

Investigation of New Photochromic Triangle Terarylenes Dyes and Their Single Crystals

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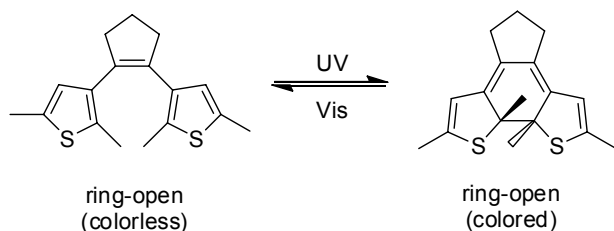
INTRODUCTION

Switchable molecules, which respond to the application of external stimuli by undergoing reversible transformations between two distinct structures, have the potential to significantly influence the development of numerous important materials science and structural biology technologies.¹ This potential is based on the fact that the dramatic changes in their electronic were realized through a reversible process, which can act as switching elements in various functional molecules and optoelectronic devices.

Compounds that interconvert between different isomers having unique absorption spectra when stimulated with light are referred to as photochromic and the process is called photochromism. In addition to the changes in color, physical properties were also modulated at the same time. The photomodulation of physical properties can be used in advance optoelectronic technologies such as waveguides,² read/write/erase optical information storage systems,³ and molecular machines.^{4,5}

Among all the photochromic systems, those possessing the hexatriene framework provided by the 1,2-dithienylethene structure have attracted special attention. This attention is well earned for its dramatic changes in physical and chemical properties satisfying for practical used in functional materials technologies. 1,2-dithienylethene undergo reversible photo-cyclization reactions between their colored ring-open and colorless ring-closed forms (Scheme 1) with an impressive of fatigue resistance and thermal irreversibility upon irradiation at appropriate wavelengths.⁶

Photoswitching effects in diarylethenes have been extensively studied for controlling various chemical and physical properties such as fluorescence intensity



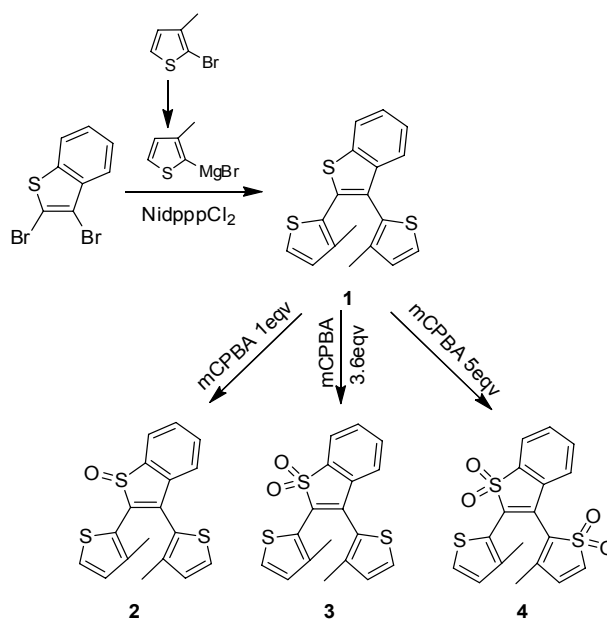
Scheme 1. Photoisomerization of the 1,2-dithienylethene backbone.

and wavelength, refractive index, dielectric properties, electronic conduction, electrochemical response, magnetic interactions, and self-assembling behavior. Most of these photoswitching effects are based, at least partly, on changes in the extent of π -conjugation in the diarylethenes in the course of photochromic reactions.

Recently, several photochromic diarylethene compounds with S=O moieties have been reported.⁷⁻⁹ A strike features of them are their highly fluorescence quantum yield in closed form and highly fatigue-resistance. Therefore, great interest has been attracted to introducing S=O into the photochromic diarylethene molecules for their special properties.

Results and Discussion

In this abstract, three photochromic triangle terarylenes with S-oxide or S,S-dioxide moieties were synthesized with high yield. The synthetic route is shown in Scheme 2. 2,3-dibromobenzothiophene was prepared according to the literature method.¹⁰ **1** was synthesized based on conventional Kumada coupling reaction between 2,3-dibromo-benzothiophene and Grignard reagent formed from 2-bromo-3-methyl-thiophene in one step.



Scheme 2. Synthesis of the triangle terarylenes.

1 can be selectively oxidized to yield **2**, **3**, or **4** by controlling the amount of oxidant in the synthetic reaction. All the target compounds were fully characterized by ^1H and ^{13}C NMR, MS spectra, element analysis and X-ray crystallography.

Spectral photochemical properties of **1-4** were studied in THF solution. **1**, **2**, and **3** exhibited good photochromic properties and could be toggled between colorless ring-open and colored ring-closed forms by alternated irradiation with ultraviolet and visible light. Upon irradiation with 254nm light, the colorless THF solution of **1-3** brought about an immediate increase of the intensity of the absorption in the visible region (440-460nm) due to the formation of the ring-closed form. Well-defined isosbestic point could be found in Fig. 1 clearly for **1-3** supporting the two-component photochromic reaction.

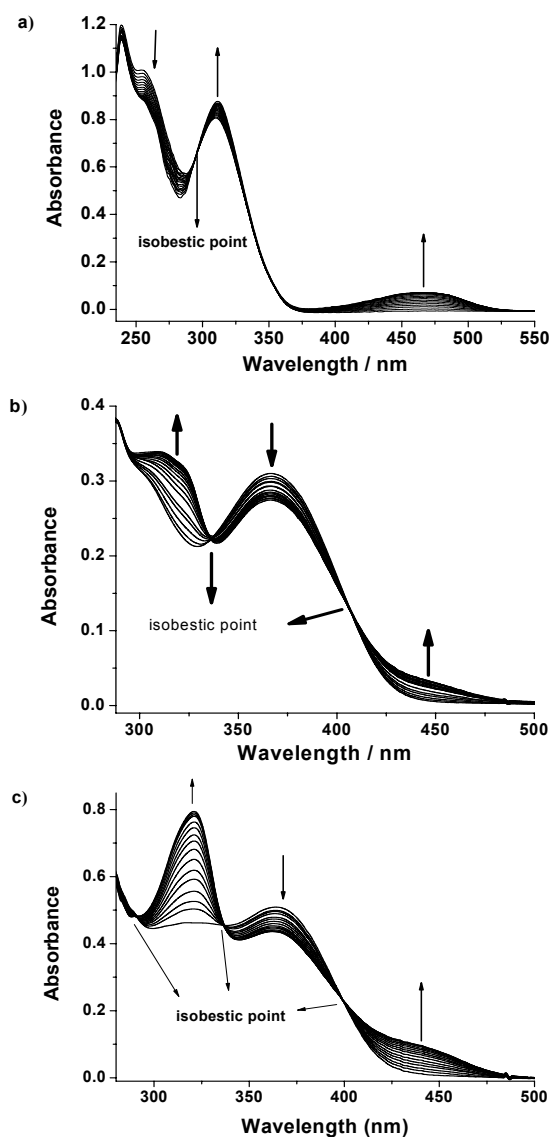
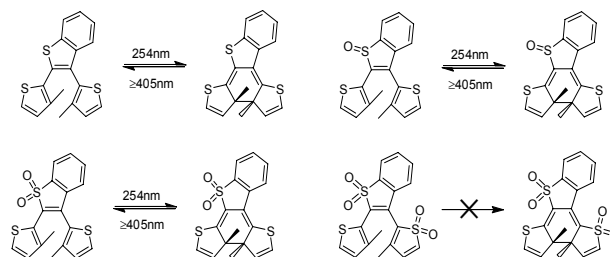


Fig. 1. Absorption changes of **1-4** in THF solution upon irradiation with 254nm light ($6.4 \times 10^{-5}\text{M}$ for **1**, $5.8 \times 10^{-5}\text{M}$ for **2**, $5.1 \times 10^{-5}\text{M}$ for **3**) every 3 seconds.

The yellowish solutions can be easily bleached upon irradiation with visible light ($\lambda \geq 405\text{nm}$), producing the absorption spectrum identical with those of the initial solution, which confirmed the completion of the back conversion and the absence of photodegradation.

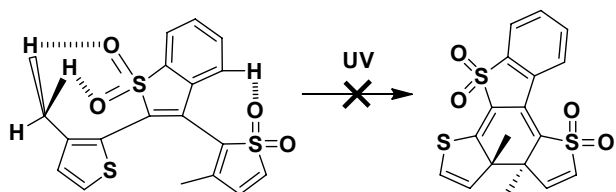
It is worth noting that dramatic absorption spectra changes were found for **2** and **3** in an “invisible region” (around 320nm). If the THF solution of **2** and **3** were irradiated with 365nm light, almost identical absorption spectra were obtained in contrast with those using 254nm light irradiation. Therefore, the photochromic behavior of **2** and **3** included “visible” and “invisible” photochromism. The color change in diarylethene derivatives is based on the change in the π -conjugation length along with the photocyclization/photocycloreversion reactions.

As the π -conjugation length becomes longer, the absorption maximum shifts to a longer wavelength. For **1**, one electron pair of sp^2 hybridized sulfur occupy a p orbital and contribute to complete the six- π -electron requirement for aromatic stabilization. While this π -conjugation was broken with the sulfur atom of benzothiophene ring oxidized to S=O groups in the ring-closed form. In contrast with **1**, the introduction of S=O group brought about the absorption around 365nm for **2** and **3**.



Scheme 3. Photoisomerization of **1-4**.

However, the THF solution of **4** did not exhibit photochromic behavior like **1**, **2**, and **3** in solution. Even if the irradiation time were prolonged to several hours, there is no new absorption band observed. As illustrated in scheme 3, the photochromic reactivity was completely suppressed. The suppressed photoactivity of **4** is considered to be the contribution of stronger intramolecular interactions including hydrogen bonding and steric hindrance (Scheme 4). The hydrogen bonds formed between S,S-dioxide moieties and corresponding hydrogen atoms fastened the two pendent thiophene rings in the photoinactive conformation. This can be confirmed by ^1H NMR measurements and molecular geometry calculations in the ground state. The steric hindrance resulting from S,S-dioxide moieties also makes the rotation of photochromic unit not so free and weakens the photochromic reactivity.



Scheme 4. Intramolecular hydrogen bonds of **4**.

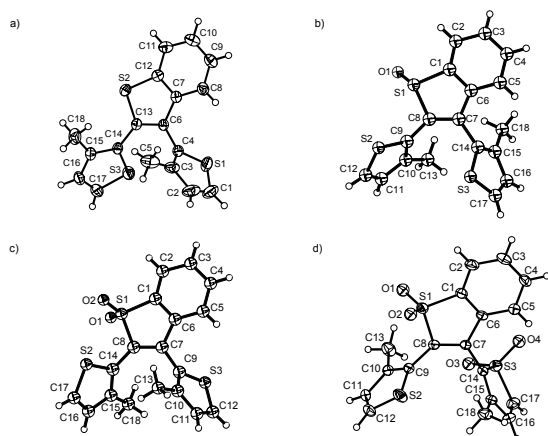


Fig. 2. Crystal structures of **1-4** with displacement ellipsoids shown at the 30% probability level.

The single crystals of **1-4** were obtained by controlling the slow evaporation speed of their solution at room temperature. The crystallographic data were available for the ring-open form only and all of them crystallized into a monoclinic crystal system. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings of **1-4** are shown in Fig. 2. The ORTEP drawings indicate that the crystals of **1**, **2**, and **4** were packed in typical parallel conformation. With the parallel conformation, the crystals lost their photochromic reactivity in solid state. In contrary, crystal **3** was packed in anti-parallel conformation. The distance between the reactive carbons (C10 to C15) was estimated to be 3.625 Å. It is shorter enough to undergo a photocyclization reaction in the crystalline phase according to the rules summarized by Irie and his co-workers.¹¹ However, the anticipate photocyclization reaction was not occurred even if the irradiation time was prolonged to several hours. Crystal **3** is one of a few reported crystals that can not proceed routine photocyclization in crystalline phase with the distance of reactive carbons shorter than 4.2 Å. Besides the distance-dependent factor, other factors also influence the photochromic reactivity of crystals, especially the packing effect.

According to the crystal data, the optimized geometric conformations of **1-4** were calculated using a BLYP/DND basis set as implement in the *Dmol³* package. The geometric conformations of **1-4** are shown in Fig. 3. It is worth noting that the optimized structure of **4** also supported the intramolecular hydrogen bonding with which the

photochromic reactivity was lost in solution. The intramolecular hydrogen bonds fixed the thiophene rings to a parallel conformation. In solution, the parallel conformation of **4** will be an overwhelming conformation. While in other optimized structures, there exists no chance for establishing intramolecular hydrogen bonds for **1-3**.

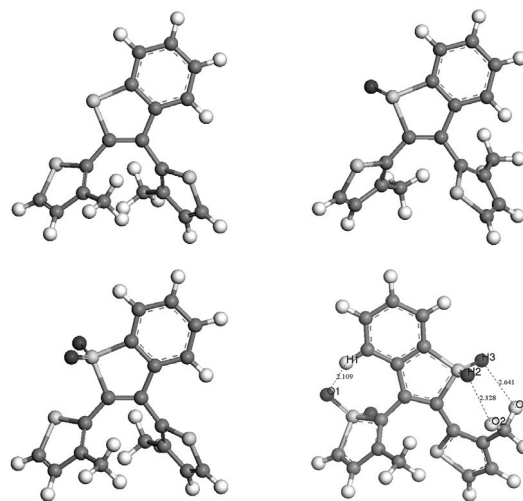


Fig. 3. Optimized molecular structures of **1** (top left), **2** (top right), **3** (bottom left), and **4** (bottom right).

In summary, a series of photochromic triangle terarylenes were synthesized. With the S=O moieties introduced, the photochromic reactivity of them were also influenced. Stronger intramolecular interactions mainly derived from hydrogen bonding prohibited the free rotation of thiophene rings. Thus, the photoactivity of **4** was lost. The conjugate benzothiophene rings is broken because of oxidized sulfur atom. After the photocyclization, the conjugate length of **2** and **3** are different from that of **1**. The broke conjugate system result in a “visible” and “invisible” photochromism for **2** and **3**. Single crystals of **1-4** were investigated. Unusual photochromic behavior of crystal **3** was found even though the distance of reactivity carbons is shorter enough. Based on the crystal data, their optimized structure were calculated with *Dmol³*. The optimized structure of **4** supported the existence of intramolecular hydrogen bond further.

Reference

1. D. Pijper, M. G. M. Jongejan, A. Meetsma, and B. L. Feringa; *J. Am. Chem. Soc.*, 130, 4541–4552(2008).
2. J. W. Kang, J. J. Kim, and E. Kim; *Appl. Phys. Lett.*, 80, 1710–1713(2002).
3. A. J. Myles and N. R. Branda; *Adv. Funct. Mater.*, 12, 167–173(2002).

4. M. Alonso, V. Rebotto, L. Guiscardo, A. San Martin, and J. C. Rodriguez-Cabello; *Macromolecules*, 33, 9480–9482(2000).
5. T. Hugel, N. B. Holland, A. Cattani, L. Moroder, M. Seitz, and H. E. Gaub; *Science*, 296, 1103–1106(2002).
6. M. Irie; *Chem. Rev.*, 100, 1685–1716(2000).
7. Y. -C. Jeong, S. I. Yang, E. Kim, and K. -H. Ahn; *Tetrahedron*, 62, 5855–5861(2006).
8. Y. -C. Jeong, J. P. Han, Y. Kim, E. Kim, S. I. Yang, and K. -H. Ahn; *Tetrahedron*, 63, 3173–3182(2007).
9. M. Ohusmi, M. Hazama, T. Fukaminato, and M. Irie; *Chem. Commun.*, 29, 3281–3283(2008).
10. G. Barbarella, L. Favaretto, A. Zanelli, G. Gigli, M. Mazzeo, M. Anni, and A. Bongini; *Adv. Funct. Mater.*, 15, 664–670(2005).
11. S. Kobatake, K. Uchida, E. Tsuchida, and M. Irie; *Chem. Commun.*, 23, 2804–2805(2002).