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Photochromism of triangle terthiophene derivatives as molecular re-router†

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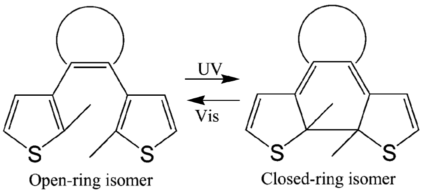
2,2′-3,3″-Terthiophene derivatives undergo photochemically reversible cyclization and cycloreversion reactions. The absorption peak wavelength changed systematically with substitution of the phenyl rings at 5-, 5′- and 5″-positions of the thiophene rings, which indicates re-routing of the π-conjugation system.

Photochromic molecules have been widely studied as photoswitching units in various photoresponsive molecules and polymers.[1] Recently, photoswitching effects in photochromic diarylethenes have been extensively studied for controlling various chemical and physical properties such as refractive index, dielectric properties, electronic conduction, electrochemical response and magnetic interactions.[2–9] Some of these photoswitching effects are based, at least partly, on changes in the extent of the π-conjugation in diarylethene upon the photochromic reactions. That is, the π-conjugation system of diarylethene extends over both sides of the molecule in the closed-ring form, while it is restricted on each side of its open-ring isomer, as shown in Scheme 1. The connection mode of the π-conjugation system is dependent on the substitution positions of the thiophene units to the ethene unit.[10] Recently, Branda *et al.* have designed dithienylethene derivatives having thiophene units on their reacting carbon atoms for a photoswitching unit of the π-conjugation pathway, although various types of photocyclization reactions are possible in these molecules and the detailed reaction mechanism must be clarified.[11] Since various types of molecular electronic devices have been designed on the basis of a π-conjugation connection pathway,[12] photon-mode switching and re-routing of the connection mode of the π-conjugation system are worthy of extensive study.

Here, we report on photochromic triangle terthiophene derivatives **1–3**, which behave as photoswitching 2-way re-routers of the π-conjugation system. These molecules include a hexatriene unit in their molecular structure and are expected to undergo photoinduced cyclization and cycloreversion reactions in a similar manner to diarylethenes. As illustrated in Scheme 2, the π-conjugation system in the open-ring isomers would extend between the 5- and 5′-positions in the central and left side thiophene rings, respectively, while it would extend between the 5- and 5″-positions in the central and right side thiophene rings in the closed-ring form isomer, respectively. In order to demonstrate the re-routing effect in the π-conjugation connection mode, molecules **1–3** having different substituents were prepared.

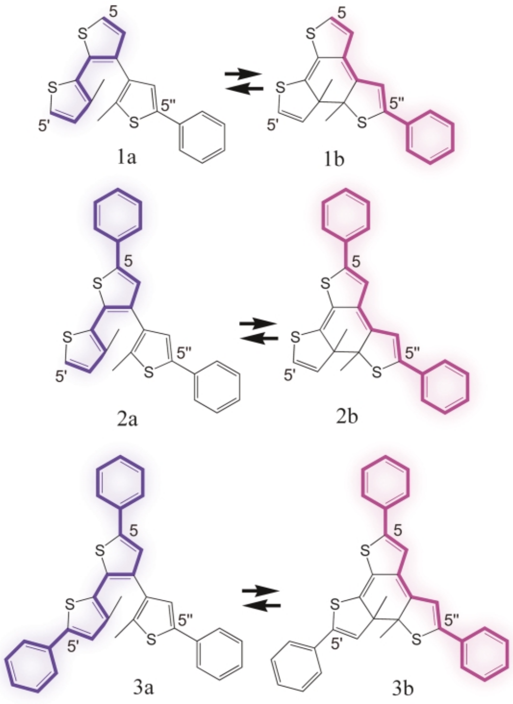
Compounds **1a–3a** were synthesized by conventional cross-coupling reactions of thiophene derivatives and their chemical structures were confirmed by elemental analysis, mass spectra and NMR spectra.† The closed-ring isomers **1b–3b** were prepared by irradiating hexane solutions of the corresponding open ring isomers **1a–3a** with UV light and were isolated by HPLC from the colored solutions. Formation of the colored isomers was confirmed by mass spectrometry and/or by ^{1}H-NMR spectroscopy in $CDCl_3$ solution. The photochromic reaction behavior and absorption spectral changes of these molecules were studied in hexane at room temperature.



Scheme 1

Colorless and yellow solutions of the open ring isomers **1a–3a** were observed to turn red or blue depending on the molecular structures upon irradiation with UV light (λ = 313 nm). These colors disappeared upon irradiation with visible light (λ > 460 nm). These coloration and bleaching cycles can be repeated many times with alternating irradiation with UV (λ = 313 nm) and visible light (λ > 460 nm).

As shown in Fig. 1, **1a** has no absorption band in the visible range and a new absorption band appeared at 558 nm upon irradiation with UV light, which corresponds to the formation of **1b**. An isosbestic point was observed at 318 nm supporting the two-component photochromic reactions shown in Scheme 2. The conversion ratio from **1a** to **1b** was 72% at the photostationary state which was achieved by irradiation with UV light (λ = 313 nm). The colored solution was completely bleached upon irradiation with visible light. Similar photochromic performance was also observed for **2** and **3**. Fig. 1(b) and (c) show absorption spectra of **1a–3a** and **1b–3b**, respectively. Their λ_{max} and ε_{max} are summarized in Table 1. The λ_{max} of the open-ring isomers showed a systematic red shift from **1a** and **3a**. This is due to the introduction of phenyl groups at the 5- and 5′-positions of the thiophene rings. These spectral shifts of indicate that the π-conjugation pathway is connected between the 5- and 5′-positions and is disconnected



Scheme 2

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† Electronic supplementary information (ESI) available: analytical data for **1a**, **2a** and **3a**. See http://www.rsc.org/suppdata/cc/b3/b311334e/

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between the 5- and 5″-positions as schematically illustrated in Scheme 2.

On the other hand, $\lambda_{\max}$ of the closed ring isomers showed a red shift in the absorption maximum upon the introduction of a phenyl ring at the 5-position of the central thiophene ring. Almost identical absorption spectra were observed for **2b** and **3b**. Substitution with a phenyl unit on the 5′-position does not affect the absorption spectrum. These spectral features indicate that the π-conjugation systems are connected between the 5- and the 5″-positions of the closed ring isomers but those between the 5- and 5′-positions are disconnected.

Similar spectral shifts were also observed in fluorescence emission wavelengths, as also listed in Table 1. Noted that the closed-ring isomers **1b** and **2b** showed fluorescence emission wavelengths different from those of **1a** and **2a**, respectively. That is, the emission wavelength can be modulated by the photochromic reaction, although their emission intensities were relatively weak as found for some diarylethene derivatives.[13]

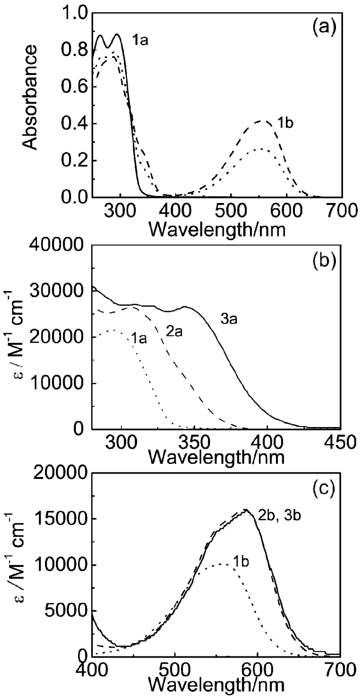

Fig. 1 (a) Absorption spectra of **1a** solution (solid line) and of the photostationary state under irradiation with UV light (λ = 313 nm) (dotted line) and absorption spectrum of **1b** solution (broken line). (b) Absorption spectra of open ring isomers **1a–3a**. (c) Absorption spectra of closed ring isomers **1b–3b**. All measurements were carried out at room temp. using hexane as solvent.

Table 1 Optical properties of photochromic terthiophenes **1–3**[a]

Compound	$\lambda_{\max}$/nm (ε/M^{-1} cm^{-1})	$\phi_{o\text{–}c}$[b]	$\phi_{c\text{–}o}$[c]	λ_{em}, λ_{ex}/nm
1a	264 (20900) 294 (21500)	0.27	—	389, 313
1b	558 (10100)	—	0.43	561, 682
2a	272 (31500) 307 (28100)	0.18	—	432, 348
2b	584 (16000)	—	0.26	716, 586
3a	274 (31500) 308 (27000) 345 (26000)	0.04	—	449, 352
3b	584 (16000)	—	0.39	—

[a] All measurements were performed at room temp. in hexane solution. [b] At 313 nm. [c] At $\lambda_{\max}$ of the closed ring isomers.

Table 1 also summarizes the photochemical quantum yields of cyclization and cycloreversion reactions of the compounds. These values were evaluated by the standard procedure using fulgide as a standard.[14] **1** showed relatively high photochemical quantum yields in both cyclization and cycloreversion reactions. Suppressed quantum yields were observed in **3a**. No marked thermal bleaching was observed in the closed ring isomers **1b**, **2b** and **3b** at room temp.

In conclusion, the triangular terthiophene derivatives presented here showed reversible photochromic reactions with relatively high photochemical quantum yields and they can re-route the connection mode of the π-conjugation system with the photochromic reaction. We expect various kinds of photo-switching effects such as electrical conductivity and optical properties with these photo-switching units. By combining these molecular re-routers, photon-mode logic gates may be realized in the future.

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