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Regulating π-conjugated pathways using a photochromic 1,2-dithienylcyclopentene

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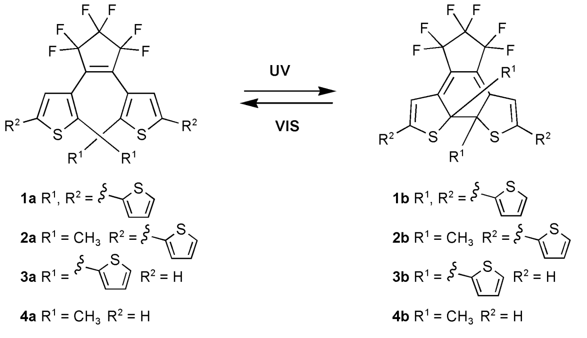
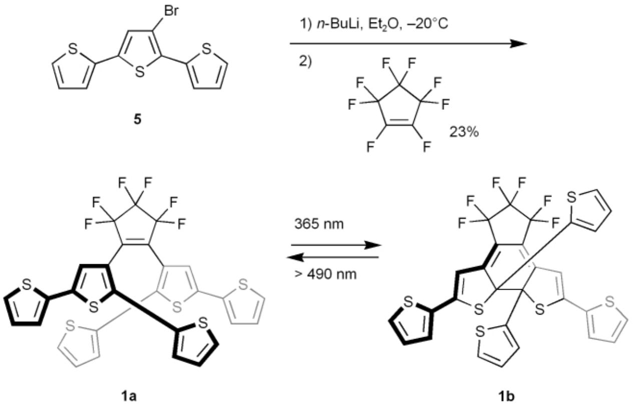
Linear π-conjugation is reversibly re-routed by irradiation of a photochromic bis(terthiophene).

Thermal irreversibility and fatigue resistance are two of the properties responsible for the growing popularity of photochromic 1,2-dithienylethene derivatives in photonic device applications such as processing digital information and gating electronic conductance.[1] This last application is feasible because the π-electrons are delocalized throughout the photochromic backbone only in the ring-closed state (**1b**–**4b**, for example) due to the linearly π-conjugated pathway that is created upon photocyclization. On the other hand, these electrons are forced to reside on the two thiophene rings in the ring-open form (**1a**–**4a**, for example) due to the lack of linear π-conjugation between the two heterocycles. Therefore, any π-electrons on the two R^2 groups can only interact with each other through the conjugated pathway in the ring-closed state. Accordingly, incorporating the photochromic dithienylethene backbone into polyene molecular wires should permit the reversible switching of conductive properties by photoirradiation. Although there are several reports that describe how this structural modification can regulate electronic communication between various R^2 groups,[1,2,3] we are unaware of any that take advantage of the changes that accompany, in our opinion, the most dramatic skeletal alteration between the two isomers: upon photochemical ring closure, the two carbon atoms involved in forming the new single bond (the 2′-positions of the heterocycles) change their hybridization from sp^2 to sp^3.

The molecular system described here is the first of its kind. Two terthiophene units have been appropriately modified so that the central thiophene rings of each make up the photochromic dithienylethene backbone (**1a**). Because oligo- and polythiophenes display promising semi-conducting properties and are being considered as prototype molecular-scale wires,[4] we chose to use terthiophene as a model oligothiophene to incorporate into the photochromic 1,2-dithienylcyclopentene. Complete delocalization of the π-electrons in a manner typical for terthiophene derivatives is anticipated only when the photochromic system is in its ring-open form (**1a**, grey and black pathways in Scheme 1). Light-activated ring-closure not only severs the conjugated pathways of the two original oligomers, it creates a new one (**1b**, grey-to-black in Scheme 1). Using this approach, π-conjugation is not just regulated on command, but also re-routed.





Scheme 1

Compound **1a** was synthesized from the known 3′-bromoterthiophene **5**[5] as shown in Scheme 1. Single crystals of **1a** suitable for X-ray crystallographic analysis were grown by slowly cooling a hot hexane solution of the compound. The structure of **1a** in the crystal† (Fig. 1) reveals that the two peripheral heterocycles of each terthiophene arm are rotated by an average of 20° and 48° for the outer and inner rings, respectively.‡ Despite this deviation from coplanarity with the central heterocycle in the solid-state, the recorded UV–VIS absorption spectra argue that, in solution, π-conjugation is still extended throughout each terthiophene arm of the photochromic system.

The crystal structure also reveals that the two overlapping terthiophene arms are within π–π stacking distances and exist in a cofacial orientation with an average distance of 3.62 Å between the stacked rings. This π–π stacking also exists in solution as shown by the fact that in CD_2Cl_2 the ^1H NMR signal corresponding to the methine protons on the central thiophene rings shift downfield from 6.40 ppm to 6.58 ppm upon photoinduced ring cyclization of **1a**. This is contrary to what is typically observed for other photochromic dithienylethene derivatives where the methine protons move upfield due to the loss of aromaticity of the heterocycles during the ring-closing

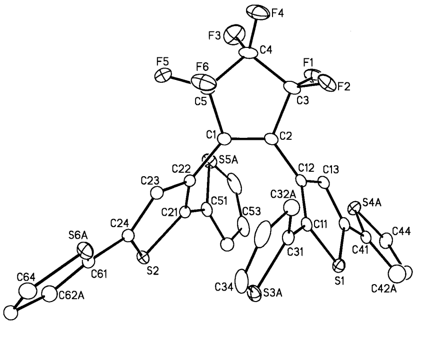


Fig. 1 Molecular structure of **1a** in the crystal. The thermal ellipsoids are drawn at the 20% probability level.

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process. The atypical downfield shift in the case of **1a** is due to the fact that in the ring-open form these protons are lying within the shielding region of the thiophenes of the neighbouring arms. This shielding effect is lost when **1a** is photochemically transformed into **1b**. Bis(dithiophene) **2a** shows typical upfield shifting of the central thiophene protons in the ^{1}H NMR spectrum upon ring closure (7.12 ppm for **2a** and 6.54 ppm for **2b**).

All of the photochromic compounds can be toggled between their ring-open and ring-closed forms by alternate irradiation with appropriate wavelengths of light. A representative example is shown by the changes in the UV–VIS absorption spectra in Fig. 2a. Irradiation of CH_2Cl_2 solutions of **1a** at 365 nm resulted in an immediate increase in the absorption intensity in the visible spectral region (λ_{max} = 632 nm) and a visual change in colour from light yellow to blue due to the appearance of the ring-closed isomer, **1b**. The photostationary state was identified by ^{1}H NMR spectroscopy as consisting of 80% of the ring-closed isomer, **1b**. Irradiation of **1b** at wavelengths greater than 490 nm resulted in the rapid ring-opening photoreaction and the regeneration of the original absorption and ^{1}H NMR spectra corresponding to **1a**.

The presence of the significant low-energy absorption for **1a** (as far out as 448 nm§) as compared to **2a**[6] (cut-off at 388 nm), which possesses only dithiophene arms, clearly indicates that each terthiophene arm of **1a** exhibits extended conjugation (Fig. 2b). The bis(dithiophene) **3a** exhibits a low-energy absorption band at λ_{max} = 320 nm which is comparable, albeit less intense, to that of **2a** (λ_{max} = 316 nm). On the other hand, compound **4a**,[6] which contains a single thiophene within each arm, exhibits an absorption band at higher energy (λ_{max} = 292 nm).

The absorption band for the ring-closed form of bis(terthiophene) **1b** (λ_{max} = 632 nm) is only slightly red-shifted when compared to bis(dithiophene) **2b** (λ_{max} = 625 nm) as shown in Fig. 2c. This observation argues that the pendant heterocycles in **1b** have little effect on the UV–VIS absorption spectrum of the ring-closed form. Therefore, the linear π-conjugated backbone in **1b** should be treated as an analogue of that in **2b**. The absorption band of bis(dithiophene) **3b** (λ_{max} = 545 nm), however, is significantly blue-shifted as compared to that of the bis(dithiophene) **2b** due to the extended π-conjugation that is maintained in the latter even in the ring-closed form. In a similar fashion, the absorption band of bis(dithiophene) **3b** is only red-shifted by 25 nm as compared to that of the photochromic bis(thiophene) **4b** (λ_{max} = 520 nm).

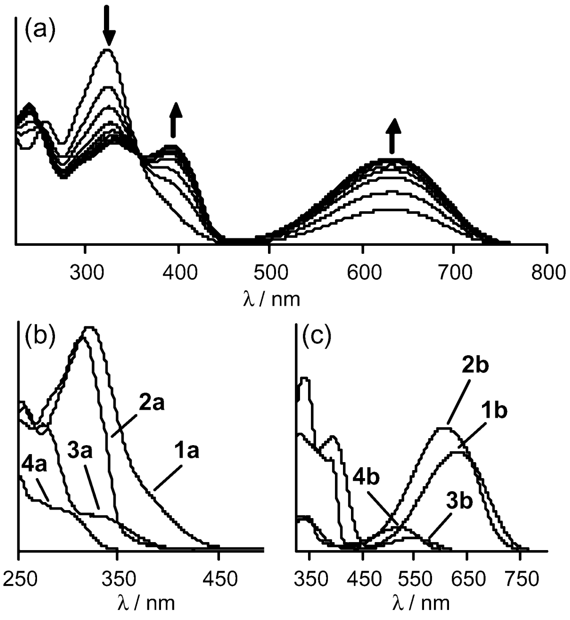

Fig. 2 (a) Changes in the UV–VIS absorption spectra of **1a** upon irradiation with 365 nm light. Irradiation periods are every 5 seconds until a 50 second period was reached. (b) UV–VIS spectra of the ring-open forms **1a**, **2a**, **3a** and **4a**. (c) UV–VIS spectra of the photostationary states containing 80% **1b**, 93% **2b**, 38% **3b** and 63% **4b**. All spectra were of CH_2Cl_2 solutions at 2×10^{-5} M. The photostationary states were obtained by irradiating solutions of **1a** and **2a** with 365 nm light and solutions of **3a** and **4a** with 313 nm light until no spectral changes were observed.

This work has demonstrated that while the ring-open isomer **1a** has two π-conjugated terthiophene arms, the ring-closed isomer **1b** has the linearly π-conjugated pathway extending through the backbone of the photochrome. The original conjugated pathways have been destroyed. This is clearly evidenced by the similarity of the absorption spectrum in the visible region between the ring-closed forms of **1b** and **2b**, the latter possessing an identical linear π-conjugation backbone but lacking the additional thiophene heterocycles.

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Notes and references

† *Crystal data* for **1a**: $C_{29}H_{14}F_6S_6$, M = 668.76, monoclinic, space group $P2_{1/c}$ (No. 14), a = 14.701(2), b = 24.818(4), c = 7.6381(12) Å, β = 90.457(3), V = 2786.7(7) Å^3, T = −80 °C, Z = 4, μ = 0.552 mm^{-1}, 5701 reflections measured, 3872 unique, $R_1(F)$ = 0.0556, $wR_2(F^2)$ = 0.1358 (all data). CCDC 187849. See http://www.rsc.org/suppdata/cc/b2/b205904e/ for crystallographic data in CIF or other electronic format.

‡ The terminal 2-thienyl groups were found to be rotationally disordered such that the sulfur atom and the carbon in the 3-position were exchanged to varying degrees (the disorder ratios being 70:30, 85:15, 55:45 and 60:40 for the four terminal thienyls). In all cases only one set of 4,5-olefinic carbon atom positions was refined, and even with the disordered sulfur and carbon atoms there was little deviation from thienyl ring planarity, as shown by the least-squares planes calculations. The one exception from planarity would be the ring containing C41, C43 and C44 and the disordered sulfurs S4A and S4B and carbons C42A and C45B. In this case the best-fit planes were calculated separately for S4A, C41, C42A, C43, C44 and for S4B, C41, C43, C44, C45B. For the former plane the deviations were minimal, while for the latter the larger deviations observed (up to 0.116(11) Å, for C45B) would in large part be due to the relatively low occupancy factors for the disordered atoms in this plane (15% occupancy for S4B, C45B *vs.* 85% for S4A, C42A).

§ An arbitrary cut-off of 0.01 absorption units was used in all cases.

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