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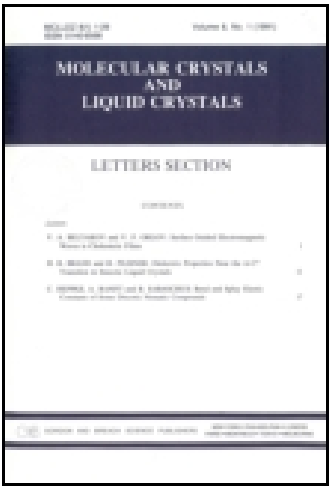

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Properties of Star Shaped Thiophene Materials Having a Build-In Photochromic Core

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A series of star shaped photochromic bisthienylethene derivatives were synthesized by Still coupling reaction and fully characterized. Their photocromic properties were investigated in solution state. With the thiophene or thiazole "arms" attached to a photochromic core, the reversible ring-open and ring-close photoismerization reactions undergoes smoothly when irradiated with ultraviolet and visible light alternately. Molecular geometric structures were optimized and HOMOs/LUMOs were calculated by Dmol^3 *package of* Material Studio. *Two key factors, the distance between reactive carbon atoms and the electron distribution in unoccupied orbitals (LUMO), favored the cyclization/cycloreversion triggered by photons.*

Keywords Star shaped; photochromic core; Stille coupling reaction; geometric structure; reactive atoms

Introduction

Molecular switches were intensively investigated in the last decades and have been applied in molecular electronic especially in optoelectronics, optical data storage, self-assembling system, and logic gate system [1–5]. Particular interest for electronics applications are molecules that can be toggled between well-defined states by external excitation. Among variety of types of molecular switch, bisthienylethenes stood out of them and attracted the interest of scientists in recent years. They exhibit excellent yields of photocyclization-photocycloreversion reactions, fatigue resistance, and thermal stability. The physical properties, such as conductance, emission intensity, viscosity, and refractive index can be modulated reversibly by the switching process [6–10].

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In this report, triangle terthiophene, a photochromic core, was extended in three directions with thiophene and thiazole rings. The star shaped molecular structure will benefit to the energy absorption. Photochromic triangle terthiophene has three α position left, in which the α-H is easy to be substituted by bromine atom. The introduced bromine atoms can be substituted by functional group according to the requirement. Still or Suzuki coupling reaction are alternatives for attaching functional "arms" to the photochromic core. The synthesis is convenient and the corresponding tin or boron reagents are commercially available. With thiophene or thiazole "arms" attached, the energy harvesting and transferring effect in the molecular system will be observed generally. Also it will be benefit for the quantum yield of photocyclization. The energy transfer efficiency depends on the type and number of "arms." Correspondingly, the opto-properties of the core will be enhanced or changed possibly based on the light harvesting effect of "arms."

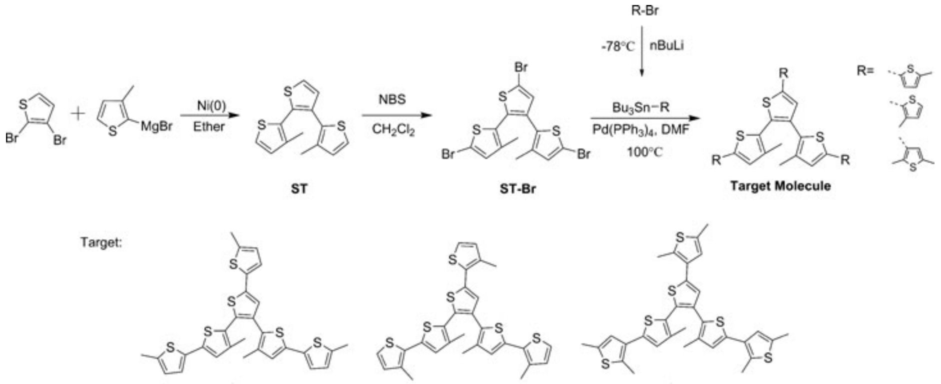
Experimental

Synthesis

The synthetic route is shown in Scheme 1. Bromonated thiophene or thiazole were purchased from Aldrich and Alfa Aesar and used as received. Photocromic core (star-shaped terthiophene, **ST)** was synthesized by conventional Kumada coupling reaction [11, 12]. Bromination of **ST** proceeded according to our published paper in 2009 [13]. The synthesis of target molecules (**ST1–3**) was carried out by Stille or Suzuki coupling reaction. Experimental results show that Stille coupling reaction is more effective than Suzuki. The synthesis procedure is as follows:

Synthesis of Sn-reagents: Bromonated thiophene or thiazole (1eq) was added to anhydrous THF in 100 mL Schlenk tube under nitrogen atmosphere. The mixture was cooled to −78°C. n-BuLi (1.1 eq) was added dropwisely. After the temperature was maintained at −78°C for 30 min, chlorotributyltin (1.1 eq) was added dropwisely. The reaction mixture was warmed to room temperature and stirred for 3 h. After normal workup, the product (pale yellow liquid) was used for next step without purification.

General procedure for the synthesis of target molecules: Under the protective of nitrogen atmosphere, **ST-Br** (1 mmol, 510 mg), Sn-reagent (4.5 mmol), Pd(PPh_3)$_4$ (35 mg) mixed with DMF (35 mL). After three freeze-thaw cycles, the mixture was heated up to



Scheme 1. Synthetic route of **ST1–3.**

100°C for 48 h. The progress of reaction was monitored by TLC. After the completion of reaction, the reaction was quenched by adding water (50 mL). This solution was extracted by CH_2Cl_2 (30 mL × 3). The combined organic phase was washed thoroughly with KF solution (40 mL, 1 M) to remove the un-reacted chlorotributyltin. The organic phase was dried over magnesium sulfate, and then the solvent was evaporated in vacuum. The residue product was chromatographed on silica gel (hexane/CH_2Cl_2 = 4:1) giving yellowish solid powder (yield: 12–49%).

ST1 Pale yellow powder, yield 49%, ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.09 (s, 1H), 7.00 (s, 1H), 6.90 (s, 2H), 6.81 (s, 2H), 6.68 (s, 1H), 6.63 (s, 2H), 2.48 (d, J = 12.6 Hz, 9H), 1.97 (d, J = 25.2 Hz, 6H), ^{13}C NMR (100 MHz, $CDCl_3$), δ: 139.8, 139.2, 138.9, 137.5, 137.2, 137.1, 136.6, 136.1, 135.2, 134.9, 134.3, 132.9, 130.4, 130.1, 127.6, 126.2, 126.1, 126.0, 123.9, 123.5, 123.3, 15.5, 15.4, 15.0, 14.8, EI+/MS: 564, HRMS: Calcd for $C_{29}H_{24}S_6$, 564.0202, found, 564.0226.

ST2 Pale yellow powder, yield 35%, ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.16 (s, 2H), 7.09 (s, 2H), 6.90 (s, 1H), 6.87 – 6.83 (m, 4H), 2.44 (s, 3H), 2.34 (s, 6H), 2.04 (s, 3H), 1.98 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$), δ: 140.1, 139.6, 138.6, 138.4, 138.2, 137,5, 137.0, 136.6, 136.0, 135.8, 135.5, 135.2, 134.9, 134.0, 133.1, 132.6, 132.2, 130.3, 127.5, 127.2, 126.6, 126.3, 126.1, 125.4, 123.7, 123.5, 122.9, 15.7, 15.2, 14.8, 14.6. EI+/MS: 564, HRMS: Calcd for $C_{29}H_{24}S_6$, 564.0202, found, 564.0210.

ST3 Pale yellow powder, yield 24%, ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.38 (s, 1H), 7.31 (s, 1H), 7.21 (s, 1H), 7.16 (s, 1H), 6.91 (s, 1H), 6.82 (s, 1H), 2.41 (s, 3H), 2.37 (s, 6H), 2.35 (s, 3H), 2.31 (s, 3H), 2.28 (s, 6H), 1.97 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$), δ: 142.5, 141.1, 139.1, 138.1, 135.8, 135.6, 134.9, 134.0, 131.4, 131.1, 130.7, 130.2, 129.1, 128.6, 127.3, 126.5, 125.7, 125.3, 124.2, 123.6, 123.3, 123.0, 121.4, 15.6, 15.2, 14.9, 14.4, 13.9, EI^+/MS: 607, HRMS: Calcd for $C_{29}H_{24}S_6$, 606.0672, found, 606.0678.

Measurements

The NMR spectra were recorded on Brucker Advance 400 spectrometer, operating at 400 MHz for proton and 100 MHz for carbon. The measurement was carried out at $CDCl_3$ solution. The chemical shifts (given as δ in ppm) was referenced to tetramethylsilane (TMS). Mass spectra measured by a Waters120 QTof. High resolution mass spectra measured on Brucker microOTOF II Focus. Absorption spectra measured with PERSEE TU-1900 spectrophotometer with an external slit width of 2.5 mm used to collect absorption. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements solutions were deoxygenated by bubbling nitrogen through them.

For the theoretical study of photophysics of the compounds in the excited states, the *Dmol*^{3} module packaged in *Material Studio* was used. The ground state geometries of the compounds were calculated by GGA (generalized gradient approximation) methods at the PBE level [14, 15]. The vibration spectrum of each star shaped compounds was calculated at the level of theory based on the ground state geometries.

Results and Discussion

The photochromic behavior of **ST**s induced by photoirradiation was measured in THF (tetrahydrofuran) at room temperature. **ST1–3** exhibited moderate photochromic properties and could be toggled between colorless ring-open and colored ring-closed forms by alternate irradiation with ultraviolet and visible light. The absorption changes of abosrption in **ST1–3** with wavelengths were shown in Fig. 1 and representative photochromic reaction was shown

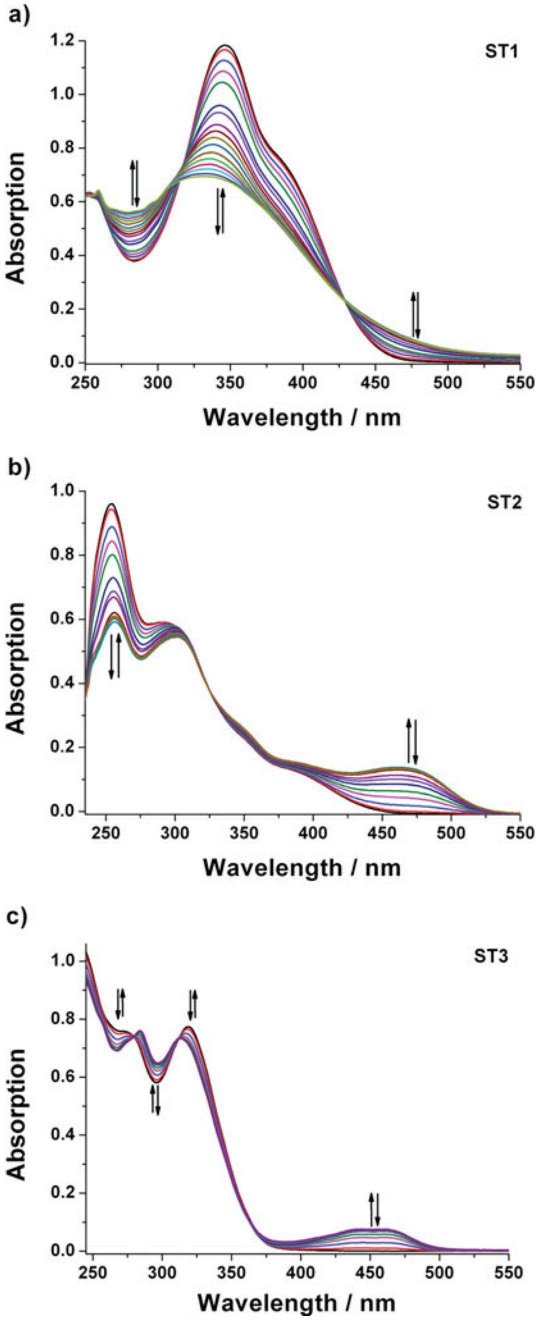


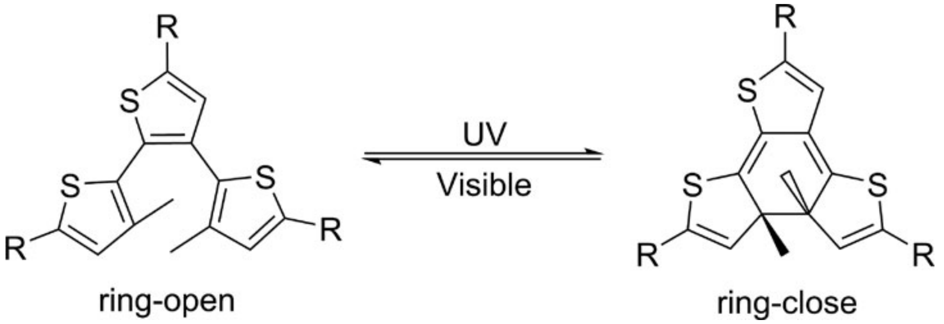
Figure 1. Absorption change of **ST1–3** in THF upon irradiation at 365 nm for **ST1**, 254 nm for **ST2** and **ST3** (1.2×10^{-5} M).

in Scheme 2. The absorption maximum of **ST1** in THF was observed at 346 nm due to a π-π^* transition. Generally, the absorption of ring-open form appeared at shorter wavelength. For the ring-closed form, the absorption peak was at a longer wavelength since π-electrons delocalized and extended to the two cyclizing thiophene rings. Upon irradiation of **ST1** in

THF with UV light ($\lambda = 365$ nm), a new absorption band centered at 475 nm ($\varepsilon = 7.2 \times 10^3$ L·M^{-}1·cm^{-1}) emerged immediately due to the formation of ring-closed form. The formation of the ring-closed form leads to a color change of the solution from colorless to light yellow. For the reverse reaction, the light yellow solution of **ST1** faded to colorless upon irradiation with visible light ($\lambda \geq 405$ nm) and the absorption band centered at 470 nm disappeared gradually. **ST2–3** exhibited similar photochromic properties with the appropriate irradiation wavelength for **ST2/ST3** (254 nm). The absorption maxima were found at 460 nm ($\varepsilon = 1.1 \times 10^4$ L·M^{-1}·cm^{-1}) and 454 nm ($\varepsilon = 6.7 \times 10^3$ L·M^{-1}·cm^{-1}) for **ST2** and **ST3**, respectively. The color of solutions turned from colorless to light yellow and faded gradually with alternated irradiation of UV and Visible light, which is similar to that of **ST1**.

According to the behavior and data mentioned above, it is worth to be noted that the variability of structure resulted in a shift of the maxima absorption of ring-closed form from 475 nm to 454 nm. The photochromic wavelength of **ST1/ST2** are shifted to longer wavelength than that of **ST3**. With the "arms" of 2,5-dimethylthiophene attached to the photochromic core (**ST),** the photochromic wavelength of **ST3** blue-shifted about 20 nm compared with that of **ST1**. The attached heterocyclic ring "arms" will be conjugated with the ring-closed photochromic core (**ST**). Obviously, the steric hindrance 2,5-dimethylthiophene is larger than that of 5-methylthiophene and 3-methylthiophene. Higher steric hindrance prevents the conjugated degree of the whole molecular system. The smaller steric hindrance "arms" of **ST1/ST2** result in expanded conjugation of π system and absorption red-shift. The intensity at photochromic wavelength for **ST2** is the largest among the four compounds. The conversion of photocyclization reaction α_{ps} at the photostationary states are determined to be 0.24 (**ST1**), 0.60 (**ST2**), and 0.40 (**ST3**) [16, 17]. The photocyclization yield of **ST2** is better than that of others. It likely indicates that the "arms" of 3-methylthiophene is helpful for the light absorbing and efficient energy transfer from the "arms" to the core. However, it does not exclude the possibility that the complicated intra- or inter-molecular interaction prevent the energy transfer from the "arms" to the core in a certain extent for **ST1** and **ST3**.

One of the key factors for photochemical reaction was the photostability. Photochemical reaction and the corresponding reverse reaction cycles should be repeated without or with a very few side reactions. **ST1–3** were stable towards photochemical decomposition. Even if 5 times of coloration and decoloration cycles, only a little intensity decrease of absorbance was observed for the ring-closed forms of **ST1–3** at the photostationary state. The thermal stability of the ring-open and ring-closed forms of **ST1–3** was also investigated, which is



Scheme 2. Photochromic reaction of **ST**s.

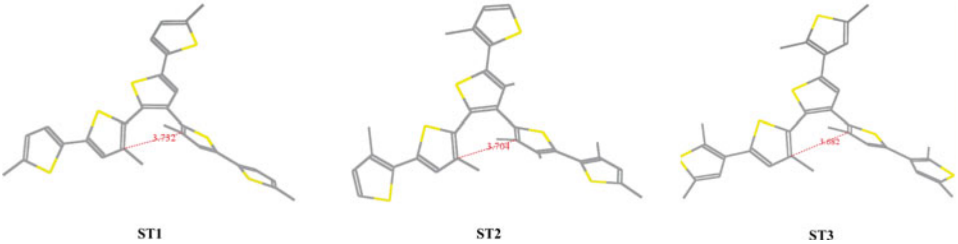


Figure 2. Optimized structure of **ST1–3** and the distance between reactive carbon atoms.

important for opto-electornic device fabrication. At room temperature, no color change can be detected by absorption spectra with the solution of **ST1–3** in THF being exposed to air for 1d in the dark. In the absence of light, the light yellow color of solutions persisted for several days, attesting to their thermal stability.

In order to get a deep insight for the photo-physical properties of the photochromic compounds, three-dimension structures of **ST1–3** were optimized by the level of density function theory using a GGA/PBE basis set as implement in the *Dmol*^{3} package. Fig. 2 shows the optimized structure of **ST1–3**. The ring-open forms of diarylethenes have two conformations, antiparallel and parallel, and two conformations interconvert with each other in solution state. Obviously, most of the molecules will adopt the conformations with lower molecular energy. The conrotatory cyclization can proceed only from antiparallel conformation. According to the literature report, the photocyclization reactivity of diarylethenes was controlled by the distance between the reactive carbon atoms in the antiparallel orientation rather than the polar and steric substituent effects [18–20]. The optimized structures of **ST1–3** (Fig. 2) indicate that these compounds are in antiparallel conformation, which facilitates the photocyclization. The distances between reactive carbon atoms were measured to be 3.732 Å, 3.704 Å, and 3.682 Å for **ST1–3**, respectively, which are shorter enough for the molecules to undergo the photocyclizaion reaction. With the distance between the reactive carbon atoms larger than 4.2 Å, the photocyclization reaction will be suppressed completely.

The absorption spectra of **ST1–3** were also investigated with Time-Dependent Density Functional Theory (TD-DFT) based on the optimized ground state. The most stable conformer exhibits a strongly transition at 377 nm (**ST1**), 332 nm (**ST2**), and 353 nm (**ST3**), which corresponds to the experimental value at 346 nm (**ST1**), 300 nm (**ST2**), and 337 nm (**ST3**). These bands are dominated by a HOMO-LUMO contribution with the calculated oscillator strengths (f) larger than 0.4. The topologies of these molecular orbitals are shown in Fig. 3, and it appears that the HOMO and LUMO have π shapes for **ST1–3**. The electron distributions are delocalized on the photochromic core mostly, which is important for photochromism. To allow the ring-close, the electron should be promoted into a state dominated by photochromic orbitals which are characterized by a bonding nature for the to-be-formed carbon-carbon bond as well as a significant density on at least one of the two reactive carbon atoms. From Fig. 3, it can be seen clearly that the electrons gathered around the reactive carbon atoms in LUMOs of **ST1–3**.

Conclusions

A series of star-shaped thiophene derivatives were designed and synthesized. Their photochrmic behavior in the THF solution was investigated in details. **ST1–3** exhibit similar

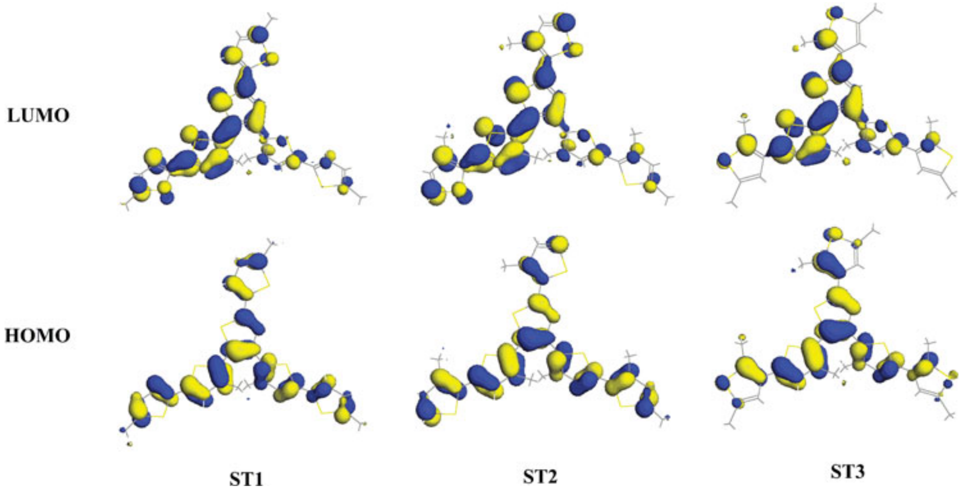


Figure 3. Frontier orbitals for **ST1–3**.

photochromic behavior with different photochromic wavelength. The photochromic wavelength of **ST2** is shifted with the 3-methylthiophene attached to the photochromic core. The ring-open and ring-closed isomers were thermal stable at room temperature, and the coloration/decoloration cycles could be repeated 5 times. Based on the optimized structures of **ST1–3**, the distances between reaction carbon atoms for **ST1–3** were estimated and shorter than the threshold (4.2 Å), which is critical to the photochromic reactivity of diarylethene derivatives. Absorption spectra for **ST1–3** were calculated based on the optimized structure. The calculated molecular orbitals indicate that the electron location at the reactive carbon atoms in LUMOs is benefit to induce photochromism. The reversible cyclization/cycloreversion can be used to modulate the fluorescence emission and well documented, which qualified photochromic bisthienylethen derivatives as a potential candidate for multifunctional OLED dopant or information storage materials. Our work along those lines is in progress.

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