Photochromic thiophene oligomers based on bisthienylethene: syntheses, photochromic and two-photon properties

Yanli Feng,^a Yongli Yan,^b Sheng Wang,^a Weihong Zhu,^a Shixiong Qian^b and He Tian^{*a}

Received 16th June 2006, Accepted 25th July 2006 First published as an Advance Article on the web 8th August 2006 DOI: 10.1039/b608545h

A series of novel, functional symmetric and unsymmetric photochromic thiophene oligomers based on bisthienylethenes (BTEs) were synthesized *via* control of the reaction condition with a Suzuki coupling method. Their optical, photochromic quantum yields, two-photon and electrochemical properties in THF as well as in poly(methylmethacrylate) (PMMA) films were measured and discussed. The fluorescence emission can be tuned reversibly by alternating irradiation with UV and visible light. These BTEs could be used as nanowires, fluorescent switch and electrochemical switch.

Introduction

Photochromism is a reversible transformation between two isomers with different absorption spectra caused by alternating irradiation with UV and visible light. Among the various types of photochromic compounds, bisthienylethene derivatives (BTEs) are one of the most promising materials because of their excellent fatigue resistance and thermal stability in both isomeric forms, picosecond switching times, and fairly high photocyclization quantum yields.^{1–4} The open- and closedring isomers of BTEs differ from each other not only in their absorption but also in various physical and chemical properties, such as luminescence, refractive indices, oxidation/ reduction potentials, chiral properties and magnetic interactions.^{5–10} Up to now, intense research efforts have been carried out in an attempt to enhance their optical data storage and optical signal processing.¹¹

Recently, thiophene oligomers have generated considerable attention for their possible applications in light-emitting diodes, lasers, field-effect transistors (FETs), photovoltaic cells¹² and molecular nanowires¹³ because of their excellent electron and energy transfer properties through the π -conjugation. Specifically, how to optically control such molecular wires of thiophene oligomers by external stimuli becomes an important theme. On the basis of our earlier work,14-16 we herein incorporated the photochromic BTE unit into thiophene oligomers via a Suzuki coupling reaction in order to develop molecular wires with photo-switching characteristics. The synthesized photochromic thiophene oligomers (BTEs) with good solubility in common organic solvents could be triggered between the colorless ring-open and colored ringclosed forms by alternating irradiation with UV and visible light in THF as well as in poly(methylmethacrylate) (PMMA) films (Scheme 1). Moreover, the effect of thiophene numbers

and the substituents on the absorption peaks as well as twophoton properties are also discussed. We expect that the thiophene oligomers could work as molecular nanowires with a photoswitch (BTE), fluorescent switch, electrochemical switch or potential application for three dimensional optical data storage.

Experimental

General procedure

¹H NMR spectra were recorded on a Bruker AM 500 spectrometer with tetramethyl silane (TMS) as internal reference. MS were recorded on EI or ESI mass spectroscopy. Absorption spectra were measured on a Varian Cary500 UV-Vis spectrophotometer. Fluorescence spectra were measured on a Varian Cary Eclipse Fluorescence spectrophotometer. Fluorescence lifetimes were measured on an Edinburgh Lifespec-Ps spectrofluorometer. The optical switch experiments were carried out using a photochemical reaction apparatus with a 200 W Hg lamp. Cyclic voltammetry measurements were carried out at a platinum electrode using millimolar solutions in CH₂Cl₂ containing 0.1 M of the support electrolyte, tetrabutylammonium perchloride, in a three electrode cell and potentiostat assembly by VersaStarII electrochemical analyzer. HPLC analyses were determined by Agilen 1100 eluted by methanol at a flow rate of 0.6 ml min⁻

Materials

Reagents and starting materials were used as received. Solvents were distilled and dried before use. 1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene was synthesized and purified according to the established procedures.^{16,17}

Synthesis of BTE1, BTE2

To the solution of 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (0.50 g, 1.52 mmol) in anhydrous THF (10 mL) was added *n*-BuLi (2.5 mL of 1.6 M solution in hexane, 4 mmol) using a syringe in 2 portions under nitrogen at -78 °C. This solution was stirred for 30 min at room temperature, then

^aLaboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China. E-mail: tianhe@ecust.edu.cn; Fax: +86 (0)21 64252288; Tel: +86 (0)21 64252756

^bDepartment of Physics, Fudan University, Shanghai 200433, P. R. China



Scheme 1 Photochromic bisthienylethene-thiophene oligomers (BTEs).

 $B(OBu)_3$ (1.2 mL, 4.2 mmol) was added in one portion. This reddish solution was stirred for 1 h at room temperature, and was then used in the Suzuki cross coupling reaction without any workup because the product is deboronized during isolation.

A mixture of 2-bromo-5-chlorothiophene (0.61 g, 3.10 mmol), Pd(PPh₃)₄ (0.20 g) and THF (10 mL) was stirred for 15 min at room temperature. Then aqueous Na₂CO₃ (10 mL, 2 M) was added. The reactive mixture was heated at a temperature of 60 °C, and the solution of bis(boronic) esters of BTE (compound 2) was added dropwise *via* a syringe. Subsequently, the mixture was refluxed for 2 h and cooled to room temperature. The reactive mixture was poured into H₂O and extracted with ether, and dried with anhydrous Na₂SO₄. After concentration, the compound was purified by column chromatography on silica (petroleum ether–ethyl acetate = 20 : 1 v/v) to yield BTE2 (0.33 g), yield 44.1%, m.p. 101–103 °C.

To a solution of 1,2-bis(5-chloro-2-methylthien-3-yl) cyclopentene (0.50 g, 1.52 mmol) in anydrous THF (10 ml) was added *n*-BuLi (1 ml of 1.6 M solution in hexane, 1.6 mmol) in 2 portions using a syringe under nitrogen at -78 °C. At the same reaction conditions with BTE2, a solution of the unsymmetric bis(boronic) esters of BTE (compound 1) was obtained. Then a mixture of 2-bromo-5-chlorothiophene (0.30 g, 1.52 mmol), Pd(PPh₃)₄ (0.10 g) was added, and BTE1 (0.21 g) was similarly obtained (petroleum ether–ethyl acetate = 25 : 2 v/v) with a yield of 34.2%, m.p. 95–96 °C.

BTE1. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 1.87 (s, 3H, -CH₃), 1.94 (s, 3H, -CH₃), 2.01–2.07 (m, 2H, -CH₂–), 2.71–2.77 (m, 4H, -CH₂C=CCH₂–), 6.59 (s, 1H, thiophene-H), 6.76 (d, *J* = 1.7 Hz, 1H, thiophene-H), 6.77 (s, 1H, thiophene-H), 6.79 (d, *J* = 3.9 Hz, 1H, thiophene-H). HRMS (*m*/*z*) [M⁺] calcd for C₁₉H₁₆S₃Cl₂: 409.9791, found: 409.9755.

BTE2. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 1.99 (s, 6H, CH₃), 2.07 (m, 2H, -CH₂), 2.81 (t, *J* = 7.4 Hz, 4H, -CH₂C=CCH₂-), 6.78–6.80 (m, 6H, thiophene-H). HRMS (*m*/*z*) [M⁺] calcd for C₂₃H₁₈S₄Cl₂: 491.9668, found: 491.9670.

Synthesis of BTE3

A mixture of 5,5'-dibromo-2,2'-bisthiophene (0.99 g, 3.10 mmol), Pd(PPh₃)₄ (0.20 g) and THF (10 mL) was stirred for 15 min at room temperature. Then aqueous Na₂CO₃ (10 mL, 2 M) was added. The reactive mixture was heated at a temperature of 60 °C and the solution of compound **2** was added dropwise *via* a syringe. Subsequently, the mixture was refluxed for 2 h and cooled to room temperature. The reactive

mixture was poured into H_2O and extracted with ether, and dried with anhydrous Na_2SO_4 . After concentration, the compound was purified by column chromatography on silica (petroleum ether–ethyl acetate = 25 : 2 v/v) to yield BTE3 (0.22 g), 19.6%, m.p. 136–138 °C.

BTE3. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 1.95 (s, 6H, –CH₃), 2.09 (m, 2H, –CH₂–), 2.81 (t, *J* = 7.4 Hz, 4H, –CH₂C=CCH₂–), 6.88 (m, 4H, thiophene-H), 6.94–6.98 (m, 6 H, thiophene-H), HRMS (*m*/*z*) [M⁺] calcd for C₃₁H₂₂S₆Br₂: 743.8413, found: 743.8393.

Synthesis of BTE4 and BTE5

To the solution of BTE2 (0.52 g, 1.05 mmol) in anhydrous THF (10 mL) was added *n*-BuLi (0.78 mL of 1.6 M solution in hexane, 1.25 mol) using a syringe in 2 portions under nitrogen at -78 °C. This solution was stirred for 30 min at room temperature, then B(OBu)₃ (0.40 mL, 1.26 mmol) was added in one portion. This reddish solution was stirred for 1 h at room temperature, and was then used in the Suzuki cross coupling reaction without any workup because the product is deboronized during isolation.

The bis(boronic) esters of BTE2 Suzuki coupling with 4-iodoanisole and 4-iodobenzaldehyde gave the corresponding compounds BTE4 and BTE5, respectively. The only difference was that the reactant was purified by column chromatography on silica (petroleum ether– $CH_2Cl_2 = 25 : 4 \text{ v/v}$) to yield a dark-green solid BTE4 (0.22 g, yield 38.1%, m.p. 123–125 °C), and purified by column chromatography on silica (petroleum ether– $CH_2Cl_2 = 25 : 2 \text{ v/v}$) to yield a green solid BTE5 (0.24 g, yield 41.2%, m.p. 108–109 °C).

BTE4. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 1.95 (s, 3H, -CH₃), 1.96 (s, 3H, -CH₃), 2.09 (m, 2H, -CH₂-), 2.82 (m, 4H, -CH₂C=CCH₂-), 3.84 (s, 3H, -OCH₃), 6.80 (d, *J* = 3.7 Hz, 1H, thiophene-H), 6.81 (s, 1H, thiophene-H), 6.88 (s, 1H, thiophene-H), 6.91 (m, 3H, thiophene-H, benzene-H), 6.99 (d, *J* = 3.8 Hz, 1H, thiophene-H), 7.07 (d, 1H, thiophene-H, *J* = 3.6 Hz), 7.51 (d, *J* = 8.7 Hz, 2H, benzene-H). HRMS (*m*/*z*) [M⁺+H] calcd for C₃₀H₂₆S₄OCI: 565.0555, found: 565.0525.

BTE5. ¹H NMR (500 MHz, CDCl₃, ppm): $\delta = 1.97$ (s, 3H, –CH₃), 1.99 (s, 3H, –CH₃), 2.06–2.09 (m, 2H, –CH₂–), 2.82–2.97 (m, 4H, –CH₂C=CCH₂–), 6.78 (d, 1H, thiophene-H, J = 3.6 Hz), 6.8 (s, 1H, thiophene-H), 6.81 (d, J = 3.8, 1H, thiophene-H), 6.84 (s, 1H, thiophene-H), 7.01 (s, 1H, thiophene-H), 7.1 (s, 1H, thiophene-H), 7.74–7.76 (d, J = 8.2 Hz, 2H, benzene-H,), 7.96–7.94 (d, 2H, benzene-H,

J = 8.1 Hz), 10.05 (s, 1H, –CHO). HRMS (m/z) [M⁺] calcd for C₃₀H₂₅S₄OCI: 562.0320, found: 562.0325.

Synthesis of BTE6

To a solution of BTE4 (83.5 mg, 0.15 mmol) in anhydrous CH₂Cl₂ (20 mL) was added BBr₃ (1 mL) using a syringe under nitrogen at -78 °C. This solution was stirred for 2 h, then poured into H₂O and extracted with ether. The organic layer was separated and dried with Na₂SO₄. After concentration, the compound was purified by column chromatography on silica (CH₂Cl₂–*n*-hexane = 1 : 1 v/v) to yield a purple-green solid BTE6 (0.054 g, 65.1% yield, m.p. 111–113 °C).

¹H NMR (500 MHz, CDCl₃, ppm): δ = 1.95 (s, 3H, -CH₃), 1.97 (s, 3H, -CH₃), 2.04-2.08 (m, 2H, -CH₂-), 2.82 (m, 4H, -CH₂C=CCH₂-), 4.86 (b, 1H, -OH), 6.8 (d, J = 4.5 Hz, 1H, thiophene-H), 6.81 (s, 1H, thiophene-H), 6.84 (d, J = 8.3 Hz, 2H, benzene-H), 6.87 (s, 1H, thiophene -H), 6.90 (d, 1H, thiophene-H, J = 4.4 Hz), 6.99 (d, 1H, thiophene-H, J = 3.5 Hz), 7.06 (d, J = 3.4 Hz, 1H, thiophene-H), 7.46 (d, J = 8.5 Hz, 2H, benzene-H). HRMS (m/z) [M⁺] calcd for C₂₉H₂₃S₄OCl: 550.0320, found: 550.0322.

Synthesis of BTE7 (shown in Scheme 2)

A mixture of BTE5 (0.1038 g, 0.18 mmol), 2-aminophenyl disulfide (0.0223 g, 0.09 mol) in anhydrous CH_2Cl_2 (20 mL) was stirred for 20 h at room temperature. After concentration, the compound was purified by column chromatography on silica (CCl_4 – $CH_2Cl_2 = 1 : 1 v/v$) to



Scheme 2 Routes for synthesizing BTEs. Reagents: (i) *n*-BuLi (1 eq.), B(OBu)₃, THF, -78 °C; (ii) *n*-BuLi (2 eq.), B(OBu₃), THF, -78 °C; (iii) 2 M Na₂CO₃, Pd(PPh₃)₄, 2-bromo-5-chlorothiophene, THF, 60 °C; (iv) 2 M Na₂CO₃, Pd(PPh₃)₄, 5,5'-dibromo-2,2'-bisthiophene, THF, 60 °C; (v) 2 M Na₂CO₃, Pd(PPh₃)₄, 4-iodoanisole, THF, 60 °C; (vi) 2 M Na₂CO₃, Pd(PPh₃)₄, 4-iodoanisole, THF, 60 °C; (vi) 2 M Na₂CO₃, Pd(PPh₃)₄, 4-iodobenzaldehyde, THF, 60 °C; (vii) BBr₃, CH₂Cl₂, 50 °C. (viii) CH₂Cl₂, 2-aminophenyl disulfide, r. t.

yield a purple-green solid BTE7 (0.013 g), yield 11.3%, m.p. 151–153 $^{\circ}\mathrm{C}.$

BTE7. ¹H NMR (500 MHz, CDCl₃, ppm): δ = 1.97 (s, 6H, CH₃), 1.98 (s, 6H, CH₃), 2.04–2.08 (m, 4H, CH₂), 2.82 (m, 8H, –CH₂C=CCH₂–), 6.77 (m, 8H, thiophene-H), 6.81 (s, 2H, thiophene-H), 7.05 (s, 2H, thiophene -H), 7.26 (s, 2H, –N=CH–), 7.41 (m, 2H, benzene-H), 7.51 (m, 2H, benzene-H), 7.72 (m, 4H, benzene-H), 7.92 (2H, benzene-H), 8.10 (m, 2H, benzene-H), 8.17 (d, *J* = 8.4 Hz, 4H, benzene-H). HRMS (*m*/*z*) [M⁺] calcd for C₇₂H₅₄S₁₀N₂Cl₂: 1336.0871, found: 1336.0869.

Results and discussion

Molecular design and synthesis

Usually, Suzuki coupling method is used to synthesize symmetric bisthienylethene derivatives. However, here BTE1, BTE4, BTE5 and BTE6 are structurally unsymmetric and are obtained by controlling the ratio of starting materials and reagents.^{18–20}

1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene (compound 1) was converted into the bis(boronic) esters 2 via *n*-BuLi–B(OBu)₃, and then directly used in the next Suzuki reaction without any workup because during isolation the bis(boronic) esters are easily deboronized. Suzuki coupling with 2-bromo-5-chlorothiophene gave the corresponding symmetric BTE2 and unsymmetric BTE1 by controlling the ratio of starting materials and reagents (Scheme 2). And treatment of bis(boronic) esters 2 with 5,5'-dibromo-2,2'bithiophene got BTE3. BTE2 was converted into the bis(boronic) esters 3 via *n*-BuLi–B(OBu)₃, then Suzuki coupling with 4-iodoanisole and 4-iodobenzaldehyde gave the corresponding compounds BTE4 and BTE5. BTE6 was obtained from BTE4 in yield up to 89% and BTE7 was got from BTE5.

Absorption spectra

All synthesized bisthienylethene substituted with oligothiophene units could readily dissolve in common organic solvents, such as chloroform, methylene chloride, THF and toluene, which overcame the insolubility of most unsubstituted thiophene oligomers.¹⁸

Such thiophene oligomers show typical photochromism. The THF solution of BTE2 gradually turned purple upon light irradiation at 365 nm, with a new absorption band at 548 nm arising from the ring-closed form of bisthienylethene. From the absorption spectrum, two isobestic points could be found at 358 and 315 nm, indicative of two existing isomers. A similar result was also obtained from Fig. 1 when unsymmetric BTE4 was irradiated at 365 nm, and the two new absorption bands appeared at 398 and 558 nm, respectively, which were ascribed to the closed form isomer.

The absorption spectral changes of BTE1, BTE3, BTE4, BTE5 and BTE6 are almost the same as the spectral changes of BTE2 and BTE4 no matter whether the compounds are symmetric or unsymmetric. Upon irradiation with 365 nm light, the solution of thiophene oligomers with a BTE unit in THF gradually coloured and attained the photo-stationary



Fig. 1 Absorption changes of BTE4 in THF ($1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$) under different irradiation times at 365 nm.

state (PSS) after about 20 min. Especially, the colored isomers (closed forms) of these compounds are very stable in the dark at room temperature. Irradiation of them in their photostationary state with visible (>540 nm) light could lead to a complete recovery of the initial absorption signal, and the purple or blue solution turning colorless. Photochromism of BTE2 in poly(methylmethacrylate) (PMMA) films was also investigated, which was almost the same with spectral changes of BTE2 in THF (Fig. 2). When irradiated by 365 nm, the PMMA film turned gradually purple and new absorption bands at 381 and 548 nm appeared due to the large π -conjugation, and attained the photo-stationary state at 40 min, which is twice as long as that of BTE2 in THF.

The absorption data of BTEs in THF for the open and closed forms are summarized in Table 1. Compared with the known bisthienylethene derivatives,¹⁹ all oligothiophenes with a BTE unit showed the characteristic photochromic properties of bisthienylethene. From the viewpoint of application to optical memory media, it is desirable to develop photochromic compounds that have sensitivity in the wavelength region of 530–650 nm (DVD).²⁰

The effect of the thiophene number on the absorption maximum was examined. When increasing the number of thiophene units, the absorption peak in THF was red shifted



Fig. 2 Absorption changes of PMMA film containing 1 wt% BTE2 under different irradiation times at 365 nm.

	(e/10 ⁴ THF)	λ^{Ab} /nm (s/10 ⁴ THF)	Photochromic quantum yields (THF)		Ratios (PSS methanol)
Compounds	(open)	(PSS)	$\Phi_{\text{o-c}} \left(\lambda_{\text{max}} / \text{nm} \right)$	$\Phi_{\text{c-o}} (\lambda_{\text{max}}/\text{nm})$	(open : closed)
BTE1	278 (9.5)	503 (6.7) 313 (10.5)	0.27 (278)	0.45 (503)	1:0.80
BTE2	333 (7.7)	548 (5.5) 379 (3.0)	0.29 (333)	0.28 (548)	1:0.91
BTE3	381 (12.7)	593 (7.9)	0.37 (381)		1:1.20
BTE4	350 (11.5)	558 (9.1) 398 (7.2)	0.34 (334)	0.42 (558)	1:1.10
BTE5	283 (12.4), 342 (9.5)	553 (7.1) 384 (4.3)	0.25 (342)		1:0.75
BTE6	349 (11.8)	557 (7.7) 396 (7.5)	0.27 (349)	0.31 (557)	1:0.83
BTE7	330 (9.0)	553 (4.3) 380 (2.9)	0.11 (330)	0.23 (553)	1:0.33

Table 1 Absorption data, the photochromic quantum yields (Φ) of thiophene oligomers and ratios of ring-open and closed forms at the photostationary state (PSS).

because of the larger π -conjugation system. For example, the absorption of BTE1 is red shifted by as much as 38 nm for ring-open isomer and 59 nm for ring-closed isomer in comparison with that reported for bisthienylethene.^{19,21} Further red shifts of the absorption of BTE2 (containing four thiophene units) and BTE3 (containing six thiophene units) were similarly observed (Table 1). It is also interesting to compare the absorption peaks of the ring-open isomer and ring-closed isomer of symmetric and unsymmetric compounds such as BTE1 and BTE2 (Table 1). The thiophene ring is rich-electronic and can contribute electron to the π -system for the inductive effect of S atom.²² The absorption maximum of BTE2 was red shifted by as much as 55 nm for ring-open isomer and 45 nm for ring-closed isomer compared with that of BTE1 in THF.

The substituent effect on the absorption maximum in THF was also studied. When the substituents at the 5- and 5'- position of the thiophene ring are strong electron-donating or electron-withdrawing groups, the corresponding absorption of the ring-open isomer and the ring-closed isomer are obviously different. The absorption peaks of BTE5 is red shifted both for ring-open isomer and ring-closed isomer with respect to that of BTE2 in THF. Larger absorption differences of BTE4 and BTE6 were also observed (Table 1).

When we set the isosbestic absorption point as the detecting wavelength, the ratio between the ring-open and closed forms is equal to the ratio of the integrated area of HPLC peaks. As an example (illustrated in Fig. 3) the HPLC retention times



Fig. 3 HPLC traces of BTE1 (in methanol, 2.0×10^{-5} mol L⁻¹) eluted by methanol at a flow rate of 0.6 ml min⁻¹ detected at the isosbestic wavelength of 332 nm: (a) before UV light irradiation, (b) under UV light irradiation of 365 nm until the photostationary state is reached.

eluted by methanol at a flow rate of 0.6 ml min^{-1} are 10.5 and 11.0 min for the ring-open and closed forms of BTE1, respectively. Thus the ratio between the ring-open and closed forms can be obtained as 1:0.80 from the ratio of the integrated area of HPLC peaks. Similarly, the ratios of other ring-open and closed forms in the photo-stationary state were listed in Table 1. Notably, HPLC is a convenient way to measure the ratio since the ring-open and closed forms of the BTEs are difficult to be separated by silica column chromatography.

Fluorescence spectra

Typical fluorescence spectral changes of the novel thiophene oligomers were shown in the photochromic reaction. The open form of BTE2 (Fig. 4) shows significant fluorescence intensity located at 398 nm upon excitation at 333 nm. A similar result was obtained from Fig. 5 when BTE4 was excited at 350 nm, and the significant fluorescence intensity appeared at 409 and 430 nm. After irradiation at 365 nm to reach the photostationary state, the fluorescence intensities of BTE2 and BTE4 in THF decreased by 82 and 90%, respectively. Moreover, in the case of BTE2 doped in the matrix of PMMA, irradiated at 365 nm to reach the photostationary state, the fluorescence intensity was decreased by 86% (Fig. 6), a very similar fluorescence quenching as that of BTE2 in THF. This is attributed to the close form as a fluorescence quencher.^{4,8,23} Clearly, the fluorescence intensity can be regulated by the photochromic reaction.

The fluorescence lifetimes of all oligothiophene BTEs (open forms) were obtained by an interactive non-linear



Fig. 4 Fluorescence changes of BTE2 in THF ($1.0 \times 10^{-5} \text{ mol L}^{-1}$, $\lambda_{\text{ex}} = 350 \text{ nm}$) under different irradiation times at 365 nm.



Fig. 5 Fluorescence changes of BTE4 in THF $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}, \lambda_{\text{ex}} = 350 \text{ nm})$ under different irradiation times at 365 nm.



Fig. 6 Fluorescence changes ($\lambda_{ex} = 333$ nm) of BTE2 in PMMA film (1 wt%) under different irradiation times at 365 nm.

deconvolution fitting procedure and the fluorescent lifetimes were well fitted with a single exponential (Table 2). For example, the fluorescence of open form of BTE2 in THF decays with a fluorescence lifetime of 8.69 ns (excited at 372 nm).

Notably, irradiation of all compounds with visible light (>540 nm) could lead to a complete recovery of the initial fluorescence signal. Fig. 7 shows that the fluorescence intensity of BTE6 at 432 nm changed reversibly upon a excitation of 330 nm by alternating irradiation with UV (365 nm) and visible (>540 nm) light. This cycle could be repeated more than 20 times, indicative of being potentially utilized as good photochromic fluorescence switches.

Table 2 Emission wavelengths (λ_{max}^{em}/nm) and fluorescent lifetimes (τ/ns) of the open forms of BTEs

Compounds	$\lambda_{\rm max}^{\rm em}/{\rm nm}$	$\lambda_{\rm max}^{\rm em}/{\rm nm}$ (PSS)	τ /ns (chi-squared)
BTE1	395	394.6	_
BTE2	398	411	8.69 (1.054)
BTE3	432, 453	423, 459	7.13 (1.033)
BTE4	409, 431	410, 433	5.09 (1.029)
BTE5	467	453.5	7.34 (1.039)
BTE6	410, 432	411, 432	5.05 (1.068)
BTE7	459	462	_ ` ` `



Fig. 7 Modulated emission intensity at a peak of 432 nm (excited at 350 nm) of BTE6 in THF during alternating irradiation at the wavelengths of 365 nm and >540 nm, respectively.



Fig. 8 Linear scan of BTE2 in dichloromethane containing tetrabutylammonium tetrafluorobrate (0.1 mol L^{-1}) at the scan rate of 100 mV s⁻¹.

Electrochemical properties

The electrochemical studies were performed on BTE2 and BTE3 by VersaStar II electrochemical analyzer. Fig. 8 shows linear scan of BTE2 in dichloromethane containing tetrabutylammonium tetrafluorobrate (0.1 M). The open-ring isomer of BTE2 shows two oxidation potentials at 1.46 and 1.30 V. After 1 h irradiation with 365 nm to reach the photostationary state, the oxidation potentials were shifted to 0.84 and 0.60 V, indicating that there exist the oxidation potential shifts by 0.62 and 0.7 V from the open form to the closed form for BTE2. Similarly (Fig. 9), the oxidation potential of BTE3 was shifted by 0.32 V from the open form (0.98 V) to the closed form (0.66 V). It clearly indicates that the communication extending throughout the thiophene unit of



Fig. 9 Linear scan of BTE3 in dichloromethane containing tetrabutylammonium tetrafluorobrate (0.1 mol L^{-1}) at the scan rate of 100 mV s⁻¹.



Fig. 10 Open-aperture Z-scan trace of BTE3. Note: the scattered circles are experimental data, the line curve is a theoretical fit.

the ring-closed isomer is more than that of the ring-open isomer, resulting in an easier oxidation to the closed form. Moreover, such an electrochemical switch *via* light stimuli can be reversibly controlled. After irradiation (>540 nm), the colored solution turned colourless, and the electrochemical properties changed to those characteristic of the ring-open isomers.

Two-photon properties

Synthesis of highly active organic two-photon materials is of considerable interest due to their potential applications in three-dimensional optical storage, two-photon laser scanning fluorescence microscopy, two-photon upconverted lasing, and two-photon optical power limiting.^{24–27} As an example, a two-photon absorption (TPA) cross section of BTE3 was determined by the femtosecond open-aperture Z-scan technique, according to a previously described method.²⁸ Fig. 10 shows the open-aperture Z-scan data of BTE3 with a TPA coefficient (β) of 9.23 × 10⁻¹¹ cm W⁻¹ and a TPA cross sections of 181GM at 800 nm.

Upon excitation at 800 nm with a 140 fs pulse (Fig. 11), BTE2 and BTE6 showed yellow–green fluorescence, while BTE3, BTE5 and BTE7 showed blue fluorescence. BTE7 in THF exhibited intense frequency up-converted fluorescence with the peak located at 475 nm, which could be observed under excitation with an unfocused pulse with and energy of several μ J. As illustrated in Fig. 12, the two-photon excited fluorescence (TPEF) spectra of BTE7 under a different laser intensity is linearly dependent on the square of the excitation intensity. Notably, the two-photon fluorescence peak of BET7 in THF is red-shifted by 16 nm with respect to that of singlephoton fluorescence in THF (Table 2), which might be explained by a reabsorption effect.²⁹



Fig. 11 Two-photon fluorescences of BTEs under an excitation with a 140 fs, 800 nm pulse.



Fig. 12 Two-photon fluorescent spectra of BTE7 in THF. Inset: the fluorescence intensity is linearly dependent on the square of excitation intensity.

Conclusions

In summary, a series of novel photochromic thiophene oligomers with a BTE unit were successfully synthesized *via* a Suzuki coupling method. Some structural symmetric or unsymmetric bisthienylethene derivatives with a BTE unit could be obtained by controlling the ratios of the starting materials and reagents. All thiophene oligomers with a BTE unit show good photochromic properties, excellent fatigue resistance, excellent solubility in the pristine state and potentially good charge carrier mobilities. Some of the compounds have switchable electrochemical and two-photon properties, which could be used as molecular wires with a photoswitch (BTE), fluorescent switch, electrochemical switch or potential application for three-dimensional optical data storage. The further investigation of the applications is currently in progress.

Acknowledgements

This work was supported by the National Foundation of China (90401026 and 20476027) and the Scientific Committee of Shanghai. W. H. Zhu thanks the foundation for National Excellent Dissertation of P. R. China (Project No.: 200143) and the Laboratory of Organic Solids, Institute of Chemistry (CAS/China).

References

- 1 M. Irie, Chem. Rev., 2000, 100, 1685-1716.
- 2 H. Tian and S. J. Yang, Chem. Soc. Rev., 2004, 33, 85-97.
- 3 L. N. van Esch, B. F. Feringa and R. M. Kellogg, *Chem. Commun.*, 2001, 759–760.
- 4 T. B. Norsten and N. R. Branda, J. Am. Chem. Soc., 2001, 123, 1784–1785.
- 5 N. Katsonis, T. Kudernac, M. Walko, S. J. van der Molen, B. J. van Wees and B. L. Feringa, Adv. Mater., 2006, 18, 1397–1400.
- 6 K. Morimitsu, K. Shibata, S. Kobatake and M. Irie, J. Org. Chem., 2002, 67, 4574–4578.
- 7 K. Uchida, M. Saito, A. Murakami, N. S. Akamura and M. Irie, *Adv. Mater.*, 2003, 15, 121–125.
- 8 A. J. Myles, T. J. Wigglesworth and N. R. Branda, Adv. Mater., 2003, 15, 745–748.

- 9 R. Sasai, H. Itoh, I. Shindachi, T. Shichi and K. Takagi, *Chem. Mater.*, 2001, 13, 2012–2016.
- 10 B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev.*, 2000, **100**, 1789–1816.
- 11 H. Rath, V. Prabhuraja, T. K. Chandrashekar, A. Nag, D. Goswami and B. S. Joshi, Org. Lett., 2006, 8, 2325–2328.
- 12 N. Kiriy, V. Bocharova, A. Kiriy, M. Stamm, F. C. Krebs and H. J. Adler, *Chem. Mater.*, 2004, **16**, 4765–4771.
- 13 J. Nishida, T. Miyagawa and Y. Yamashita, Org. Lett., 2004, 6, 2523–2526.
- 14 G. Jiang, S. Wang, W. Yuan, L. Jiang, Y. Song, H. Tian and D. Zhu, *Chem. Mater.*, 2006, **18**, 235–237.
- 15 S. Wang, W. Shen, Y. L. Feng and H. Tian, *Chem. Commun.*, 2006, 1497–1499; S. Wang, X. Li, B. Chen, Q. Luo and H. Tian, *Macromol. Chem. Phys.*, 2004, **205**, 1497–1507.
- 16 H. Tian, B. Qin, R. X. Yao, X. L. Zhao and S. J. Yang, Adv. Mater., 2003, 15, 2104–2107; B. Qin, R. Yao, X. Zhao and H. Tian, Org. Biomol. Chem., 2003, 1, 2187–2191.
- 17 L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155–166.

- 18 C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, 14, 99–117.
- 19 M. Irie and K. Sayo, J. Phys. Chem., 1992, 96, 7671–7674.
- 20 Y. Chen, D. X. Zeng and M. G. Fan, Org. Lett., 2003, 5, 1435–1437.
- 21 M. Irie and M. Mohri, J. Org. Chem., 1988, 53, 803-808.
- 22 X. D. Sun, J. L. Zhang and B. He, J. Photochem. Photobiol., A, 2005, 172, 283–288.
- 23 L. Giordano, T. M. Jovin, M. Irie and E. A. Jares-Erijman, J. Am. Chem. Soc., 2002, **124**, 7481–7489.
- 24 W. Denk, J. H. Strickler and W. W. Webb, Science, 1990, 248, 73.
- 25 K. D. Belfield and K. J. Schafer, Chem. Mater., 2002, 14, 3656.
- 26 A. Abbotto, L. Beverina, R. Bozio, S. Bradamante, C. Ferrante, G. A. Pagani and R. Signorini, *Adv. Mater.*, 2000, **12**, 1963.
- 27 J. L. Hua, B. Li, F. S. Meng, D. Fang, X. Q. Shi and H. Tian, *Polymer*, 2004, **45**, 7143–7149.
- 28 B. Li, R. Tong, R. Zhu, F. Meng, H. Tian and S. X. Qian, J. Phys. Chem. B, 2005, 109, 10705–10710.
- 29 T. Lin, G. He, P. N. Parasad and L. Tan, J. Mater. Chem., 2004, 14, 982–991.

Chemical Science

An exciting news supplement providing a snapshot of the latest developments across the chemical sciences

Free online and in print issues of selected RSC journals!*

Research Highlights – newsworthy articles and significant scientific advances Essential Elements – latest developments from RSC publications Free access to the originals research paper from every online article

*A separately issued print subscription is also available

RSCPublishing

www.rsc.org/chemicalscience

