

# Synthesis of a novel family of photochromic amorphous molecular materials based on dithienylethene, their photochromic properties and application for dual image formation

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A novel family of photochromic amorphous molecular materials containing a dithienylethene moiety, 1-{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-2-(2,5-dimethylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene, 1-{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-2-(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene and 1,2-bis{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-3,3,4,4,5,5-hexafluorocyclopentene, have been designed and synthesised. These compounds, together with their photocyclised products, were found to readily form amorphous glasses with well-defined glass transition temperatures and to undergo photochromism as amorphous films as well as in solution. These compounds are characterised by high quantum yields for the photocyclisation reactions, very low quantum yields for the reverse ring-opening reactions and, hence, almost 100% fractions of the photocyclised form at the photostationary state in solution. These results suggest that the anti-parallel conformer is more populated than the parallel conformer. Optical dichroism was induced by irradiation of coloured films of the photocyclised compounds with linearly polarised red light, and dual image formation at the same location was realised by utilising this phenomenon.

Photochromic materials have recently attracted renewed interest in view of their potential technological applications for visible image formation, optical data storage and optical switching. Photochromic materials applied for such practical uses may be used in the form of solid films and, hence, extensive studies have been made of photochromic polymers and molecularly dispersed polymer systems, where low molecular weight photochromic compounds are dispersed in polymer binders.<sup>1-4</sup> In contrast to polymers, low molecular weight organic compounds generally do not form smooth and uniform films, since they tend to crystallise readily. We have performed a series of studies on the creation of low molecular weight organic compounds that readily form stable amorphous glasses above room temperature, namely amorphous molecular materials, and investigated their structures, reactions, properties and applications.<sup>5</sup> We have proposed several new concepts for photo- and electroactive amorphous molecular materials, which include electrically conducting amorphous molecular materials,<sup>6,7</sup> photochromic amorphous molecular materials,<sup>8-10</sup> molecular resists for nanolithography<sup>11-14</sup> and materials for photovoltaic devices<sup>15-17</sup> and organic light-emitting diodes.<sup>18-25</sup>

Photochromic amorphous molecular materials constitute a novel class of photochromic molecular materials that form uniform amorphous thin films by themselves in the absence of any polymer binder. They have the advantage that there is no dilution of photochromic chromophores relative to photochromic polymers and composite polymer systems, where low molecular weight organic photochromic compounds may crystallise at high concentration. Based on this concept, we have created a novel family of photochromic amorphous molecular materials containing an azobenzene moiety.<sup>8,9</sup>

It is of great interest and significance to create photochromic amorphous molecular materials containing a dithienylethene moiety, since dithienylethene derivatives have recently received attention as promising photochromic compounds with thermal stability and excellent fatigue-resistant properties.<sup>26-31</sup> We report

here the synthesis of a novel family of photochromic amorphous molecular materials containing a dithienylethene moiety, 1-{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-2-(2,5-dimethylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (TPTTC), 1-{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-2-(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (TPTBC) and 1,2-bis{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-3,3,4,4,5,5-hexafluorocyclopentene (BTPTC), their glass-forming and photochromic properties, and application for dual image formation at the same location. Part of this work has been reported in a previous communication.<sup>10</sup>

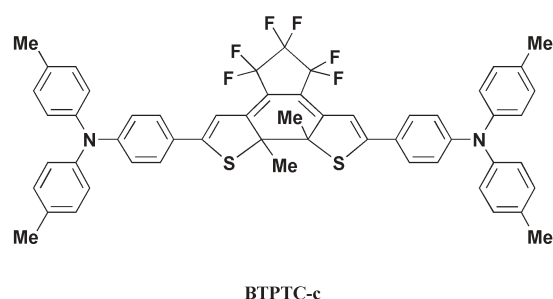
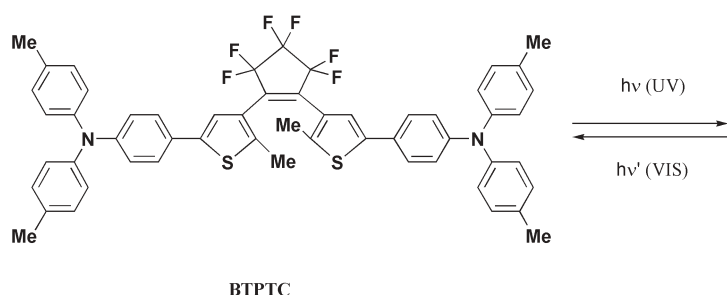
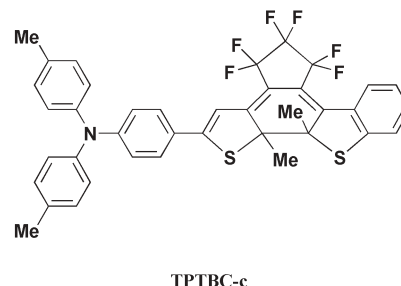
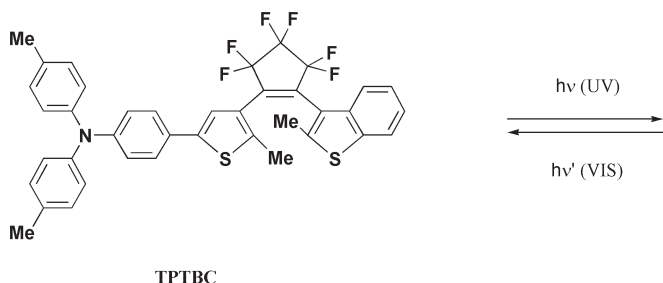
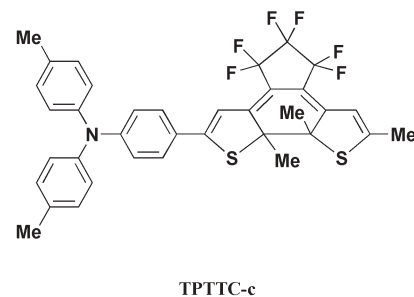
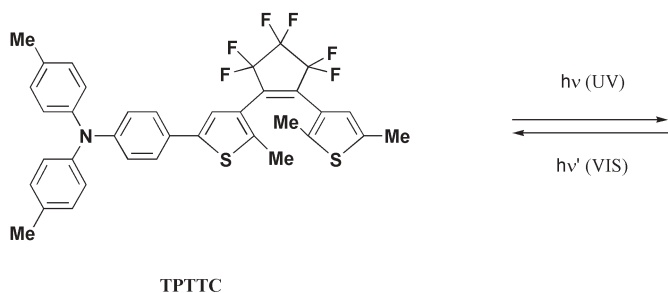
## Experimental

### Materials

Tetrakis(triphenylphosphine)palladium(0), 1.6 N hexane solution of *n*-butyllithium and 1,2,3,3,4,4,5,5-octafluorocyclopentene are commercially available and were used without further purification. 3-Bromo-2-methylthiophene-5-boronic acid<sup>29</sup> and 3-bromo-2,5-dimethylthiophene<sup>32</sup> were prepared as described in the literature.

### Synthesis of 1-{5-[4-(di-*p*-tolylamino)phenyl]-2-methylthiophen-3-yl}-2-(2,5-dimethylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (TPTTC)

A THF solution (70 ml) containing *N,N*-bis(4-methylphenyl)-4-bromoaniline (11.0 g, 31 mmol) and tetrakis(triphenylphosphine)palladium(0) (3.35 g, 2.9 mmol) was slowly added to a THF solution (75 ml) of 3-bromo-2-methylthiophene-5-boronic acid (10.1 g, 46 mmol). To this was added an aqueous solution (100 ml) of potassium carbonate (1.0 mol dm<sup>-3</sup>) and the resulting mixture was refluxed for 10 h. Then, the solution was extracted with benzene, washed with water, and dried over sodium sulfate. After removal of the solvent, the product was purified by silica gel column chromatography using a mixture



of hexane and toluene (10:1 v/v) as the eluent, followed by recrystallisation from a mixed solvent of hexane and toluene to give 3-bromo-5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophene (**1**) as a colourless powder. Yield: 10.3 g (50%). M.p.: 123 °C. <sup>1</sup>H NMR (750 MHz, CDCl<sub>3</sub>) δ (ppm): 2.32 (s, 6H), 2.40 (s, 3H), 6.97 (d, 2H, *J* = 8.7), 6.98 (s, 1H), 7.00 (d, 4H, *J* = 8.1), 7.08 (d, 4H, *J* = 8.1), 7.30 (d, 2H, *J* = 8.7 Hz). MS(EI) *m/z*: 448 (M<sup>+</sup>). Found: C, 66.77; H, 4.80; N, 3.08; calcd. for C<sub>25</sub>H<sub>22</sub>NBrS: C, 66.96; H, 4.95; N, 3.12%.

A hexane solution of n-butyllithium (20 mmol) was added to a THF solution (50 ml) of **1** (6.6 g, 15 mmol) at -78 °C under a nitrogen atmosphere and the mixture stirred for 1 h to produce 3-lithio-5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophene (**2**). To this was added 1,2,3,3,4,4,5,5-octafluorocyclopentene (3.5 ml, 26 mmol) at -78 °C and the solution was stirred for 24 h. The reaction mixture was extracted with ether and then washed successively with dilute hydrochloric acid and water. After removal of the solvent, the product was purified by silica gel column chromatography using a mixture of hexane and toluene (10:1 v/v) as the eluent, followed by recrystallisation from a mixed solvent of THF and ethanol to give 1-(5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**3**) as a pale yellow powder. Yield: 2.25 g (28%). M.p.: 129 °C. <sup>1</sup>H NMR (750 MHz, CDCl<sub>3</sub>) δ (ppm): 2.32 (s, 6H), 2.45 (s, 3H), 7.00 (d, 2H, *J* = 8.9), 7.01 (d, 4H, *J* = 8.5), 7.08 (d, 4H, *J* = 8.5), 7.11 (s, 1H), 7.35 (d, 2H, *J* = 8.9 Hz). MS(EI) *m/z*: 561 (M<sup>+</sup>). Found: C, 64.20; H, 3.97; N, 2.51; calcd. for C<sub>30</sub>H<sub>22</sub>F<sub>7</sub>NS: C, 64.17; H, 3.95; N, 2.49%.

A hexane solution of n-butyllithium (14 mmol) was added to a THF solution (30 ml) of 3-bromo-2,5-dimethylthiophene (1.6 g, 8.4 mmol) at -78 °C under a nitrogen atmosphere and the mixture stirred for 1 h. To this was added a THF solution

(35 ml) of **3** (2.2 g, 4.0 mmol) at -78 °C and the mixture stirred for 24 h. Dilute hydrochloric acid was then added and the solution washed with water. After removal of the solvent, the product was purified by silica gel column chromatography using a mixture of hexane and toluene (10:1 v/v) and gel permeation chromatography (GPC) using benzene as the eluent, followed by recrystallisation from a mixture of THF and ethanol to give a pale yellow powder. Yield: 0.79 g (30%). M.p.: 158 °C. <sup>1</sup>H NMR (750 MHz, THF-d<sub>8</sub>) δ (ppm): 1.89 (s, 3H), 1.91 (s, 3H), 2.28 (s, 6H), 2.41 (s, 3H), 6.80 (s, 1H), 6.94 (d, 2H, *J* = 8.5), 6.96 (d, 4H, *J* = 8.1), 7.06 (d, 4H, *J* = 8.1), 7.24 (s, 1H), 7.40 (d, 2H, *J* = 8.5 Hz). MS(EI) *m/z*: 653 (M<sup>+</sup>). Found: C, 65.94; H, 4.51; N, 2.13; calcd. for C<sub>36</sub>H<sub>29</sub>F<sub>6</sub>NS<sub>2</sub>: C, 66.14; H, 4.47; N, 2.14%.

#### Synthesis of 1-(5-{4-[bis(4-methylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-2-(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (TPTBC)

A hexane solution of n-butyllithium (11 mmol) was added to an ether solution (200 ml) of 3-bromo-2-methylbenzo[*b*]thiophene (3.4 g, 15 mmol) at -78 °C under a nitrogen atmosphere and the solution stirred for 1 h. To this was added 1,2,3,3,4,4,5,5-octafluorocyclopentene (3.2 ml, 24 mmol) at -78 °C and the mixture stirred for 24 h. Dilute hydrochloric acid was then added and the resulting solution washed with water. After removal of the solvent, the product was purified by sublimation (57 °C, 2.0 mmHg) to give 1-(2-methylbenzo[*b*]thiophen-3-yl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**4**) as colourless prisms. Yield: 3.6 g (72%). M.p.: 74 °C. <sup>1</sup>H NMR (750 MHz, CDCl<sub>3</sub>) δ (ppm): 2.35 (s, 3H), 7.36 (t, 1H, *J* = 8.0), 7.40 (t, 1H, *J* = 8.0), 7.49 (d, 1H, *J* = 8.0), 7.79 (d, 1H, *J* = 8.0 Hz). MS(EI) *m/z*:

340 (M<sup>+</sup>). Found: C, 49.36; H, 2.07; calcd. for C<sub>14</sub>H<sub>7</sub>F<sub>7</sub>S: C, 49.42; H, 2.07%.

To a solution of **2**, prepared by the reaction of **1** (3.5 g, 7.8 mmol) with *n*-butyllithium (9.6 mmol) in THF (50 ml), was added a THF solution (30 ml) of **4** (3.0 g, 8.8 mmol) at -78 °C under a nitrogen atmosphere and the mixture stirred for 24 h. Dilute hydrochloric acid was then added and the resulting solution washed with water. After removal of the solvent, the product was purified by silica gel column chromatography using hexane as the eluent, followed by recrystallisation from a mixture of THF and ethanol to give a pale yellow powder. Yield: 1.8 g (33%). M.p.: 158 °C. <sup>1</sup>H NMR (600 MHz, benzene-d<sub>6</sub>) δ (ppm): 1.65 (s, 3H), 1.97 (s, 3H), 2.10 (s, 6H), 6.91 (d, 4H, *J* = 8.3), 6.92 (t, 1H, *J* = 8.0), 7.00 (d, 2H, *J* = 8.9), 7.05 (t, 1H, *J* = 8.0), 7.05 (d, 4H, *J* = 8.3), 7.15 (d, 2H, *J* = 8.9), 7.18 (s, 1H), 7.30 (d, 1H, *J* = 8.0), 7.64 (d, 1H, *J* = 8.0 Hz). MS(EI) *m/z*: 653 (M<sup>+</sup>). Found: C, 67.83; H, 4.26; N, 2.04; calcd. for C<sub>39</sub>H<sub>29</sub>NF<sub>6</sub>S<sub>2</sub>: C, 67.91; H, 4.24; N, 2.03%.

#### Synthesis of 1,2-bis[5-[4-(*di-p*-tolylamino)phenyl]-2-methylthiophen-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (BTPTC)

To a solution of **2**, prepared by the reaction of **1** (5.4 g, 12 mmol) with *n*-butyllithium (18 mmol) in THF (50 ml), was added 1,2,3,3,4,4,5,5-octafluorocyclopentene (1.25 ml, 9.3 mmol) at -78 °C under a nitrogen atmosphere and the mixture stirred for 24 h. Dilute hydrochloric acid was then added and the resulting solution washed with water. After removal of the solvent, the product was purified by silica gel column chromatography and GPC using a mixture of hexane and toluene (4 : 1 v/v) and benzene, respectively, as the eluents, followed by recrystallisation from a mixture of THF and ethanol to give a pale yellow powder. Yield: 2.5 g (45%). M.p.: 207 °C. <sup>1</sup>H NMR (600 MHz, benzene-d<sub>6</sub>) δ (ppm): 1.72 (s, 6H), 2.11 (s, 12H), 6.92 (d, 8H, *J* = 8.4), 7.04 (d, 4H, *J* = 8.6), 7.07 (d, 8H, *J* = 8.4), 7.25 (d, 4H, *J* = 8.6 Hz), 7.28 (s, 2H). MS(EI) *m/z*: 919 (M<sup>+</sup>). Found: C, 72.41; H, 4.94; N, 3.12; calcd. for C<sub>55</sub>H<sub>44</sub>N<sub>2</sub>F<sub>6</sub>S<sub>2</sub>: C, 72.51; H, 4.87; N, 3.07%.

#### Synthesis of the photocyclised isomers TPTTC-c, TPTBC-c and BTPTC-c

A benzene solution (*ca.* 300 ml) of TPTTC (*ca.* 40 mg) was irradiated with 365 nm light from a 500W super-high pressure mercury lamp for *ca.* 10 min. After removal of the solvent, the resulting photocyclised isomer TPTTC-c was purified by GPC using benzene as the eluent, followed by reprecipitation from THF-acetonitrile. The other photocyclised isomers, TPTBC-c and BTPTC-c, were prepared and purified by similar procedures.

**TPTTC-c.** <sup>1</sup>H NMR (750 MHz, THF-d<sub>8</sub>) δ (ppm): 2.07 (s, 3H), 2.08 (s, 3H), 2.22 (s, 3H), 2.30 (s, 6H), 6.11 (s, 1H), 6.64 (s, 1H), 6.92 (d, 2H, *J* = 8.9), 7.00 (d, 4H, *J* = 8.2), 7.11 (d, 4H, *J* = 8.2), 7.43 (d, 2H, *J* = 8.9 Hz). MS(EI) *m/z*: 653 (M<sup>+</sup>). Found: C, 65.97; H, 4.68; N, 2.12; calcd. for C<sub>36</sub>H<sub>29</sub>F<sub>6</sub>NS<sub>2</sub>: C, 66.14; H, 4.47; N, 2.14%.

**TPTBC-c.** <sup>1</sup>H NMR (600 MHz, benzene-d<sub>6</sub>) δ (ppm): 1.99 (s, 3H), 2.00 (s, 3H), 2.09 (s, 6H), 6.64 (s, 1H), 6.71 (t, 1H, *J* = 7.4), 6.73 (t, 1H, *J* = 7.4), 6.82 (d, 1H, *J* = 7.4), 6.86 (d, 2H, *J* = 8.9), 6.91 (d, 4H, *J* = 8.9), 7.00 (d, 4H, *J* = 8.6), 7.09 (d, 2H, *J* = 8.9), 7.99 (d, 1H, *J* = 7.4 Hz). MS(EI) *m/z*: 653 (M<sup>+</sup>). Found: C, 68.07; H, 4.26; N, 2.09; calcd. for C<sub>39</sub>H<sub>29</sub>NF<sub>6</sub>S<sub>2</sub>: C, 67.91; H, 4.24; N, 2.03%.

**BTPTC-c.** <sup>1</sup>H NMR (600 MHz, benzene-d<sub>6</sub>) δ (ppm): 2.09 (s, 6H), 2.19 (s, 12H), 6.67 (s, 2H), 6.89 (d, 4H, *J* = 8.9), 6.91 (d, 8H, *J* = 8.2), 7.02 (d, 8H, *J* = 8.2), 7.12 (d, 4H, *J* = 8.9 Hz). MS(EI) *m/z*: 919 (M<sup>+</sup>). Found: C, 72.28; H, 4.94; N, 2.95; calcd. for C<sub>55</sub>H<sub>44</sub>N<sub>2</sub>F<sub>6</sub>S<sub>2</sub>: C, 72.51; H, 4.87; N, 3.07%.

#### Preparation of amorphous films

Amorphous films of the synthesised compounds were prepared on transparent glass substrates by spin coating from their benzene solutions (*ca.* 1–5 × 10<sup>-2</sup> mol dm<sup>-3</sup>), dried overnight under reduced pressure and used for the measurements of electronic absorption spectra.

#### Photochromic reactions

The synthesised compounds, TPTTC, TPTBC and BTPTC, were irradiated in benzene solution and as amorphous films with UV light (365 nm) from a 500 W super-high pressure mercury lamp through a combination of cut-off glass filters (UV-35 and UV-D33S, Toshiba) and an aqueous solution of NiSO<sub>4</sub>. The photocyclised compounds, TPTTC-c, TPTBC-c and BTPTC-c, were irradiated in toluene solution and as amorphous films with visible light (> 580 nm) from a 500 W Xenon lamp through a cut-off glass filter (O-58, Toshiba).

#### Measurements and apparatus

Gel permeation chromatography (GPC) was performed by using an LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) with two columns for the separation of low molecular weight organic compounds, JAIGEL-1H and JAIGEL-2H (a kind of styrene polymer gel).

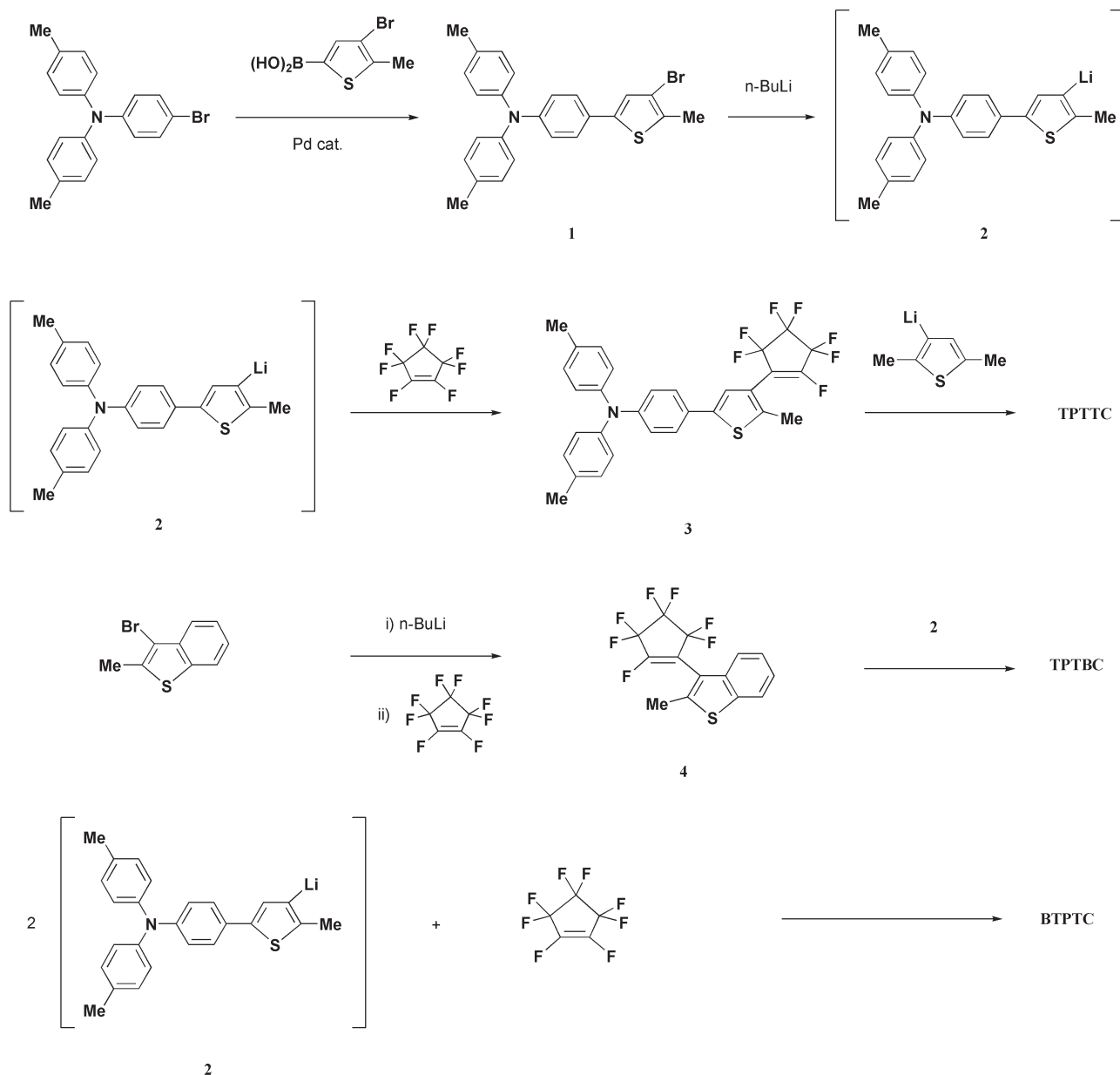
Quantum yields for the photocyclisation reactions were measured with a potassium ferrioxalate actinometer by irradiation with 365 nm light. Quantum yields for the photochemical ring-opening reactions were measured with an optical power meter (ML910A, Anritsu) by irradiation with 600 nm light with a bandwidth of 10 nm from a 500 W Xenon lamp through an interference filter (IF-S 600, Vacuum Optics Co.). Photochromic reactions were analyzed by monitoring the change of the electronic absorption spectra with a spectrophotometer (U-3200, Hitachi).

Differential scanning calorimetry (DSC) was carried out with a Seiko DSC220C instrument. X-Ray diffraction (XRD) measurements were carried out with a M18XHF-SRA diffractometer (MAC Science Co., Ltd.). Polarising microscopy was performed with a OPTIPHOT X2 (Nikon) microscope fitted with a TH-600PM hot stage (Linkam) and crossed polarisers.

## Results and discussion

#### Molecular design and synthesis of photochromic amorphous molecular materials based on dithienylethene

For the purpose of developing a novel class of photochromic amorphous molecular materials based on dithienylethene, we have designed and synthesised TPTTC, TPTBC and BTPTC. The synthetic procedures for the preparation these compounds are shown in Scheme 1. These new compounds were synthesised using 3-bromo-5-[4-[bis(4-methylphenyl)amino]phenyl]-2-methylthiophene (**1**) prepared by the reaction of *N,N*-bis(4-methylphenyl)-4-bromoaniline with 3-bromo-2-methylthiophene-5-boronic acid in the presence of palladium catalyst. TPTTC was obtained by the reaction of 1,2,3,3,4,4,5,5-octafluorocyclopentene with an equimolar amount of 3-lithio-5-[4-[bis(4-methylphenyl)amino]phenyl]-2-methylthiophene (**2**), prepared by lithiation of **1**, followed by reaction with 3-lithio-2,5-dimethylthiophene, prepared by lithiation of 3-bromo-2,5-dimethylthiophene. TPTBC was synthesised by



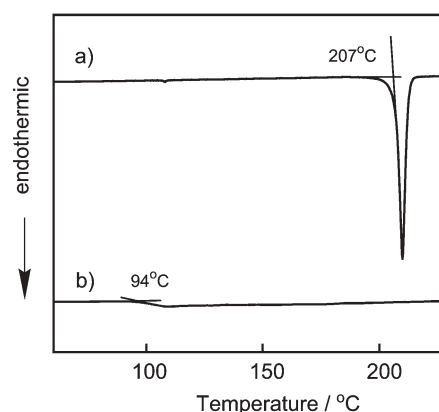
**Scheme 1** Synthetic procedures for the preparation of new compounds containing a dithienylethene moiety.

the reaction of **2** with an equimolar amount of 1-(2-methylbenzo[*b*]thiophen-3-yl)-2,3,3,4,4,5,5-heptafluorocyclopentene (**4**) derived from 3-bromo-2-methylbenzo[*b*]thiophene. BTPTC was synthesised by the reaction of 1,2,3,3,4,4,5,5-octafluorocyclopentene with two molar equivalents of **2**. They were obtained as polycrystals by recrystallisation from solution. Their photocyclised isomers, TPTTC-*c*, TPTBC-*c* and BTPTC-*c*, were obtained by irradiation of the corresponding open forms in solution with 365 nm light. They were obtained as amorphous solids, in spite of attempted recrystallisation from solution.

#### Glass-forming properties of TPTTC, TPTBC, BTPTC and their photocyclised compounds

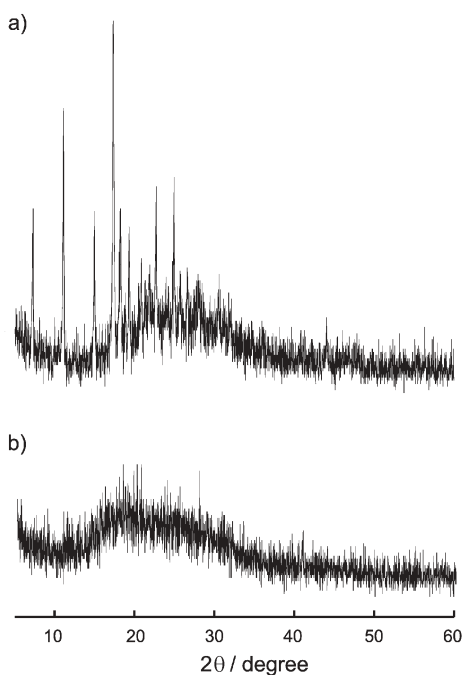
The synthesised new compounds containing a dithienylethene moiety, TPTTC, TPTBC and BTPTC, and their photocyclised isomers were found to readily form stable amorphous glasses with well-defined glass transition temperatures ( $T_g$ ), as evidenced by DSC, XRD and polarising microscopy. Fig. 1 shows DSC curves for BTPTC. When a crystalline sample, obtained by recrystallisation from THF–ethanol solution, was heated,

an endothermic peak due to melting was observed at 207 °C. When the isotropic liquid was cooled on standing in air, an amorphous glass was spontaneously formed *via* a supercooled



**Fig. 1** DSC curves for BTPTC. (a) Crystalline sample obtained by recrystallisation from solution. (b) Glass sample obtained by cooling the melt. Heating rate: 5 °C min<sup>-1</sup>.





**Fig. 2** XRD patterns of BTPTC. (a) Crystalline sample obtained by recrystallisation from solution. (b) Glass sample obtained by cooling the melt.

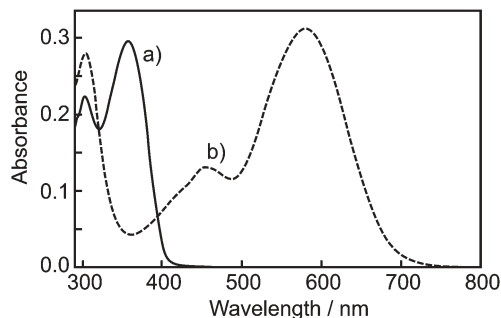
liquid state. When the glass sample was heated again, a glass transition phenomenon was observed at 94 °C. No crystallisation was observed on further heating above the  $T_g$ . Similar results were obtained for TPTTC and TPTBC.

Formation of an amorphous glass was also confirmed by XRD. As Fig. 2 shows, the XRD pattern of a polycrystalline sample of BTPTC obtained by recrystallisation from solution displays sharp peaks characteristic of crystals, whereas that of the glass sample obtained by cooling a BTPTC melt sample shows a broad halo. Similar results were obtained for TPTTC and TPTBC.

Table 1 summarises the  $T_g$  and melting points ( $T_m$ ) of TPTTC, TPTBC and BTPTC, and their photocyclised isomers, TPTTC-c, TPTBC-c and BTPTC-c. These photochromic amorphous molecular materials have relatively high  $T_g$  values. It is of interest to note that the  $T_g$  values of the photocyclised isomers are higher than those of the corresponding open forms. It is understood that the molecular structures of the cyclised forms are more rigid than those of the corresponding open forms, leading to higher  $T_g$  values for the cyclised forms. Increases in  $T_g$  values as a result of incorporation of rigid moieties has been reported for other amorphous molecular materials.<sup>5,8,33–35</sup> All these compounds form uniform amorphous films by spin coating.

**Table 1** Glass transition temperatures ( $T_g$ ) and melting points ( $T_m$ ) of photochromic amorphous molecular materials based on dithienylethene

Compound	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$
TPTTC	51	158
TPTTC-c	57	—
TPTBC	66	158
TPTBC-c	73	—
BTPTC	94	207
BTPTC-c	104	—



**Fig. 3** Electronic absorption spectra of (a) TPTBC and (b) TPTBC-c in benzene solution ( $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ).

**Table 2** Electronic absorption maxima ( $\lambda_{\text{max}}$ ) of photochromic amorphous molecular materials in benzene, together with their molar extinction coefficients ( $\epsilon$ )

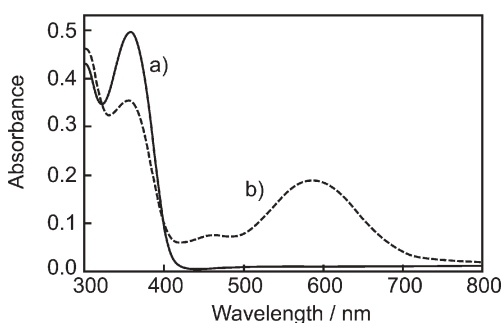
Compound	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )		
TPTTC	304 (2.3)	358 (3.3)	
TPTTC-c	298 (2.2)	428 (1.3)	575 (2.4)
TPTBC	302 (2.2)	357 (2.9)	
TPTBC-c	303 (2.8)	455 (1.3)	580 (3.1)
BTPTC	304 (3.9)	362 (6.2)	
BTPTC-c	300 (3.6)	442 (2.6)	635 (3.9)

#### Electronic absorption spectra of TPTTC, TPTBC and BTPTC

Fig. 3 shows the electronic absorption spectra of TPTBC and its photocyclised isomer TPTBC-c. Table 2 summarises the electronic absorption maxima and the molar extinction coefficients of TPTTC, TPTBC, BTPTC and their photocyclised isomers in benzene solution. The absorption bands of the cyclised forms in the visible region undergo increasing red shifts in the order TPTTC-c < TPTBC-c < BTPTC-c; this may be due to the increasing extent of  $\pi$ -conjugation in this series. The electronic absorption spectra of these compounds as amorphous films were found to be similar to those in solution.

#### Photochromic properties of TPTTC, TPTBC and BTPTC

The new compounds containing a dithienylethene moiety, TPTTC, TPTBC and BTPTC, were found to exhibit photochromism as amorphous films as well as in solution. Fig. 4 shows the electronic absorption spectral changes of an amorphous film of TPTBC prepared by spin coating from benzene solution. Upon irradiation with 365 nm light, the band with a maximum at around 360 nm gradually decreased in intensity and new absorption bands with maxima at around 455 and 580 nm appeared in the visible region due to the



**Fig. 4** Electronic absorption spectral changes of an amorphous film of TPTBC. (a) Before photoirradiation. (b) Photostationary state upon irradiation with 365 nm light.

**Table 3** Quantum yields for the photocyclisation ( $\Phi_{o-c}$ ) and the reverse photochemical ring-opening ( $\Phi_{c-o}$ ) reactions together with the fractions ( $Y_{\text{pss}}$ ) of the photocyclised forms at the photostationary state

System	$\Phi_{o-c}$	$\Phi_{c-o}$	$Y_{\text{pss}}$
TPTTC in benzene solution	0.81	0.001	1.00
TPTTC as amorphous film	0.28	0.001	0.68
TPTBC in benzene solution	0.79	0.015	1.00
TPTBC as amorphous film	0.33	0.010	0.36
BTPTC in benzene solution	0.61	0.001	1.00
BTPTC as amorphous film	0.33	0.001	0.77

transformation of the open form into the closed form *via* photocyclisation; the reaction system finally reached a photostationary state (irradiated for *ca.* 3 min at 0.5 mW cm<sup>-2</sup>). Similar spectral changes were observed for amorphous films of TPTTC and BTPTC. The reverse ring-opening reaction of the cyclised form to regenerate the open form took place on irradiation with visible light of wavelength longer than 580 nm for all the compounds.

Table 3 summarises quantum yields for the photocyclisation ( $\Phi_{o-c}$ ) and the reverse photochemical ring-opening ( $\Phi_{c-o}$ ) reactions, together with the fractions ( $Y_{\text{pss}}$ ) of the photocyclised form at the photostationary state for all the compounds. The fraction  $Y_{\text{pss}}$  represents the molar ratio of the photocyclised molecule to the total amount of the starting and photocyclised molecules at the photostationary state upon irradiation with 365 nm light, which is experimentally determined from eqn. 1,

$$Y_{\text{pss}} = (1 - A_{\text{pss}}/A_0)/(1 - \varepsilon_c/\varepsilon_o) \quad (1)$$

where  $A_0$  and  $A_{\text{pss}}$  represent the absorbances of the film before photoirradiation and at the photostationary state, respectively, and  $\varepsilon_o$  and  $\varepsilon_c$  stand for the molar extinction coefficients of the open and cyclised forms at the wavelength of incident light, respectively.

As Table 3 shows, the quantum yields for the photocyclisation reactions ( $\Phi_{o-c}$ ) of TPTTC, TPTBC and BTPTC in solution were found to be much higher than those reported for other dithienylethene derivatives in solution, which are mostly in the range 0.3 to 0.5 as reported for *e.g.* 1,2-bis(5-phenyl-2,4-dimethylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (0.41) and 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (0.35).<sup>36,37</sup> It is known that dithienylethene derivatives assume two conformers, *i.e.* an “anti-parallel” (ap) conformer having two thienyl moieties with C<sub>2</sub> symmetry and a “parallel” (p) conformer having two thienyl moieties with mirror symmetry, and that only the ap-conformer undergoes the photocyclisation reaction.<sup>26,27</sup> It is thought that dithienylethene derivatives usually take up the p- and ap-conformations in a *ca.* 1 : 1 molar ratio in solution and, hence, the quantum yields for the photocyclisation reactions of these compounds are less than 0.5. The fact that the quantum yields for the photocyclisation reactions of TPTTC, TPTBC and BTPTC in solution are much higher than 0.5 suggests that the ap-conformer is more populated than the p-conformer for these molecules, probably due to the presence of the bulky bis(4-methylphenyl)aminophenyl substituents. A high quantum yield has also been reported for the photocyclisation reaction of a photochromic polymer with a dithienylethene backbone (0.86); this result is attributed to the existence of only the ap-conformation in the polymer backbone.<sup>38</sup> The values of  $\Phi_{o-c}$  for the amorphous films were found to be lower than those for solutions of all the compounds. This result can be explained in terms of molecular motions for the cyclisation reaction being restricted due to the presence of surrounding molecules in the amorphous film. In addition, intermolecular interactions in the solid state may cause enhanced radiationless deactivation, decreasing  $\Phi_{o-c}$  for the amorphous films relative to solution.

On the other hand, the quantum yields for the reverse ring-opening reactions ( $\Phi_{c-o}$ ) of TPTTC-c, TPTBC-c and BTPTC-c to regenerate the corresponding open forms in solution were approximately two orders of magnitude smaller than those reported for other cyclised dithienylethene derivatives, *e.g.* 1,2-bis(2,4-dimethylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene and 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (0.13 and 0.41, respectively).<sup>36,39</sup> The very low quantum yields observed for TPTTC-c, TPTBC-c and BTPTC-c are in accord with the report that the presence of extended  $\pi$ -conjugation significantly reduces the quantum yield for the photochemical ring-opening reaction, as observed for 1,2-bis(3,5-dimethyl-5'-cyano-2,2',5':2"-terthiophen-4-yl)-3,3,4,4,5,5-hexafluorocyclopentene ( $1.3 \times 10^{-4}$ ).<sup>39</sup> The quantum yields for the reverse ring-opening reactions of TPTTC-c, TPTBC-c and BTPTC-c as amorphous films were similar to those for solution. It is thought that the ring-opening reaction does not require significant molecular motion.

The fraction of the photocyclised form at the photostationary state,  $Y_{\text{pss}}$ , is theoretically determined from eqn. 2.

$$Y_{\text{pss}} = \varepsilon_o \Phi_{o-c} / (\varepsilon_o \Phi_{o-c} + \varepsilon_c \Phi_{c-o}) \quad (2)$$

The  $Y_{\text{pss}}$  values for TPTTC, TPTBC and BTPTC in solution were almost 100% because of the high  $\Phi_{o-c}$  and the very low  $\Phi_{c-o}$ . The  $Y_{\text{pss}}$  values for the amorphous films of TPTTC and BTPTC were greater than 0.5, as confirmed by HPLC of the benzene solution obtained by dissolving the film at the photostationary state. Since it is thought that the transformation between the p- and ap-conformer does not take place in the amorphous film, the values of  $Y_{\text{pss}}$  being greater than 0.5 for the amorphous films of TPTTC and BTPTC suggests that the ap-conformer is more populated than the p-conformer in the amorphous films. The  $Y_{\text{pss}}$  value of TPTBC is less than 0.5, but it is thought that TPTBC also preferentially takes the ap-conformer, as described later.

In order to gain further information on the population of the ap-conformer, the value of  $Y_{\text{pss}}$  was measured for the amorphous films of the open form with only the ap-conformation, which were obtained from the 100% cyclised amorphous films of TPTTC-c, TPTBC-c and BTPTC-c by irradiation with visible light (> 580 nm). The results show that the  $Y_{\text{pss}}$  values obtained for these films were 0.69, 0.38 and 0.79 for TPTTC, TPTBC and BTPTC, respectively, being almost the same as those for the corresponding films obtained by spin coating from solutions of the unirradiated compounds in the open forms (Table 3). These results indicate that almost all molecules take up the ap-conformation in the amorphous films. The result that the  $Y_{\text{pss}}$  values for the amorphous films do not reach 1.0 suggests that there are ap-conformers which cannot undergo photocyclisation in the film, probably because the local free volume around the remaining molecules is less than that required for the photocyclisation reaction. The lower  $Y_{\text{pss}}$  value for TPTBC than those for TPTTC and BTPTC is probably due to the requirement of a larger free volume for the photocyclisation of TPTBC, as suggested from the CPK models of these molecules. That is, while the photocyclisation of TPTTC and BTPTC requires only partial rotation of the thiophene moiety around the single bond connecting the thienyl group and cyclopentene ring in the ap-conformer, the photocyclisation of TPTBC requires partial rotation of the larger benzothiophene moiety.

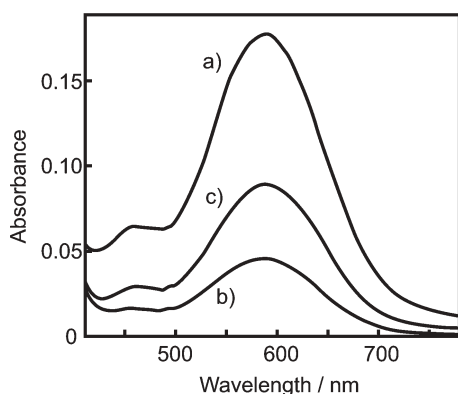
#### Polarised light-induced dichromism and dual image formation

Photoinduced dichroism and birefringence of photochromic solids is the subject of considerable interest. There are two types of polarised light-induced dichroism and birefringence. One is due to a change in the molecular alignment by polarised light irradiation, which is known as the “Weigert effect”.<sup>40</sup>

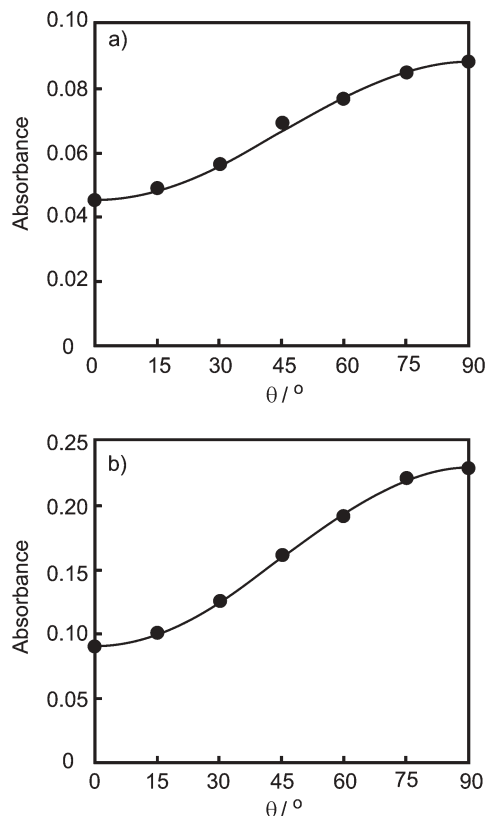
Utilising this effect, modulation of the molecular alignment of polymer liquid crystals<sup>41,42</sup> and liquid crystal monolayers<sup>43</sup> containing azobenzene chromophores has been performed. The other type of polarised light-induced dichroism is due to the bleaching of photochromic molecules lying in a specific direction in isotropic solids by irradiation with polarised light. This was first demonstrated for fulgide-doped poly(methyl methacrylate).<sup>44,45</sup> Recently, polarised light-induced dichroism and birefringence have also been reported for a sol-gel glass containing a dithienylethene moiety.<sup>46</sup> In the present study, the polarised light-induced dichroism of the dithienylethene-based photochromic amorphous molecular materials as amorphous films was investigated.

Irradiation of the amorphous films of open form TPTBC and BTPTC on glass substrates with non-polarised 365 nm light at *ca.* 20 mW cm<sup>-2</sup> caused a colour change from almost colourless to blue and green for TPTBC and BTPTC, respectively, due to the photocyclisation reactions to give TPTBC-c and BTPTC-c. After the system had reached the photostationary state, the coloured film was then irradiated with linearly polarised light of wavelength longer than 580 nm at *ca.* 20 mW cm<sup>-2</sup> to induce the reverse photochemical ring-opening reaction.

Fig. 5(a) shows the electronic absorption spectrum of the coloured film obtained by irradiation of a TPTBC film with non-polarised 365 nm light. When this coloured film was irradiated with linearly polarised red light to induce the reverse ring-opening reaction of TPTBC-c, the colour of the film gradually faded. Fig. 5(b) and (c) show the absorption spectra of the film after irradiation with polarised red light for 2 min. The intensity of the absorption band at 580 nm depended on the angle ( $\theta$ ) between the polarisation directions of the irradiated red light and probe light, as seen from the spectra for  $\theta = 0^\circ$  [Fig. 5(b)] and  $90^\circ$  [Fig. 5(c)]. Similar phenomena were observed for the amorphous film of BTPTC, although colour fading took place more slowly relative to the amorphous film of TPTBC because of the one order of magnitude smaller quantum yield for the photoinduced ring-opening reaction of BTPTC-c. Fig. 6 shows the dependence of the angle  $\theta$  on the absorbances at 580 and 630 nm for the amorphous films prepared by irradiation of the coloured films of TPTBC and BTPTC with polarised red light for 2 and 60 min, respectively. The absorbances of the films of TPTBC and BTPTC at 580 and 630 nm, respectively, increased with increasing  $\theta$ , being least for  $\theta = 0^\circ$  and greatest for  $\theta = 90^\circ$ . The transition moment for the absorption giving rise to bands peaking at 580 and 630 nm for TPTBC-c and BTPTC-c is thought to be in a direction almost parallel to the longest molecular axis (horizontal direction for the molecules drawn in Scheme 1). The closed isomers, which are in random orientations, absorb red light more effectively



**Fig. 5** (a) Electronic absorption spectrum of the coloured film obtained by irradiation of the TPTBC film with non-polarised 365 nm light. Electronic absorption spectra of the film after irradiation with polarised red light for 2 min with  $\theta = 0^\circ$  (b) and  $90^\circ$  (c).



**Fig. 6** Dependence of the angle  $\theta$  on the absorbances at 580 and 630 nm for amorphous films of (a) TPTBC and (b) BTPTC after irradiation with polarised red light for 2 and 60 min, respectively.

when the angle between the irradiated polarised red light and the longest molecular axis is small. Thus, the number of coloured molecules remaining unfaded becomes larger with increasing  $\theta$ .

Dichroism was evaluated according to eqn. 3,<sup>46</sup>

$$D = \Delta I/I_0 = 10^{-A_{\parallel}} - 10^{-A_{\perp}} \quad (3)$$

where  $I_0$  represents the intensity of the incident probe light,  $\Delta I$  the difference in the intensity of the transmitted probe light between  $\theta = 0$  and  $90^\circ$ , and  $A_{\parallel}$  and  $A_{\perp}$  the absorbances of the film for  $\theta = 0$  and  $90^\circ$ , respectively. The maximum values of  $D$  for the amorphous films of TPTBC and BTPTC were *ca.* 0.10 and *ca.* 0.11, respectively, which were larger than that for the dithienylethene-doped sol-gel glass (*ca.* 0.06).<sup>46</sup>

Utilising the phenomenon of linearly polarised light-induced dichroism, dual image formation at the same location of the amorphous film was demonstrated. The amorphous films of TPTBC and BTPTC with a thickness of 5 to 10  $\mu\text{m}$  were prepared by sandwiching a melt sample between two glass substrates and then cooling in air. The amorphous film of TPTBC was irradiated with non-polarised 365 nm light for 5 min and then the resulting blue-coloured film was irradiated with polarised red light of horizontal polarisation for 30 s through a mask of a letter "H", where the area other than the letter H is exposed, followed by irradiation with polarised red light of vertical polarisation for another 30 s through another mask of a letter "V", where the area other than the letter V is exposed.

Fig. 7 shows photographs of the dual images formed at the same location on the TPTBC amorphous film. When the film is viewed through a polariser with  $\theta = 0^\circ$ , the letter "H" is visible [Fig. 7(a)], while the letter "V" is visible through a polariser with  $\theta = 90^\circ$  [Fig. 7(b)]. Such dual image formation was also

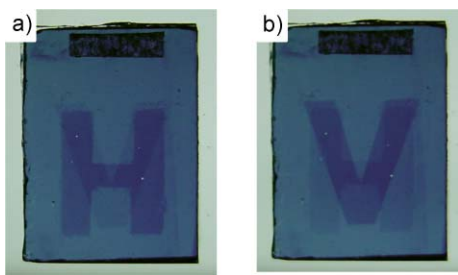


Fig. 7 Photographs of dual images formed on an amorphous film of TPTBC, viewed through polarisers with  $\theta = 0$  (a) and  $90^\circ$  (b).

realised for a BTPTC film. These images were stable for more than three months in the dark at room temperature. These two images could be erased by irradiation with intense non-polarised red light, and new dual images could be formed repeatedly by the same procedures described above. The formation of dual images at the same location can be applied for the formation of a stereo image.

## Summary

A new class of photochromic amorphous molecular materials containing a dithienylethene moiety, TPTTC, TPTBC and BTPTC, were designed and synthesised. These compounds, together with their photocyclised products, were found to readily form amorphous glasses with well-defined glass transition temperatures and to undergo photochromism as amorphous films as well as in solution. While the quantum yields for the photocyclisation reactions ( $\Phi_{o-c}$ ) of these compounds in solution were very high, those for the ring-opening reactions ( $\Phi_{c-o}$ ) of the photocyclised compounds were very low. Because of the high  $\Phi_{o-c}$  and the very low  $\Phi_{c-o}$ , the fractions ( $Y_{pss}$ ) of the photocyclised forms for these compounds in solution were almost 100%. The results that the  $\Phi_{o-c}$  of these compounds in solution are much larger than 0.5 and the  $Y_{pss}$  of TPTTC and BTPTC as amorphous films upon irradiation with 365 nm light are greater than 50% suggest that the anti-parallel conformer is more populated than the parallel conformer for the present molecules.

Polarised light-induced dichroism in amorphous films of the dithienylethene-based photochromic amorphous molecular materials was investigated, and dual image formation at the same location was realised by taking advantage of this phenomenon.

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