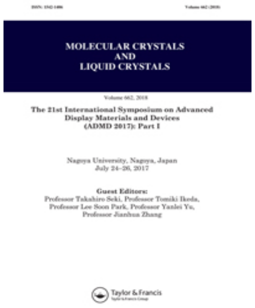

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Reversed photochromism reactivity of malononitrile attached bisthienylthene

Xiaochuan Li[a,b], Yujie Han[a], Myeong Jin Kim[c], and Young-A Son[c]

[a]Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan, P. R. China; [b]Henan Key Laboratory of Green Chemical Media and Reactions, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, P. R. China; [c]BK21, Department of Advanced Organic Materials Engineering, Chungnam National University, South Korea

ABSTRACT
An electron acceptor, malononitrile, was attached to bisthienylethene derivative. The significant influence of electron nature result a reversed phtochromism. Investigation of MT in THF demonstrates the reversible ring-open and ring-close. Upon irradiation of 405 nm laser, the solution color changed from yellowish to colorless, which is different from most of the photochromic colored phenomenon. Upon 254 nm irradiation, the original yellowish state can be recovered. Due to the attachment of malononitrile, the photo-/thermal-stability were enhanced. The ring-open/ring-closed forms were optimized by *Dmol*^{3}. The distance between photocyclizing atoms in aptiparallel conformation meets the requirement for photochromic reaction. And the calculated absorption values were also in agreement with the experimental ones.

KEYWORDS
Bisthienylethene; malononitrile; photo- and thermal-stability; photocyclizing atoms; reversed photochromism

Introduction

Molecules that respond to the external stimuli and could precede a reversible transformation between two distinct configurations/confirmations have the potential to significantly influence on the physical properties of molecules, which could be developed in numerous materials science and structural biological technologies [1–5]. This potential is based on the reversibly change in their electronic and topological characteristics. Thus, a switching elements or dynamic components in various optoelectronic devices or smart materials could be established [6, 7]. Photons are particularly appealing tools because modern laser pulse can be used to achieve fast response times, to focus a fine-tuned stimulus on a small localized domains without significant diffusion and to trigger photochemical events. Photochromism is referred as that molecule that can interconvert between different isomers have unique absorption spectra when stimulated with light. Accompanied with the conformation change, it is also resulted variations of other practical physical properties such as luminescence (switch "on" or "off"), reactivity, chirality, signal encoding, and electronic communication [8–18]. Modulation of these properties is of significant in functional device fabrication. Up to now, three or

CONTACT Prof. Xiaochuan Li lixiaochuan@htu.edu.cn School of Chemistry and Chemical Engineering, Henan Normal University, East Jianshe Rd. 46, Xinxiang, Henan 453007, China; Young-A Son yason@cnu.ac.kr Department of Advanced Organic Materials Engineering, Chungnam National University, 99 Daehakro, Yuseong, Daejeon 34134, South Korea.
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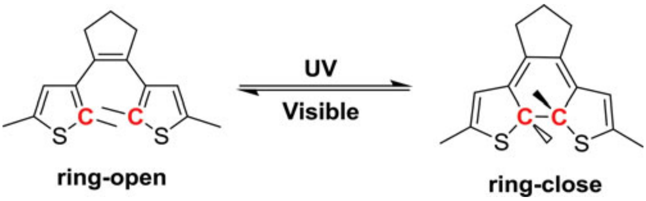


Scheme 1. A typical bisthienylethene in its open and closed forms, the cyclopentene ring being the bridging group. The reactive carbon atoms are in red.

more photochromic elements, together with fluorescent units, were integrated together for multi-color modulation have been documented, which could be applied to photo-switchable full-color displays [19–22]. And the multi-response toward external stimuli advances the device configuration of smart-logic displays.

Among various types of photo switches, bisthienylethenes (**BTE**), is one of most promising candidate due to its high quantum yield, favorable photo-thermal stability, and highly fatigue resistance [23]. The skeleton of **BTE** possesses the hexatriene framework, with which a reversible conrotatory 6π-cyclization reaction could be occur upon photo stimuli (Scheme 1) [24, 25]. Up to now, structural variation of symmetric and asymmetric **BTE**s have been intensively developed and investigated. Generally, the modification is focused in two aspects, the swing units and the bridge. For the bridge variation, it is limited in contrast to the swing units. Typical bridge units are perfluorocyclopentene, maleic anhydride, maleic imide, or aromatic heterocyclic. However, higher degree of aromaticity of the central unit could lead to rapidly thermal back reaction due to the loss of aromatic stabilization energy upon photo-cyclization from the ring open to close isomers [26]. In this contribution, a strong electron withdrawing group, malononitrile, is attached to the bridge thiophene ring by condense reaction. And the photo-physical properties were investigated.

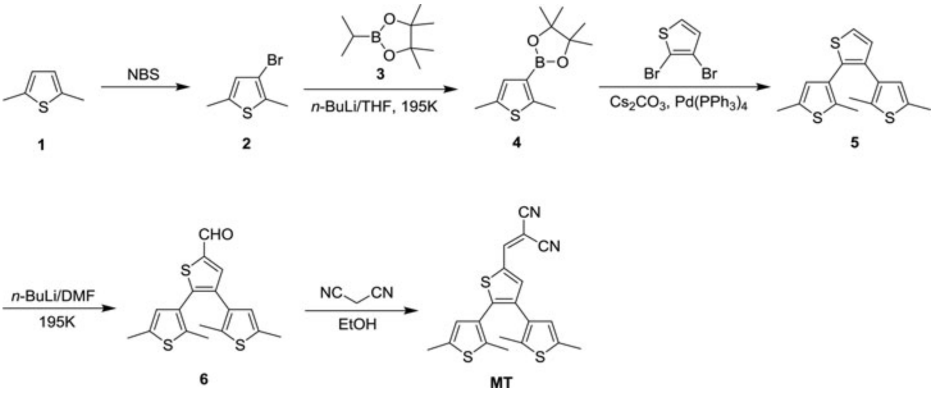
Experimental

General procedures and materials

The solvents used in the reaction were carefully dried according to the standard procedure and stored over 4Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC./Alfa Aesar-A Johnson Matthey Company (South Korea) and used without further purification. All synthesized compounds were routinely characterized by TLC and ^{1}H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

^{1}H/^{13}C NMR and high resolution mass spectroscopy

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in $CDCl_3$. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz. High resolution mass spectra (HRMS) were measured on a Bruker autoflex X III instrument.



Scheme 2. The synthesis of **MT**.

UV-Vis spectra

The absorption spectra were measured with a PERSEE TU-1900 and an Agilent 8453 spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds (2×10^{-3} M) was prepared, and a fixed amount of these concentrated solutions (2×10^{-5} M) were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.

Theoretical calculations

For the theoretical study of excited state photo-physics of the compound, the *DMol*^{3} program packaged in Material Studio (Accelrys Software Inc., United States) was used. The ground state geometries and the frontier molecular orbital of the compound were calculated using the density function theory (DFT) with the B3LYP hybrid functional and the double numerical plus *d*-functions (DNP) atomic orbital basis set.

Synthesis

The synthesis of 2,3-Bis(2,5-dimethylthiophen-3-yl)-5-methylenemalononitrile-thiophene (**MT**) is depicted in Scheme 2. Commercially available 2,5-dimethylthiophene was used as the starting materials and it was conveniently bromized. Then, it was transformed to 2-(2,5-dimethylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**) when treated with *n*-BuLi and 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**). Photochromic unit, 2,3-bis(2,5-dimethylthiophen-3-yl)thiophene (**5**), was obtained by Suzuki coupling method between **4** and 2,3-dibromothiophene [27]. Aldehyde was introduced by treating **5** with *n*-BuLi/DMF. Finally, the target compound **MT** was obtained by condensing **6** and malononitrile in ethanol.

3-bromo-2,5-dimethylthiophen (2)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 6.54 (1H, *s*), 2.38(3H, *s*), 2.31(3H, *s*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 137.0, 132.1, 128.8, 108.4, 15.9, 14.7.

2-(2,5-dimethylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.28 (1H, *s*), 7.03 (1H, *s*), 6.48 (1H, *s*), 6.43 (1H, *s*), 2.38 (6H, *s*), 2.03 (3H, *s*), 2.01 (3H, *s*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 136.7, 135.1, 125.4, 122.3, 88.9, 24.5, 16.1, 15.6.

2,3-Bis(2,5-dimethylthiophen-3-yl)thiophene (5)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.29 (1H, *s*), 7.04 (1H, *s*), 6.47 (1H, *s*), 6.44 (1H, *s*), 2.36 (6H, *s*), 2.01 (3H, *s*), 1.99 (3H, *s*). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 141.6, 135.4, 135.1, 134.1, 133.9, 133.1, 132.4, 130.9, 128.1, 127.8, 126.9, 15.2, 15.1, 13.7, 13.6.

2,3-Bis(2,5-dimethylthiophen-3-yl)thiophenecarbaldehyde (6)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 9.88 (1H, *s*), 7.68 (1H, *s*), 6.47 (1H, *s*), 6.41 (1H, *s*), 2.38 (6H, *d*, J = 4.4 Hz), 2.06 (6H, *d*, J = 15.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.8, 144.4, 140.9, 138.9, 136.2, 136.0, 135.9, 135.6, 133.6, 131.8, 129.6, 127.0, 126.6, 15.1, 15.0, 14.0, 13.7.

2,3-Bis(2,5-dimethylthiophen-3-yl)-5-methylenemalononitrile-thiophene (MT)

Malononitrile (72 mg, 1.09 mmol) and **6** (200 mg, 0.6 mmol) were dissolved in ethanol (15 mL) and stirred for 30 min. Then, sodium acetate (73 mg, 0.89 mmol) was added to the above solution. The mixture was stirred at room temperature. After the **6** was fully reacted, as confirmed by TLC, the solvent was evaporated. The residue was loaded onto the silica gel column chromatography. Pure sample was obtained with petroleum ether as the eluent, affording brown oil 190 mg (83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.76 (1H, *s*), 7.67 (1H, *s*), 6.49 (1H, *s*), 6.39 (1H, *s*), 2.38 (6H, *s*), 2.07 (3H, *s*), 2.04 (3H, *s*); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 150.5, 146.8, 140.8, 137.1, 136.8, 136.4, 136.3, 134.2, 132.9, 130.8, 128.8, 126.8, 126.4, 114.2, 113.3, 15.1, 15.0, 14.2, 13.7. MS (EI, 70 eV) m/z 380 (M^+); HRMS: [M^+] $C_{20}H_{16}N_2S_3$ requires 380.0476; found [M^+] 380.0473.

Results and discussion

The photochromic behavior of **MT** is investigated in THF solution with the concentration 2.0×10^{-5} M at room temperature. The absorption change was shown in Fig. 1(a) irradiated with 405 nm laser light (hand-held LED lamp, 405 nm/50 mW). Before irradiation with 405 nm light, the longest absorption maximum is observed at 410 nm ($\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}), which is fitting well to the commercially available LED laser lamp (405 nm). This absorption band steps into visible region and exhibits yellowish color. Together with the shoulder band at the blue side (330 nm, $\varepsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}), $S_0 \rightarrow S_1$ transition could be assigned with the bands on the high- and low-energy side corresponding to 0–1 and 0–0 vibration transition, respectively. Upon irradiation with 405 nm light, the 410 nm absorption decreases gradually to totally disappearance. The absorption around 280 nm also significantly decreases and reaches to optically transparent almost. In contrast, a significant absorption increase is observed around 240 nm ($\varepsilon = 2.4 \times 10^4$ M^{-1} cm^{-1}) and 295 nm ($\varepsilon = 1.4 \times 10^4$ M^{-1} cm^{-1}). Finally, a photo-stationary state (PSS) is reached after 7 min irradiation of

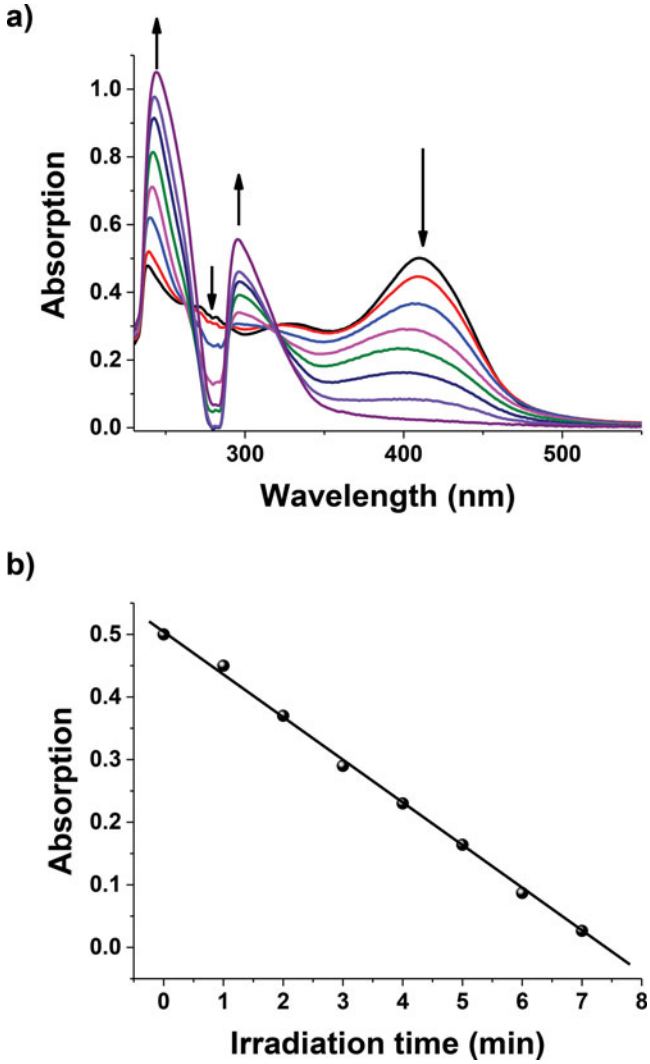
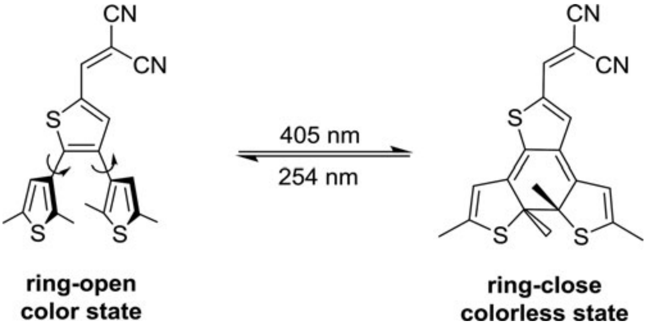


Figure 1. (a) Absorption change of **MT** in THF (2.0 × 10^{-5} M) upon irradiation with 405 nm laser light. (b) Decrease of absorbance at 410 nm with respect to irradiation time.

405 nm light. The absorptivity at 240 and 295 nm is almost doubled with the molar extinction coefficient 5.3×10^4 and 2.8×10^4 M^{-1} cm^{-1}, respectively. Finally, the solution color changed from yellowish to colorless completely. The newly appeared 240 nm band is fitting well to the 254 nm UV lamp (hand held UV lamp, 8 W) used in the lab for TLC detection. Irradiation with 254 nm light, the absorption around 410 nm is appeared again gradually and the solution color recovered to yellowish. Obvious isobestic points are found at 235, 265, 290, 318 nm. It suggests the existence of only two species in the reversible process, which in this case are the ring-open and ring-closed isomers of **MT**. It should be noted that the photochromic behavior is different from most of the published diarylethene derivatives. The cyclization and cycloreversion quantum yields of **MT** were determined to be 0.30 and 0.13. In contrast with the photochromic behavior of **5** (reversible between colorless and colored state), the photochromism of **MT** is reversible between colored and colorless state, which is defined as "invisible photochromism" [28]. Figure 1(b) shows the absorption change at 410 nm with



Scheme 3. Photochromic reaction of **MT**.

respect to irradiation time and an excellent linear relationship could be established between absorption and irradiation time, which indicates a smooth photochromic process.

The photochromic reaction upon alternation irradiation of 405/254 nm light is shown in Scheme 3. In theory, the dithienylethene molecule has two conformations with the two thiophene rings in mirror symmetry (parallel conformation) and in C_2 symmetry (unparallel conformation). The photo-isomerization can only proceed from the antiparallel confirmation, which accounts for half of the totally two conformation. Generally, the absorption of the ring-opened form appeared at a shorter wavelength side, while that of the ring-closed form would shift to longer wavelength due to the delocalized π-electrons. However, it is reversed due to the introduction of electron-acceptor unit. The absorption of ring-opened form appeared at longer wavelength side in visible region. Once the ring-closed, the absorption band in visible region disappeared, moving to invisible region (UV region). According to the well-defined isobestic point, the relative conversion of photo-cyclization was determined to be 0.55 at the photo-stationary state [29].

The photo- and thermal-stability were also investigated. The photo-stability measurements were performed under the irradiation of UV light exposure (broad band, 240–400 nm, 16 W). The isobestic absorption of 318 nm was monitored for decomposition. The absorption decrease indicates the degradation of **MT** induced by UV light Fig. 2(a). After 1 h's exposure of UV light, 5% of **MT** degraded, corresponding to an acceptable photo-stability. Thermal stability of the ring-closed forms was also investigated at room temperature and 323 K in the dark. Figure 2(b) shows thermal induced absorption increase at 410 nm. In the dark, the ring-closed form is stable and the colorless solution could maintain for 24 h. With the temperature rising, the thermal induced cycloreversion rate speeds up. The solution color recovered to color state, reverting back to the ring-opened form. Therefore, the ring-closed form is both light-sensitive and thermal-sensitive.

To better understand the geometric, electronic, and optical properties of **MT**, a comprehensive computational investigation was undertaken using Materials Studio software package. To reduce the initial run times, the ground state energy-minimized structures were calculated using DFT and the LDA/DN basis set. Further refinement and optimization of the structure were achieved using time-dependent DFT (TDDFT) with B3LYP/DND basis set, as implemented in the *Dmol*^{3} package [30, 31].

Figure 3 shows optimized antiparallel conformation, which is required for light-induced conrotatory cyclization. The key factor for the reactivity of conrotatory cyclization is the distance between the photo-cyclizing carbon atoms must shorter than 4.2 Å [32–34]. Once the distance is larger than 4.2 Å, light-induced conrotatory cyclization will be totally inhibited. According to the optimized structure of **MT**, the distance between the two carbon atoms

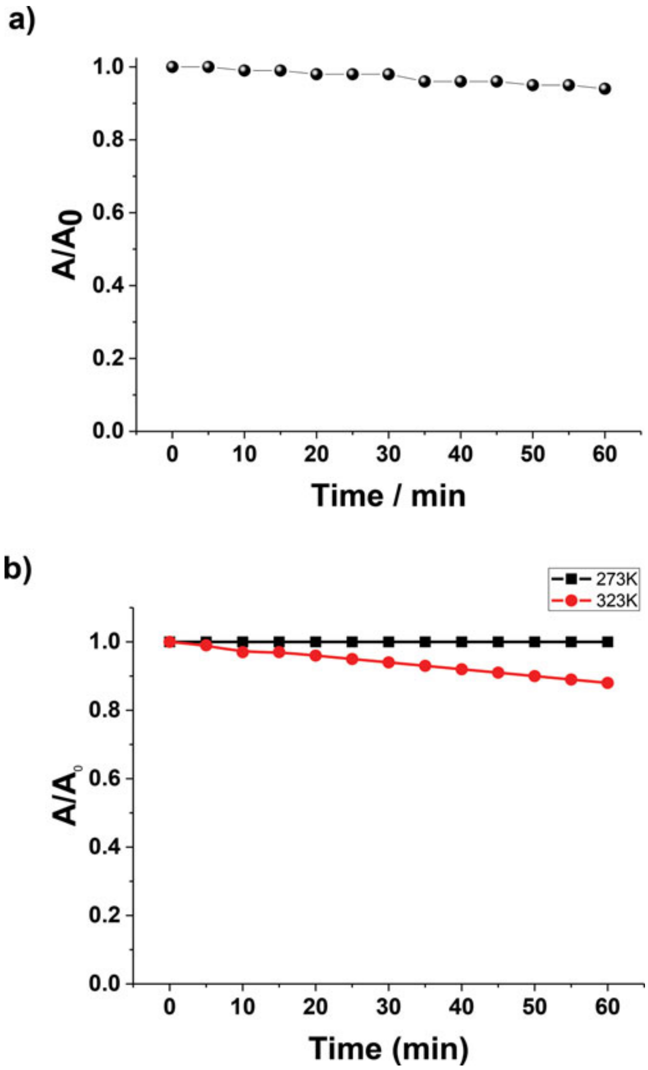


Figure 2. (a) Photo-stability of **MT** upon exposure to UV light; (b) absorption change versus time with the temperature at 273 and 323 K.

involved in the cyclization is 3.591Å, which is meet the requirement for photochromism. The distance between the reactive carbon atoms should be steric control of photochromic reactivity. Apart from that, the electronic features control the photochromic reactivity in another aspect. The nature of the states, topology of the molecule orbitals corresponding to the UV peaks provides more detailed insights towards the photochromic reactivity Fig. 4. For ring-open form, the transition of HOMO-3→LUMO and HOMO→LUMO+1 are contribute to the strong absorption of 420 and 342 nm with the oscillator strength (f) 0.281 and 0.240, respectively. It is agreement with the experimental value 410/330 nm. The molecular orbital (MO) topology of the ring-open form Fig. 4(a) indicates that the orbitals have π shapes. The electron density distributes over the photochromic group in LUMO+1, which has the bonding character of to be formed C-C bond. Due to the electron-withdrawing nature, the LUMO distributes toward the malononitrile group. For the ring-closed form, the electron transition is dominated by HOMO-1→LUMO+2 with f being 0.240 Fig. 4(b). Once the ring-closed, the

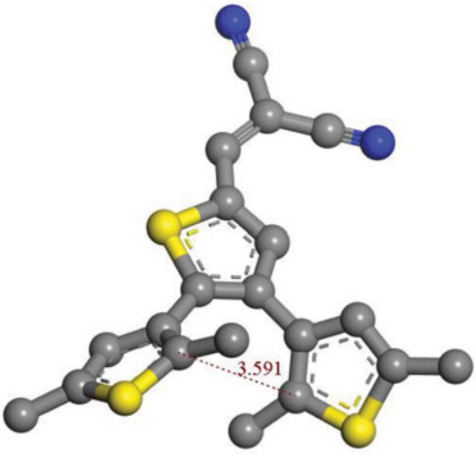


Figure 3. Optimized structure of **MT** and the calculated between reactive carbon atoms. Hydrogen atoms were omitted for clarity.

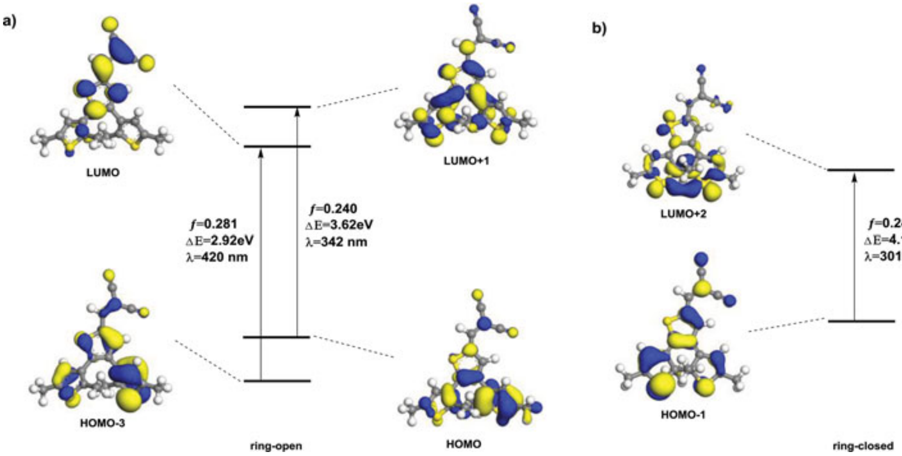


Figure 4. Frontier orbitals for **MT**. (a) Ring-open form; (b) ring-closed form.

energy gap for electron transition is enlarged to 4.12 eV and led to the absorption band shift to higher energy band. The calculated absorption wavelength of ring-closed form is identical to that of the experimental value (295 nm). In addition, the electron density gathered around in the photochromic core in HOMO-1 and LUMO+2. By comparison of the MO topologies between the ring-open and ring-closed form, the significant densities on the reactive carbons moves to higher energy orbitals. This leads to the absorption of ring-closed form shifts to shorter wavelength.

Conclusions

In summary, a robust photochromic bisthienylethene derivative was synthesized, and was full characterized. Its photochromic behavior was investigated in THF solution. It is interesting that the photochromic compound exhibit reversed photochromism. The ring-open form is colored and changed to colorless when irradiated with 405 nm laser. Due to the introduction of malononitrile, the strong absorption at longer wavelength was observed at 410 nm, which is fitting well to the commercially available laser LED lamp. After the PSS state reached, the 410 nm absorption is nearly optical transparent and absorption band around 295 and 240 nm enhanced. Upon irradiation with 254 nm light, the solution color changed from colorless to yellowish, recovering the original color of **MT**. The photo- and thermal-stability measurements show that **MT** is robust towards light and temperature. The calculation provides further insight about the reversed photochromism. Strong electron-acceptor results the electron densities in reactive carbons to higher energy orbitals and thus shifted absorption of ring-closed form to shorter wavelength.

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ORCID

Xiaochuan Li http://orcid.org/0000-0002-6903-9574

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