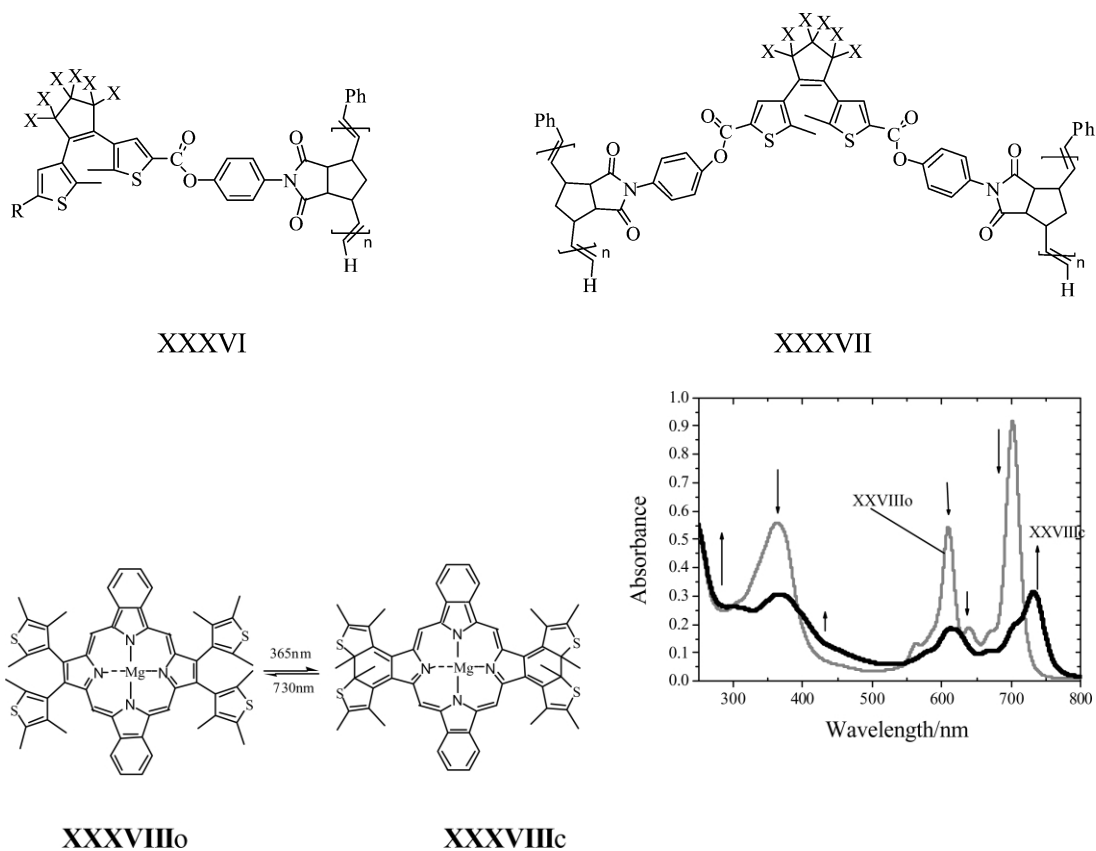
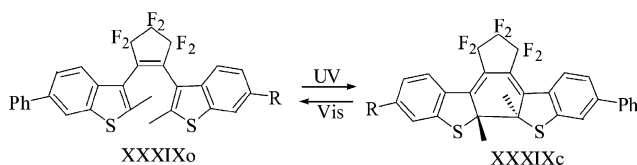


Fig. 7 Realization of non-destructive read-out by the changes in Q-band absorption of XXXVIII.

out. Among them, reversible changes in luminescence are one of the most attractive candidates for the non-destructive read-out because of high performance such as sensitivity, resolution, high contrast and all-photon mode.<sup>10–12,32</sup>

The use of a monochromatic visible irradiation leaves the state of the system almost unaffected. So the combination of different kinds of photochromic molecules or introduction of different kinds of photochromic compounds into a molecule offers a route towards non-destructive read-out capability in high-density optical memory data storage. Memory media capable of processing more than two pieces of information at the same storage site is an illustrative example of an application of the use of multi-addressable switching strategies.<sup>32,34,36</sup> For a single crystal containing two different kinds of diarylethenes, four kinds of information could be written into the crystal by changing the wavelength of irradiating light.<sup>36</sup> The recording density for the two-wavelength recording using two-component photochromic crystal is twice as high as for common one-component crystal systems.



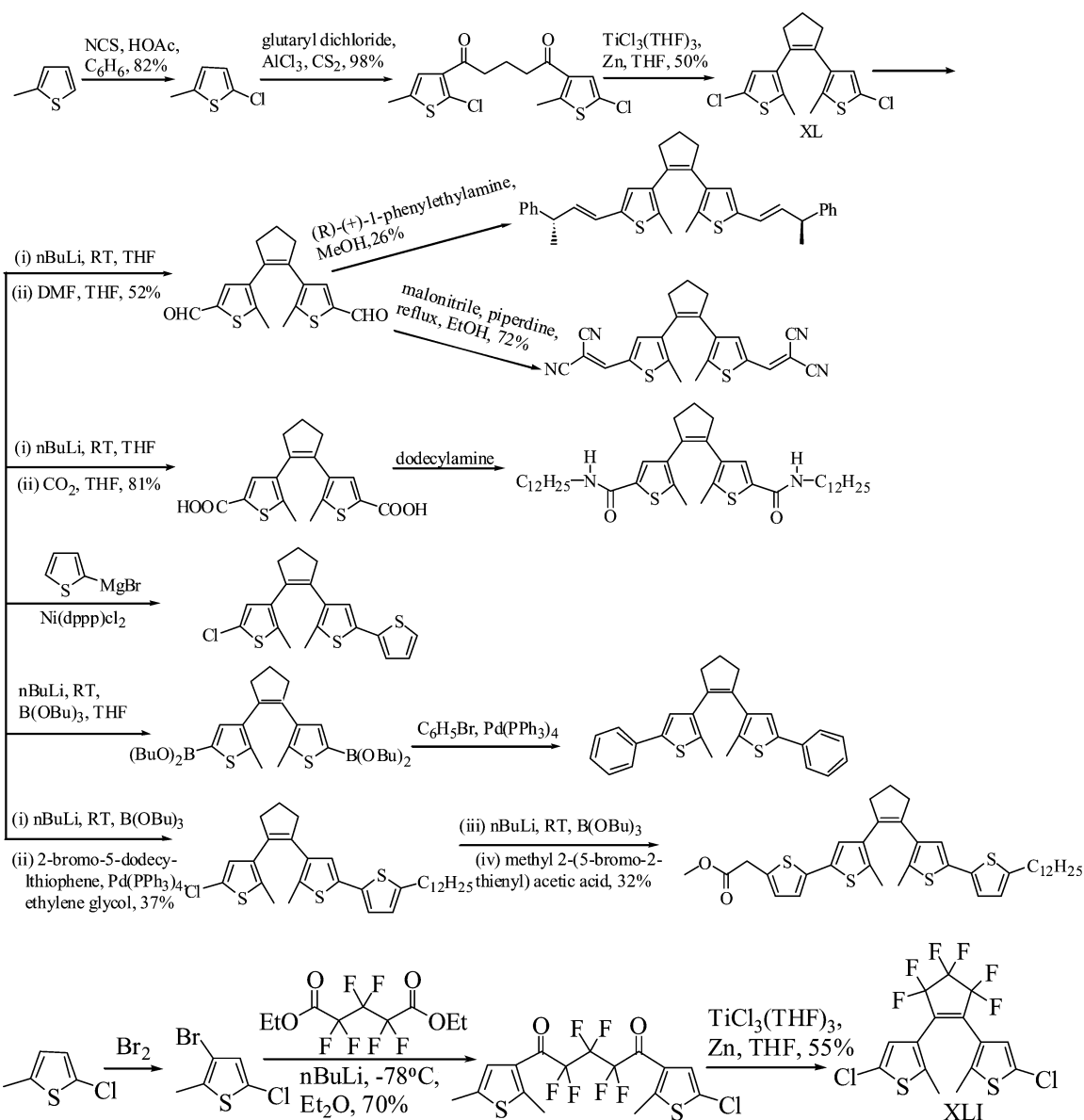
Recently, the diarylethene derivative having benzothiophene derivatives XXXIX was found to exhibit a remarkable IR spectral change around  $1590\text{ cm}^{-1}$  upon irradiation. Uchida *et al.*<sup>46</sup> doped the compound into Zeonex polyolefin polymer, which has no absorption between  $1500$  and  $1700\text{ cm}^{-1}$ . Initially the film was homogeneously irradiated with UV light. Then, a mask pattern was placed on the film and irradiated with visible light. After irradiation with visible light, purple image remained. Even after prolonged read-out of the image using IR light, no decrease in the signal-to-noise (S/N) ratio was observed. Upon irradiation with visible light, the image disappeared and the recorded information was erased.

## 5 Synthetic methods

Although many functionalized diarylethene derivatives with highly attractive photochromic properties have been synthesized, the synthesis of diarylethenes is not trivial. There are several 1,2-bis(thien-3-yl) systems containing maleic anhydride, malimide, perfluorocyclopentene, and cyclopentene units that have been employed so far. Each unit has its advantages and disadvantages. Diarylethenes with a perfluorocyclopentene bridging unit, for instance, exhibit excellent photochromic properties. However, the expensive and rather volatile (bp.  $26\text{--}28\text{ }^{\circ}\text{C}$ ) starting material octafluorocyclopentene is a major disadvantage. Both diarylmaleic anhydrides and diarylmaleimides are readily accessible but are sensitive to acidic conditions.

Feringa *et al.*<sup>47</sup> reported recently a new facile synthetic procedure for perhydrocyclopentene **XL** and perfluorocyclopentene **XLI**. The procedure, as shown in Scheme 1, can be performed on large scales with relatively cheap starting chemicals. The two basic switches **XL** and **XLI** can easily be prepared to provide access to a wide variety of diarylcyclopentene photochromic switches by a convergent synthetic route. Because of the low yields of the Suzuki coupling for perfluorocyclopentenenes, this route should be well suited for the convergent synthesis of other functionalized perhydrocyclopentene molecular switches, but less suitable for the corresponding perfluorocyclopentenenes.

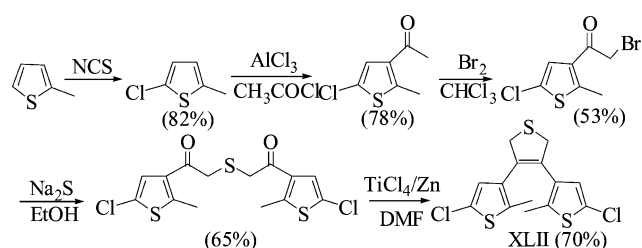
The photochromic behavior of perhydro- and perfluorocyclopentene photochromic switches is remarkably similar. Both perhydrocyclopentene and perfluorocyclopentene molecular switches combine excellent quantum yields (0.6) with high degrees of photoconversion ( $>0.85$ ).<sup>48</sup> The main difference, they found, was lower photochemical and thermal stability of the perhydrocyclopentene molecular switches. And some perhydrocyclopentene derivatives undergo almost quantitative photochemical rearrangements while the perfluoro counterparts did not.<sup>1</sup> Despite that, the switches can still undergo multiple switching cycles without notable photodecomposition, with half lives for thermal interconversion between the open and closed forms in all cases



**Scheme 1** The new facile synthetic procedure of perhydrocyclopentene and perfluorocyclopentene.

exceeding 3 h at 100 °C. Therefore, perhydrocyclopentenes should be excellent alternatives to perfluorocyclopentenes in most cases, while perfluorocyclopentenes might be better suited for applications such as data storage, which depend critically on fatigue resistance and thermal stability.

Recently, Fan *et al.* also reported a novel synthetic route to preparing new symmetric and non-symmetric functional dithienylethene derivatives with a 2,5-dihydrothiophene unit (Scheme 2).<sup>49</sup>



**Scheme 2** The novel synthetic route to preparing functional dithienylethene derivatives.

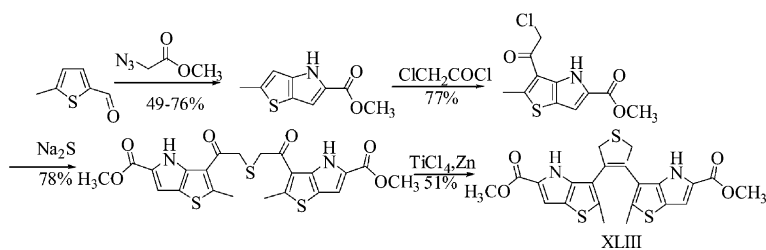
Compound **XLII** can easily be derived to provide a wide variety of photochromic switches. The synthesis can be performed on large scales with cheap starting materials.

For the first time, Krayushkin *et al.*<sup>50</sup> synthesized thienopyrrole-based photochromic 1,2-dihetarylethene **XLIII** in which thienopyrrole fragments are linked by the tetrahydrothiophene, as described in Scheme 3. **XLIII** exhibited typical photochromic properties and underwent at least 20 cycles of the photoinduced transition from the open form to the cyclic form and back in acetonitrile solution. Without irradiation, the cyclic form was stable for at least 200 h.

## 7 Future perspectives

In recent years there has been an ever growing interest in photochromic switches, and this tendency is related to the wide ranging possibilities of their applications as active elements for various optical devices, such as data recording and storage, holography, multi-color displays *etc.* Glassy nematic liquid crystals present new opportunities for non-destructive rewritable optical memory and high-speed photonic switches, including spatial light modulators, filters, polarizers and beam splitters for optical communication and image processing.<sup>31</sup> Photochromic single crystals have potential applications as photo-driven nanometer-scale actuators and three-dimensional memory.<sup>35</sup>

An important motive to research organic photochromic switches is to develop materials particularly well suited as erasable memory media for erasable laser discs. Obviously, for long-term stability



**Scheme 3** The synthetic steps for thienopyrrole-based photochromic 1,2-dihetarylethene.

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. The quantum yields and the response times for photochromic conversion in both directions between the two isomers in the thin solid films need to be improved significantly.

Single crystals of diarylethene have good thermal stability for both of their isomers. They have high photo-cyclization quantum yields and rapid response times in less than 10 ps.<sup>2,35,36</sup> As a result, they can be applied to optoelectronic devices, such as optical memory, optical switching, and optical displays. The recording density for two-wavelength recording using a two-component photochromic crystal is twice as high as for common one-component crystal systems.<sup>36</sup> In order to obtain high performance photochromic solids with large areas, multi-component photochromic copolymers should be explored in the future. Meanwhile, diarylethenes with three primary colors, yellow in particular, should be developed for photon-mode rewritable full color printing or full color displays.

Near-field recording can avoid the density limit caused by the wavelength of light to great extent, when near-field IR is used; it is possible to develop ultrahigh density optical memory with non-destructive read-out capability.<sup>46</sup> Since the wavelength is one of the critical factors limiting the optical density of data storage, and the wavelength of conventional IR (or NIR) is far longer than that of UV/Vis, so we believe that reversible changes in UV/Vis absorption bands of photochromic switches are still one of the most favorable methods for non-destructive and high-density memory systems. In this case, commercial, integrated, and low cost semiconductor lasers can be used as the light sources for read, write, and erase, functions. High-density data storage can be realized by modifying the chemical structures of photochromic compounds and shifting the wavelengths of the color form to a shorter spectral region. Two critical conditions must be met for this strategy to be effective: 1) there must exist one narrow absorption band in photochromic switches for read-out and this absorption band must not overlap with the absorption bands where photochromic reaction is excited; 2) The open and closed isomers must display significantly different absorption spectra in the read-out region. Of course, for all organic photochromic memory media, high fatigue resistance and very stable write/read states are prerequisites.

## Acknowledgements

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