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One-step synthesis and photochromic properties of a stable triangle terthiophene

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Abstract—A new photochromic compound based on the hexatriene backbone was prepared by one-step coupling. The photochromic backbone, composed of three thiophene ring, undergoes reversible ring-opening and ring-closing photoisomerization reactions when irradiated with ultraviolet and visible light, respectively. It exhibited fatigue resistance and thermally irreversible photochromic properties. The ring-open form exhibits appreciable fluorescence, while quenched by the ring-closed form.
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Photochromism is the reversible transformation by photoirradiation of a chemical species between two forms that have different absorption spectra. Photochromic compounds have attracted much attention because of their potential application for photonic devices, such as optical memory media[1] and optical switches.[2] Among various types of photochromic compounds, dithienylethene is one of the most promising photochromic molecule owing to (1) its high efficiency of 'ring-closure' and 'ring-opening' photoisomerization for excitation at different wavelengths, (2) sufficient thermal stability of both the 'open' and 'closed' forms, (3) very high resistance to photofatigue, and (4) large differences in ability of the transmission of electronic interactions (electronic π-conjugation is interrupted in the open form, while electronic π-conjugation is extended over the closed form).[3] However, an additional factor that cannot be downplayed is the lack of highly efficient synthesis of photochromic compounds from cheaper starting materials. To date, several 1,2-bis(thien-3-yl) systems containing maleic anhydride,[4] maleimide,[5] perfluorocyclopentene,[6] or cyclopentene,[7] have been employed. Each unit has its advantages and disadvantages. Diarylethenes with the perfluorocyclopentene bridging unit, for instance, exhibit excellent photochromic properties. However, the expensive and rather volatile starting material of octafluorocyclopentene is the major disadvantage for the synthesis. Both diarylmaleic anhydride and diarylmaleimide are readily accessible, but sensitive to acidic conditions. Their drawbacks limit the scope of their applications for optical devices.

In recent years, some new bridging units emerged in developing new type photochromic compounds and new synthetic routes, for example, 2,5-dihydrothiophene,[8] 2,5-hydrofuran,[8a] quinones,[9] phenanthroline[10] and thiophene bridging units.[11] Among various bridging units employed in designing the skeleton of photochromic compounds, there are a few reports about thiophene as the bridging unit. Herein, we report a highly efficient synthesis of a new photochromic compound with thiophene ring as the bridging unit. Its photochromic property is also presented. Comparing to the previous bridging units used in the syntheses, the merits of the current work are based on (1) one-step efficient synthesis (using conventional Kumada coupling reaction) and (2) commercially available starting materials and catalyst. The synthesis can be performed on a large scale.

The synthetic route for photochromic triangle terthiophene (TTT) is shown in Scheme 1. The key starting materials, 2,3-dibromothiophene and 2-bromo-3-methylthiophene, were commercially available and used without further purification. The Grignard reagent formed from 2-bromo-3-methylthiophene and magnesium was slowly added to the mixture of 2,3-dibromothiophene and NidpppCl$_2$ in diethyl ether at 0 °C, then the reaction mixture was warmed to room temperature and kept overnight. The triangle terthiophene was obtained with

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Keywords: One-step synthesis; Photochromic properties; Fluorescence.

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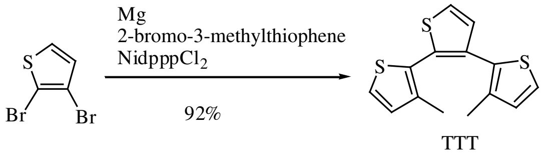
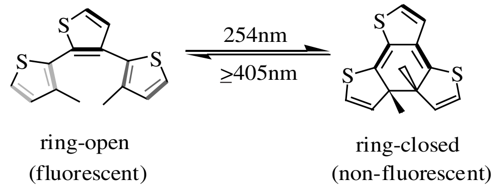


Scheme 1. Synthesis of TTT.



Scheme 2. Photochromic reaction of TTT.

92% yield after simple workup and column chromatographic purification.

The triangle thiophene exhibited good photochromic properties and could be toggled between colourless ring-open and coloured ring-closed forms by alternate irradiation with ultraviolet and visible light. The photochromic behavior is illustrated in Figure 1 and Scheme 2. Figure 1 shows the changes of absorption of triangle terthiophene solution (5×10^{-5} M in THF) upon irradiation at the maximum absorbance (254 nm). It could also be seen clearly that an isobestic point appeared at 315 nm ($\varepsilon = 8.0 \times 10^3$ M^{-1} cm^{-1}). This fact indicated that only two isomers existed when TTT underwent photoisomerization reaction. In general, the absorption of the ring-open form appeared at a shorter wavelength, while the absorption peak of the ring-closed form was at a longer wavelength since π-electrons delocalized and extended to the two thiophene rings. In fact, irradiation of the colourless THF solution of TTT at 254 nm brought about an immediate increase of the intensity of the absorption bands in the visible region centred at 465 nm due to the formation of the closed form of TTT, as described in Scheme 2. This is a new kind of yellow colour photochromic diarylethenes. A few yellow coloured photochromic diarylethenes have been reported in the literature.[12] Moreover, yellow as one of the three primary colours is needed in order to realize a photon-mode rewritable full colour print. Although yellow fulgides or oxazolyfulgides, spirooxazine and chromene derivatives have been synthesized,[13] stable yellow photochromic diarylethenes still need to be developed to realize photon-mode full colour tuning based on the same chemical analogue with the same stability and compatibility. In addition, TTT displayed well-defined isosbestic point. Thus, one can calculate the relative conversion of photocyclization reaction α_{ps} following the expressions based on the absorbance of the two forms.[14] The conversion of photocyclization reaction α_{ps} at the photostationary state was determined as 0.37 for TTT.

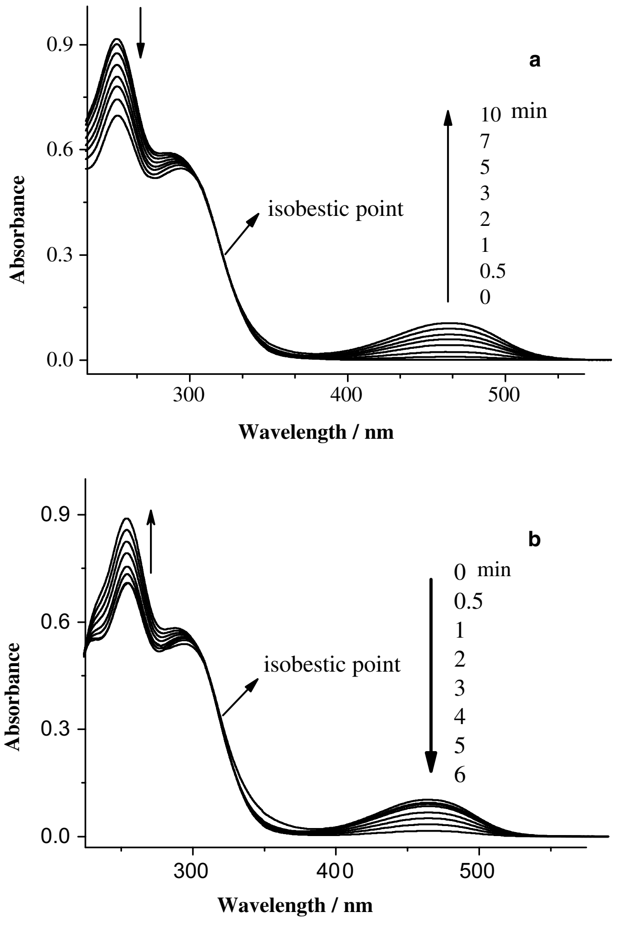


Figure 1. Absorption changes of TTT in THF upon irradiation at 254 nm (5×10^{-5} M, a) and its photochromic bleaching upon irradiation at ⩾405 nm (5×10^{-5} M, b).

The photochromic bleaching of the coloured solution was performed using the light longer than 405 nm and resulted in the disappearance of the band centred at 465 nm illustrated in Figure 1. It showed that the ring-closed form could be easily reversed back to ring-open form upon irradiation (⩾405 nm) in solutions. Obviously, there was an isobestic point at 315 nm, and it indicated the equilibrium of two isomers (ring-open and ring-closed forms) existed in isomerization upon irradiation. The cyclization and cycloreversion quantum yields of TTT in THF were 0.33 and 0.30, respectively. The properties of photochromism of the triangle terthiophene were also measured in other solvents, such as hexane, ethanol and acetonitrile. Very similar results were obtained. The polarity of solvent did not bring to observable difference in its UV–vis absorption spectra and photochromic properties.

The triangle terthiophene exhibited fluorescence at 440 nm in THF when it was excited at 300 nm. The fluorescence quantum yield of TTT in THF solution was measured using anthracene ($\Phi = 0.46$) as a reference and determined to be 0.13. The fluorescence intensity decreased along with the photochromism from the ring-open form to the ring-closed form upon irradiation at 254 nm, as shown in Figure 2. The obvious emission quenching at the photostationary state (PS) should be attributed to the formation of the closed TTT form,

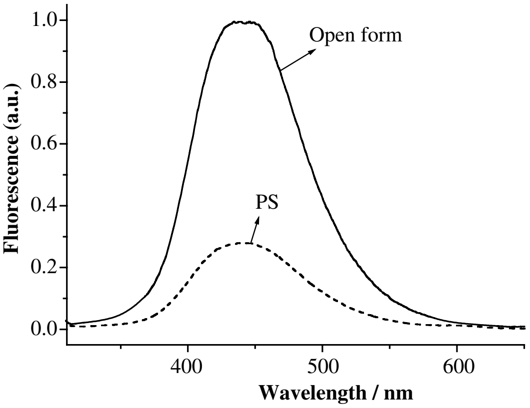


Figure 2. Fluorescence spectral changes of TTT in THF (5×10^{-5} M, excited at 300 nm) at room temperature: before irradiation with 254 nm light (solid line) and after irradiation (dashed line).

whose maximum absorption was at this region. This was also confirmed by the fluorescence excitation spectra of TTT measured at 440 nm. The excitation spectrum with a peak around 310 nm region was parallel to the absorption of the open form of TTT. The blue fluorescence of the solution could be recovered using light longer than 405 nm irradiation upon the photostationary state (PS). The fluorescence decayed with two exponential kinetics with the lifetimes of 0.39 ns and 3.63 ns.[†] It should be noted that the Stokes Shift of the fluorescence was relatively large and the fluorescence spectra edge showed a red-shift in comparison with the absorption edge.

Another favorable property of TTT was its photostability (fatigue resistance). Photochemical colouration and decolouration cycles should be repeated without or at least with very few side reactions. Repeated irradiation with ultraviolet light at 254 nm and visible light longer than 405 nm revealed that TTT was very stable towards photochemical decomposition. As shown in Figure 3, a little decrease in the absorption of the coloured form at photostationary state (PS) was observed even if 10 times of colouration and decolouration cycles. In the absence of visible light, the yellow colour persisted even if laid aside more than several days at 50 °C, attesting to the thermal stability of the photochromic compound.

The single crystals of TTT were obtained from petroleum ether by controlling the concentration of the compound, the crystallization temperature and the velocity of crystallization. And the crystallographic data were available only for the ring-open form.[†] The Oak Ridge Thermal Ellipsiod Plot (ORTEP) drawings of the compound was shown in Figure 4. The single crystal adopted a monoclinic space group. In fact, the single crystal of TTT did not show any photochromism in the crystalline phase even if irradiated for 24 h.

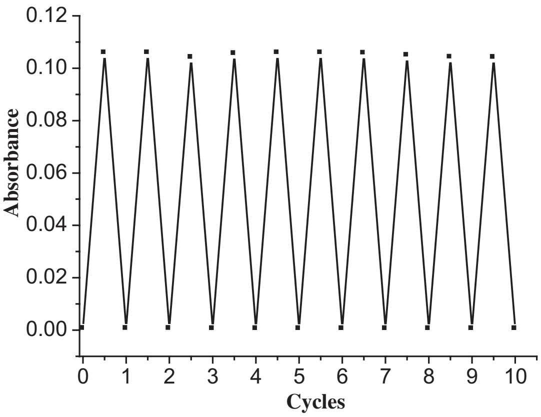


Figure 3. Cycling between the open and closed forms of TTT by repetitive irradiation at $\lambda = 254$ nm and $\lambda \geqslant 405$ nm at room temperature in THF. The ordinate shows the formation of the ring-closed form as monitored the absorbance at 465 nm.

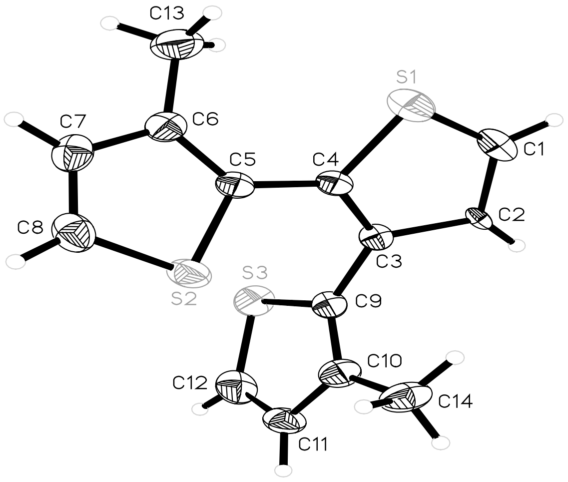


Figure 4. The ORTEP plot of the X-ray crystal structure of TTT. Thermal ellipsoids are drawn at 50% probability level.

The ring-open form diarylethenes have two conformations, antiparallel and parallel, and two conformations interconvert with each other in a solution. The conrotatory cyclization can proceed only from antiparallel conformation.[3] In crystals, on the other hand, there is no interconversion between the two conformations. According to the report of Irie, the photocyclization reactivity of diarylethenes in the single-crystalline phase was controlled by the distance between the reactive carbon atoms in the antiparallel orientation rather than polar and steric substituent effects.[15] X-ray crystallographic analysis of the single crystal of TTT indicated that the triangle terthiophene molecules in the crystal phases were packed neither in the photoactive antiparallel conformation nor in the photoinactive parallel conformation. The two non-bridging thiophene ring is almost perpendicular (the dihedral angles between the two non-bridging thiophene ring is 80.9°).[†] And the distance between the reactive carbon atoms (C6 and C10 shown in Fig. 4)[16] was measured to be 0.524 nm, which is too long for the molecule to undergo the

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[†] Experimental procedures, characterization relating to the synthesis, timed-resolved fluorescence spectra are available in Supplementary data.

photocyclization reaction in the crystal. When the distance between the reactive carbon atoms is larger than 0.42 nm, the photocyclization reaction in crystals was suppressed.[15]

In summary, a new yellow photochromic triangle terthiophene with the thiophene ring as the bridging unit was synthesized by one-step coupling reaction. The starting materials for the synthesis were commercially available reagents and the coupling reaction was completed overnight at room temperature with a high yield. The photo-generated ring-closed isomers were thermal stable at room temperature, and the cyclization/cycloreversion could be repeated more than ten times. The luminescence changes of this new triangle terthiophene can be regulated in a reversible manner by the photoisomerization. This character will make it the potential use in full-colour (using absorption) photo-electronic device, rewritable materials.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.05.142.

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16. Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 268462. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)-1223-336033 or email: deposit@ccdc.cam.ac.uk). Crystal data: Colorless plates, $C_{14}H_{12}S_3$, $FW = 276.42$, $T = 293(2)$ K, monoclinic, space group $P2(1)/c$, $a = 12.3963(13)$ Å, $\alpha = 90°$, $b = 6.8990(7)$ Å, $\beta = 105.039(2)°$, $c = 16.1589(16)$ Å, $\gamma = 90°$, $V = 1334.6(2)$ Å^3, $\rho_{(\text{calcd.})} = 1.376$ Mg/m^3, $\mu = 0.529$ mm^{-1}, $Z = 4$, reflections collected: 6990, independent reflections: 2617 ($R_{\text{init}} = 0.0551$), final R indices [$I > 2\sigma I$]: $R_1 = 0.0742$, $wR_2 = 0.2322$; R indices (all data): $R_1 = 0.0829$, $wR_2 = 0.2417$.