

“Lock and Key Control” of Photochromic Reactivity by Controlling the Oxidation/Reduction State

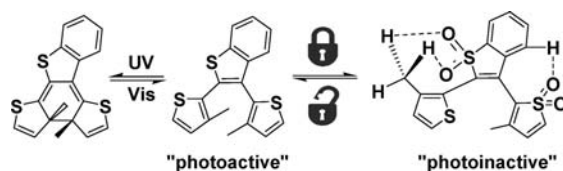
Xiaochuan Li,^{*,†} Yuzhen Ma, Bingcai Wang, and Gongan Li

College of Chemistry and Environmental Science, Henan Normal University,
Xinxiang, Henan, 453007, People's Republic of China

lixiaochuan@henannu.edu.cn

Received June 24, 2008

ABSTRACT



A photochemical active triangle terarylene was synthesized and the photochromic behavior was investigated. Its photochromic reactivity can be strongly suppressed by selected oxidization of the sulfur atoms in the molecules. Reactivated photochromic reactivity was obtained by deoxidation of the S,S-dioxide moieties. The suppressed photoactivity of the oxidation state was attributed to the stronger intramolecular hydrogen bonding interactions.

Switchable molecules 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 a given physical property can be modulated through the action of some external trigger, which can act by switching elements in various functional molecules and optoelectronic devices.²

Among the switchable materials, considerable attention has been paid to photochromic molecules, especially on photo-

chromic dithienylethene (DTE), which undergo reversible photoisomerizations between pairs of bistable isomers with different absorption spectra upon irradiation at appropriate wavelengths.³ Some novel photochromic molecules of this type based on the change of π -conjugation connection pathways in DTEs have been reported recently on designing and synthesis.⁴ Photoswitch effects of DTEs have been widely studied for photomodulations of chemical and physical properties such as fluorescence intensity or wavelength,^{5a–h} Lewis acidity of boron,⁵ⁱ and electronic conductance.^{5j}

A property that is strongly desired but is still inadequate is gated photochromic reactivity. Gated reactivity is the property that the on/off photoactivity of molecules depends on the inducement of another external stimulus such as

[†] Henan Normal University.

(1) (a) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999. (b) Feringa, B. L. *Molecule Switches*; Wiley-VCH: Weinheim, Germany, 2001. (c) Irie, M. *Photo-Reactive Materials for Ultrahigh-Density Optical Memory*; Elsevier: Amsterdam, The Netherlands, 1994. (d) Matsuda, K.; Irie, M. *Functional Organic Materials*; Muller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, Germany, 2007; Chapter 9. (e) Volgraf, M.; Gorostiza, P.; Szobota, S.; Helix, M. R.; Isacoff, E. Y.; Trauner, D. *J. Am. Chem. Soc.* **2007**, *129*, 260. (f) Dohno, C.; Uno, S.; Nakatani, K. *J. Am. Chem. Soc.* **2007**, *129*, 11898.

(2) (a) Fukaminato, T.; Umemotom, T.; Iwata, Y.; Yokojima, S.; Yoneyama, M.; Nakamura, S.; Irie, M. *J. Am. Chem. Soc.* **2007**, *129*, 5932. (b) Whalley, A.; Steigerwald, M. L.; Guo, X.; Nuckolls, C. *J. Am. Chem. Soc.* **2007**, *129*, 12590. (c) Lee, P. H.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2007**, *129*, 6058. (d) Takami, S.; Kuroki, L.; Irie, M. *J. Am. Chem. Soc.* **2007**, *129*, 7319. (e) Pijper, D.; Jongejan, M. G. M.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2008**, *130*, 4541.

(3) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685. (b) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85. (c) Wigglesworth, T. J.; Myles, A. J.; Branda, N. R. *Eur. J. Org. Chem.* **2005**, *7*, 1233. (d) Tian, H.; Fei, Y. *J. Mater. Chem.* **2008**, *18*, 1617. (e) Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781.

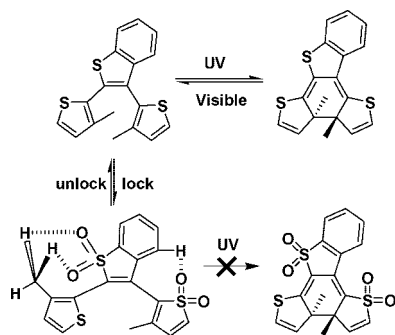
(4) (a) Nakashima, T.; Atsumi, K.; Kawai, S.; Nakagawa, T.; Hasegawa, Y.; Kawai, T. *Eur. J. Org. Chem.* **2007**, *19*, 3212. (b) Yahyaoui, A. E.; Felix, G.; Heynderickx, A.; Moustrou, C.; Samat, A. *Tetrahedron* **2007**, *63*, 9482. (c) Jeong, Y.-C.; Yang, S. I.; Ahn, K.-H.; Kim, E. *Chem. Commun.* **2005**, *19*, 2503. (d) Yan, S. F.; Bbelov, V. N.; Bossi, M. L.; Hell, S. W. *Eur. J. Org. Chem.* **2008**, *15*, 2531.

additional photons of different wavelengths,⁶ reactive chemicals,⁷ or heat.⁸ Such threshold reactivity is indispensable for application to display and memory technologies.

Among the gated DTE photochromic systems hitherto reported, several strategies have been employed to regulate the photochromic reactivity including reversible processes of esterification reactions,^{7e} [4 + 2] cycloaddition reactions,^{7f} acid/base reactions,^{7c} redox,^{7a} and the formation of hydrogen bonds.^{7a,b} In each of these cases, the basic principle for regulating photoactivity is based on the reversible processes of limited/unlimited rotation of the two pensile heterocyclic rings. According to the Woodward–Hoffmann rule, the photocyclization proceeds in a contrarotational mode. The contrarotational cyclization of five-membered carbon rings is allowed only from the antiparallel conformation. Therefore, the key point is how to manipulate the orientation of the 1,3,5-hexatriene portion of the photoswitchable DTEs.

In this Letter, we report an innovative system based on regulation of the intramolecular interactions, with which the on/off photoactivity of photochromism can be achieved. The principle is illustrated in Scheme 1 and represents a promis-

Scheme 1. The Principle of the “Lock and Key” Process of Photochromic Reactions



ing way of manipulating the conformations of thiophene rings. Construction and destruction of the specific hydrogen bonding interaction in the photochromic molecules is one of the best ways of fastening and unfastening the rotating

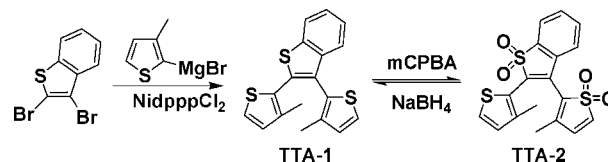
(5) (a) Straight, S. D.; Liddell, P. A.; Terazono, Y.; Moore, T. A.; Moore, A. L.; Gust, D. *Adv. Funct. Mater.* **2007**, *17*, 777. (b) Traven, V. F.; Bochkov, A. Y.; Krayushkin, M. M.; Yarovenko, V. N.; Nabatov, B. V.; Dolotov, S. M.; Barackevsky, V. A.; Beletskaya, I. P. *Org. Lett.* **2008**, *10*, 1319. (c) Zhao, Z.; Xing, Y.; Wang, Z.; Lu, P. *Org. Lett.* **2007**, *9*, 547. (d) Zhou, Z.; Xiao, S.; Xu, J.; Liu, Z.; Shi, M.; Li, F. *Org. Lett.* **2006**, *8*, 3911. (e) Lim, S. J.; Seo, J.; Park, S. Y. *J. Am. Chem. Soc.* **2006**, *128*, 14542. (f) Browne, W. R.; Pollard, M. M.; Lange, B.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 12412. (g) Yumoto, K.; Irie, M.; Matsuda, K. *Org. Lett.* **2008**, *10*, 2051. (h) Finden, J.; Kunz, T. K.; Branda, N. R.; Wolf, M. O. *Adv. Mater.* **2008**, *20*, 1998. (i) Lemieux, V.; Spantulescu, M. D.; Baldrige, K. K.; Branda, N. R. *Angew. Chem., Int. Ed.* **2008**, in press. (j) Kronemeijer, A. J.; Akkerman, H. B.; Kudernac, T.; Wees, B. J.; Feringa, B. L.; Blom, P. W. M.; Boer, B. *Adv. Mater.* **2008**, *20*, 1467.

(6) (a) Murakami, M.; Miyasaka, H.; Okada, T.; Kobatake, S.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14764. (b) Lemieux, V.; Gauthier, S.; Branda, N. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6820. (c) Uchida, M.; Irie, M. *J. Am. Chem. Soc.* **1993**, *115*, 6442. (d) Miyasaka, H.; Murakami, M.; Itaya, A.; Guillaumont, D.; Nakamura, S.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 753. (e) Muraoka, T.; Kihbara, K.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 11600.

thiophene rings of the photochromic unit. The “lock” process could be realized by fabricating specific intramolecular hydrogen bonding interactions in the photochromic molecules and the photoactivity was lost, in which the photoswitchable unit was fastened in a photoinactive conformation. Conversely, the “key” process can be achieved by destroying the corresponding hydrogen bonding interaction and the photoactivity would be reactivated.

The synthetic route for photochromic triangle terarylenes (TTA) is shown in Scheme 2. 2,3-Dibromobenzothiophene

Scheme 2. Synthesis of Triangle Terarylenes



was prepared according to the literature method.⁹ TTA-1 was synthesized based on the conventional Kumada coupling reaction between 2,3-dibromobenzothiophene and Grignard reagent formed from 2-bromo-3-methylthiophene in one step with 23% yield.^{4c,10} TTA-2 was prepared by selected oxidation of sulfur atoms of TTA-1, using *m*-chloroperbenzoic (mCPBA) acid with 60% yield.¹¹ TTA-2 can be deoxidized by NaBH₄ to give TTA-1 at room temperature in nearly quantitative yield. Their structures were confirmed with ¹H and ¹³C NMR, MS spectra, element analysis, and X-ray crystallography.

Spectral photochemical properties of TTA-1 and TTA-2 were studied in THF solution. TTA-1 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. The photochromic behavior is illustrated in Figure 1a and Scheme 1. Figure 1a shows the changes of absorption of TTA-1 (6.4 × 10⁻⁵ M in THF) upon irradiation with 254 nm light. In fact, irradiation of the colorless THF solution of TTA-1 at 254 nm brought about an immediate increase of the intensity of the absorption bands in the visible region

(7) (a) Irie, M.; Miyatake, O.; Uchida, K.; Eriguchi, T. *J. Am. Chem. Soc.* **1994**, *116*, 9894–9900. (b) Irie, M.; Miyatake, O.; Uchida, K. *J. Am. Chem. Soc.* **1992**, *114*, 8715. (c) Kawai, S. H.; Gilat, S. L.; Lehn, J.-M. *Eur. J. Org. Chem.* **1999**, *9*, 2359. (d) Huck, N. P. M.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1995**, 1095. (e) Ohsumi, M.; Fukaminato, T.; Irie, M. *Chem. Commun.* **2005**, 3921. (f) Lemieux, V.; Branda, N. R. *Org. Lett.* **2005**, *7*, 2969. (g) Kuhni, J.; Belsler, P. *Org. Lett.* **2007**, *9*, 1915.

(8) (a) Irie, M.; Eriguchi, T.; Takata, T.; Uchida, K. *Tetrahedron* **1997**, *53*, 12263. (b) Irie, M.; Miyatake, O.; Uchida, K. *J. Am. Chem. Soc.* **1992**, *114*, 8715. (c) Dulic, D.; Kudernac, T.; Puzys, A.; Feringa, B. L.; Wees, B. J. *Adv. Mater.* **2007**, *19*, 2898.

(9) Barbarella, G.; Favaretto, L.; Zanelli, A.; Gigli, G.; Mazzeo, M.; Anni, M.; Bongini, A. *Adv. Funct. Mater.* **2005**, *15*, 664.

(10) Li, X.; Tian, H. *Tetrahedron Lett.* **2005**, *46*, 5409.

(11) (a) Jeong, Y.-C.; Han, J. P.; Kim, Y.; Kim, E.; Yang, S. I.; Ahn, K.-H. *Tetrahedron* **2007**, *63*, 3173. (b) Jeong, Y.-C.; Yang, S. I.; Kim, E.; Ahn, K.-H. *Tetrahedron* **2006**, *62*, 5855. (c) Jeong, Y.-C.; Park, D. G.; Kim, E.; Ahn, K.-H.; Yang, S. I. *Chem. Commun.* **2006**, *17*, 1881. (d) Ohsumi, M.; Hazama, M.; Fukaminato, T.; Irie, M. *Chem. Commun.* **2008**, in press.

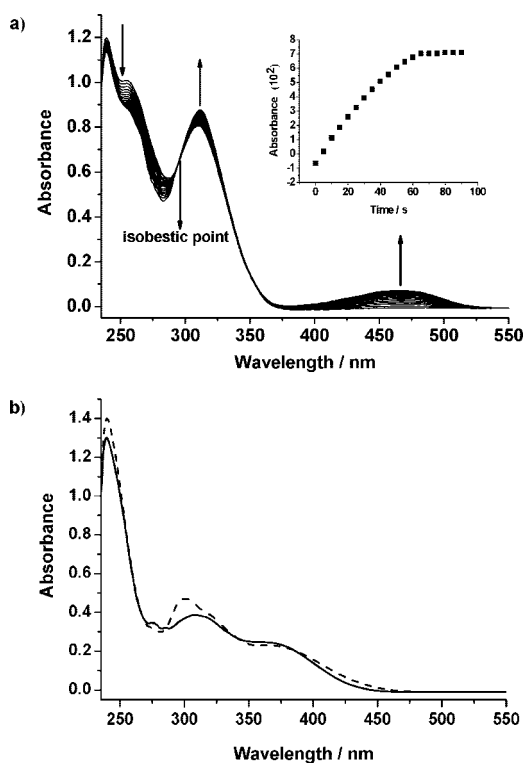


Figure 1. (a) Absorption changes of **TTA-1** in THF solution upon irradiation with 254 nm light (6.4×10^{-5} M) every 5 s. Insert: Increase of absorbance at 465 nm with respect to irradiating time. (b) Absorption changes of **TTA-2** in THF solution before (solid line) and after (dashed line) irradiation with 254 nm light.

centered at 465 nm due to the formation of the ring-closed form of **TTA-1**. A well-defined isosbestic point appeared at 292 nm ($\epsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) supporting the two-component photochromic reaction as shown in Scheme 1. The yellowish solution can be easily bleached upon irradiation with visible light ($\lambda \geq 405 \text{ nm}$), producing an absorption spectrum identical with that of the initial solution of **TTA-1**. The identity of the final and original spectra of the open form confirmed the completion of the back conversion and the absence of photodegradation. The conversion efficiency (α_{ps}) between ring-open and ring-closed forms at the photo-stationary state, achieved by irradiation with UV light ($\lambda = 254 \text{ nm}$), was estimated to be 0.59, which can be calculated following the expressions based on the absorbance of the two forms.¹²

The absorption spectrum of **TTA-2** in THF solution at room temperature is shown in Figure 1b. **TTA-2** did not exhibit photochromic behavior like **TTA-1** in THF solution when irradiated with 254 nm light, which suggested no photocyclization occurred. Its photochromic reactivity was suppressed completely.

The suppressed photoactivity of **TTA-2** is considered to be the contribution of stronger intramolecular interactions of **TTA-2** than that of **TTA-1**. The stronger intramolecular

interactions of **TTA-2** include hydrogen bonding interaction and steric hindrance. The sulfone moieties provide the probability for the formation of intramolecular hydrogen bonds between *S,S*-dioxide moieties and corresponding hydrogen atoms, which fastened the two pendent thiophene rings in the photoinactive conformation (Scheme 1). This can be confirmed by ^1H NMR measurements and molecular geometry calculations in the ground state.¹³ The hydrogen bonds like springs limited the rotation of two pendent thiophene rings. The steric hindrance resulting from *S,S*-dioxide moieties also makes the rotation of photochromic unit not so free and weakens the photochromic reactivity. The ring-open form of **DTE** usually has two conformations, parallel and antiparallel, which interconvert with each other in solutions. This interconversion in **TTA-2** was prohibited by both hydrogen bonds and steric hindrance. These factors stabilize and enrich the photoinactive parallel conformation in solution, resulting in completely suppressed photochromic reactivity of **TTA-2**.

TTA-2 can be deoxidized back to give **TTA-1** with the photochromic reactivity being reactivated at the same time. By selected oxidation of sulfur atoms of **TTA-1**, **TTA-2** was obtained with strongly suppressed photochromic reactivity. Therefore, two different types of **DTE** derivatives with distinctively opposite photoactivity could be reversibly controlled by the redox processes. Namely, the “lock and key” control of the photoactivity could be realized by this reversible process.

The single crystals of **TTA-1** and **TTA-2** were obtained by controlling the slow evaporation speed of their solutions at room temperature. The two crystallographic data were available for the ring-open form only and both of them crystallized into a monoclinic crystal system. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings of **TTA-1** and **TTA-2** are shown in Figure 2. The ORTEP drawing of **TTA-1** indicates that a typical parallel conformation packed in the crystals and the two dihedral angles between the two thiophene rings and the benzothiophene ring were evaluated to be $61.78(4)^\circ$ and $-69.45(5)^\circ$, respectively. While the packed structure of **TTA-2** is different from that of **TTA-1**, a typical antiparallel conformation is observed in the crystalline phase and the two dihedral angles between the two thiophene rings and the benzothiophene ring were evaluated to be $87.36(7)^\circ$ and $76.71(5)^\circ$, respectively. According to the rule reported by Irie, photocyclization reactivity of the **DTE** crystals with antiparallel conformational molecules depends on the distance between the reactive carbon atoms in the single-crystalline phase rather than polar and steric substituent effects. When the distance is longer than 4.2 \AA , the photocyclization is suppressed.¹⁴ The distances between the reactive carbon atoms of **TTA-1** (C3–C15) and **TTA-2** (C10–C15) were estimated to be $4.327(3)$ and $4.595(4) \text{ \AA}$, respectively. It is too long for them to undergo a photocyclization reaction in the crystalline phase, although the

(13) See the Supporting Information for details.

(14) (a) Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, 23, 2804. (b) Shibata, K.; Muto, K.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2002**, 106, 209. (c) Kobatake, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **2004**, 77, 195.

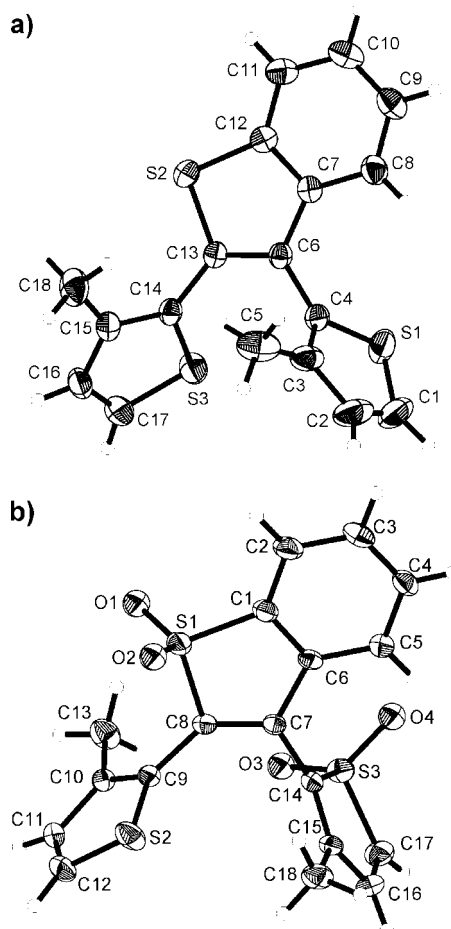


Figure 2. Crystal structures of **TTA-1** (a) and **TTA-2** (b) with displacement ellipsoids shown at the 30% probability level.

crystal of **TTA-2** was packed in the photoactive antiparallel conformation. Therefore, two crystals showed no photochromic performance even if they were irradiated with 254 nm light for a longer time.

Actually, no intramolecular hydrogen bond was established in the two crystals. In the crystalline phase, the conformations

of two molecules were determined mainly by intermolecular hydrogen bonds. In the crystal of **TTA-1**, two pensile thiophene rings were fixed in a parallel conformation by two hydrogen bonds. However, two pensile thiophene rings were fixed to the antiparallel conformation by six hydrogen bonds in the crystal of **TTA-2**. The existence of an S=O group provided more probability for the formation of hydrogen bonds, and the strength of C–H \cdots O in the crystal of **TTA-2** is stronger than that of C–H \cdots S in the crystal of **TTA-1**. Predominant interactions in the crystal are intermolecular interactions and are different from those in dilute solutions, where intramolecular interactions are predominant. Therefore, it is reasonable that the photochromic behavior can be distinctively different between the crystalline phase and the solution phase.

In summary, a chemically gated **DTE** switch system was developed, whose photochromic activity can be manipulated by a reversible process between the oxidation state and the reduction state. It offers a new approach to further functionalize photoresponsive molecular switches based on the **DTE** scaffold. We expect these triangle terarylene derivatives to play a considerable role in photoswitched molecular devices, memory media, as well as molecular logic gates.

Acknowledgment. This work was supported by the National Natural Science Foundation of China for the Youth (No. 20702011), the Startup Fund of Henan Normal University (No. 051004), and the Science Foundation for the Youth of Henan Normal University (No. 2006033). We also thank Professor Young-A Son (Chungnam National University/Korea) for his help in molecular geometry calculations.

Supporting Information Available: Synthetic and experimental details and CIF files for **TTA-1** and **TTA-2**. This material is available free of charge via the Internet at <http://pubs.acs.org>. The data for crystal structure for **TTA-1** (CCDC 691479) and **TTA-2** (CCDC 691480) can also be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44(0)1223-336033; e-mail deposit@ccdc.cam.ac.uk; or <http://www.ccdc.cam.ac.uk>). OL8013655