A Novel Photochromic Amorphous Molecular Material Based on Bisthienylethene with a Spiro-linker

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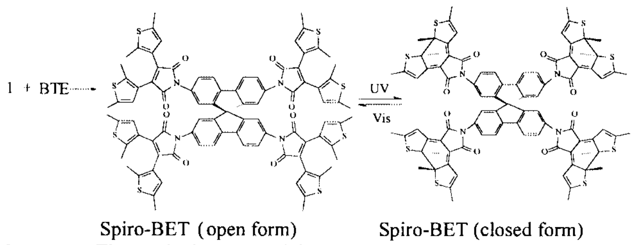
A novel photochromic amorphous molecule (Spiro-BTE) based on bisthienylethene with a spirobifluorene linker has been synthesized. The relative high photochromic quantum yields were obtained for the Spiro-BTE and the switching stability was observed for more than 200 photochromic cycles. The introduction of the spiro center for photochromic molecules provides a new guideline for the exploring new amorphous photochromic materials with high T_g, good photostability.

Bisthienylethenes (BTEs) are the most promising photochromic compounds for the photoelectronic applications, such as photoresponsive laser dye, photocontrolled self-assembly of molecular switches and long-term target for non-destructive optical data memory media, because of their fatigue resistance and thermally irreversible properties.[1,2] Several characteristics of BTE, such as cyclization and recyclization quantum yield, absorption coefficients and non-destructive readout capability, are still required to be improved. Photoluminescence has been suggested as a viable alternative for non-destructive readout, as long as changes in emission coincide with the photochromic transformation.[1b,2a] Branda et al.[1b] described supramolecular photochromic switches based on BTE, which utilized the luminescent changes to achieve non-destructive readout. A series of BTE-based photochromic amorphous molecular materials were developed,[3] in which there is no dilution of photochromic chromophores relative to a composite polymer systems, where low-molecular-weight compounds may crystallize at high concentration.

In this letter, new bisthienylethene-based material with a spirobifluorene (Spiro-BTE, shown in Scheme 1) was synthesized. Compounds based on this spiro linkage have meanwhile found applications in solar cells and OLEDs.[4] Spirobifluorene (SBF) has strong absorption in UV (308 nm, ε = 1.32 × 10^4 M^{-1}cm^{-1} in ethanol) and offered the unique opportunity to maintain the electronic properties of the corresponding monomeric units and gain a significant enhancement of morphological stability. Therefore, it is expected that the spiro center introduced enhances significantly the thermal stability of the photochromic material with a high glass transition temperature (T_g). In addition, the concentration of the photochrome per molecule, which is one of the properties to be urgently improved, would be easily improved for Spiro-BTE as the multi-substitution of bisthienylethene.

The spiro compound was prepared according to the methods described in literatures[4a,4c] and BTE was prepared in the known way.[2c,2d,2g] Spiro-BTE was synthesized by the reaction between 2,2',7,7'-tetraiodo-9,9'-spirobifluorene (**1**) and 2,3-bis-(2,5-dimethyl-3-thienyl)maleimide (BTE)[2c] in refluxing ethanol in the presence of K_2CO_3 and trace of CuI for 30 h. The product Spiro-BTE was purified twice by column chromatography on silica gel (CH_2Cl_2 and hexane–CH_2Cl_2 3/2 v/v). The colorless Spiro-BTE: ^{1}H NMR (500 MHz, $CDCl_3$) ppm: 1.71 (s, 12H, –CH_3), 2.22 (s, 12H, –CH_3), 2.68 (s, 12H, –CH_3), 2.75 (s, 12H, –CH_3), 6.57 (d, 4H, J = 5.05 Hz, thienyl), 6.81 (d, 4H, J = 5.37 Hz, thienyl), 7.36 (d, 4H, J = 7.90 Hz), 7.55 (d, 4H, J = 7.91 Hz), 7.81 (s, 4H). MALDI-TOF-MS: 1578 [M$^+$]. Infrared spectra: 1820, 1750 (C=O), 1440, 1410, 670 (S–C, aromatic thienyl) cm^{-1}. The closed form of Spiro-BTE obtained by irradiation with 365 nm for 10 h: ^{1}H NMR (500 MHz, $CDCl_3$) ppm: 1.96 (s, –CH_3), 2.22 (s, –CH_3), 2.75 (s, –CH_3), 2.90 (s, –CH_3), 6.25 (s, thienyl), 6.97 (s, thienyl), 7.55–7.58 (m, 4H), 7.65–7.75 (m, 4H), 8.01 (s, 4H). UV–vis absorption (shown in Figure1) of Spiro-BTE in CCl_4 (solubility approx. 4 mg/ mL): 392.4 nm (open form, ε = 2.3 × 10^4 M^{-1} cm^{-1}); closed form: 535 nm (ε = 4.74 × 10^3 M^{-1} cm^{-1}), 366nm (ε = 1.17 × 10^4 M^{-1} cm^{-1}). The absorption of BTE in CCl_4: 393.4 nm (open form, ε =7.63 × 10^3 M^{-1} cm^{-1}); 531.6 nm (closed form, ε =1.91 × 10^3 M^{-1}cm^{-1}). Comparing with BTE, the extinction coefficient of Spiro-BTE (open and closed forms both) was improved nearly



Scheme 1. The synthetic route and the photochromic process of Spiro-BTE

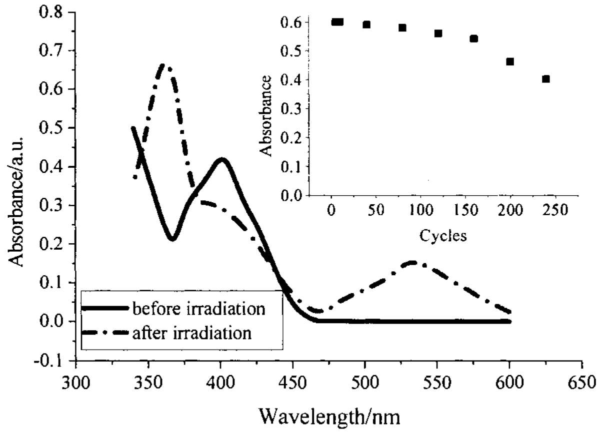


Figure 1. Absorption spectra of Spiro-BTE in CCl_4: before irradiation and after irradiation with 365-nm light. The inset figure is the absorption changes at 405 nm of Spiro-BTE in the PC film with switching cycles. The PC film was fabricated directly with the CH_2Cl_2 solution (1 × 10^{-5} M) of the compound in polycarbonate matrix under vacuum dry, the thickness (~10 μm) of the film was not exactly measured.

Table 1. Quantum yields at room temperature and absorption maximum (λ_{max} /nm) and fluorescence maximum of the open form (λ^{Fl}_{max} /nm, excited at 365 nm) of the compounds synthesized in the study (1×10^{-5} M in solution or in the film)

Compound(λ_{max} (open)/ λ_{max} (closed))	$\phi_{O \to C}$ (%) [a]	$\phi_{C \to O}$ (%) [a]	λ^{Fl}_{max}
Spiro-BTE in CCl_4 (392.4/535, 366)	25.4	70.4	658
Spiro-BTE in PC film (405/556)	11.6	43.3	660
BTE in CCl_4 (393.4/531.6)	46.3	50.8	656

a $\phi_{O \to C}$ cyclization yield determined by 365-nm light irradiation of BTE or Spiro-BTE. $\phi_{C \to O}$ opening ring yield determined by 538-nm light irradiation of BTE or Spiro-BTE (closed form prepared by 365-nm light irradiation for 35 min)

three times as expected due to the multi-substitution of bisthienylethene. The Spiro-BTE has strong absorption at 308 and 366 nm due to the intrinsic absorption of SBF, which is very important for efficient dye laser operation in order to absorb the pump energy: a frequent situation in pumping by an excimer laser at 308 nm.[1c,5] SBF core is acting as energy absorbing antenna. The strong fluorescence quenching of SBF was observed in Spiro-BTE, which is attributed to the efficient energy transfer from the excited SBF to the BTE units because of the overlap between the emission band of SBF and the absorption of BTE. The high photochrome concentration per molecule in Spiro-BTE will increase the fluorescence quantum yield because of non-aggregate of the spiro center with multi-BTE, whereas aggregation would generally quench the emission of BTE. Spiro-BTE here exemplifies the use of the reversible luminescent changes, especially for photoresponsive laser dye because SBF is an effective antenna to absorb UV pump energy.[1] Laser experiments of Spiro-BTE are being carried out.

The photochromic experiments were carried out in air using a 400-W super-high pressure Hg lamp. The distance between sample and the lamp is 20 cm, and in the front of the sample there is a cut-filter or quartz cell with water. The quantum yields[6] of photochromic processes were listed in Table 1. Compound Spiro-BTE exhibited relative high ϕ_{C-O} (70.4%) in solution.[7] Meanwhile, the ring opening quantum yield of Spiro-BTE in a PC film reaches to 43.3%. The low quantum yield (11.6%) for cyclization of Spiro-BTE in a PC film may be due to the low kinetics in the solid phase and/or to some filter effect of PC matrix. The fatigue resistance of Spiro-BTE in the film determined by the decreasing of absorption maximum at 405 nm was observed for > 200 optical switching cycles. One optical switching cycle was defined as follows: the film sample was under irradiation with 538-nm light for 30 min, then exposure to 365 nm for 15 min. Since the degraded products (if there exist) of the photochromic material have no possiblility to absorb visible light, the many switching recycles irradiated with 538-nm light indicate that this photochromic material has better fatigue resistance properties in the solid film. The so-call reservoir and concentration effects on fatigue resistance should be very small and eliminated due to the diluted concentration used in our experiments ($\sim 10^{-5}$ M). The reason for the high photochromic quantum yield of Spiro-BTE may be due to the stability of the maleic imide and the spiro center. The glass-transition temperature (T_g) is 117.5 °C for Spiro-BTE, as determined by differential scanning calorimetry (DSC, Waters 1040). The higher T_g of Spiro-BTE would be very helpful for the application in the film and the operation of laser dye in solid.

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