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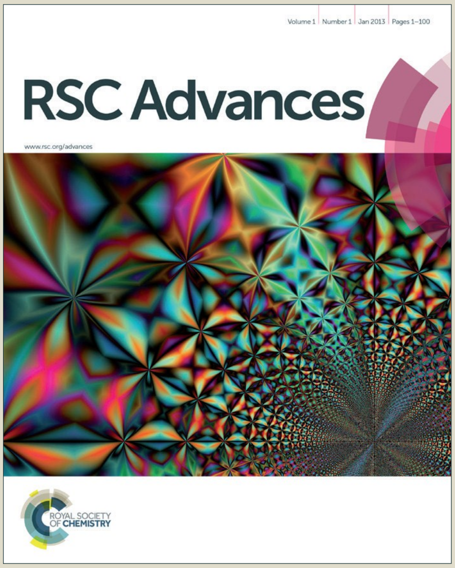

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ARTICLE

Substitution effect on photochromic properties of benzo[*b*]thiophene-1,1-dioxide based diarylethenes†

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Benzo[*b*]thiophene-1,1-dioxide based diarylethenes (DAEs), BTT-1 to BTT-4, containing methyl, phenyl, formyl and triphenylamine groups at the 5,5'-position of thiophene rings have been developed for insight into substituent effects on the absorption and photochromic properties. Electron-donating substituents, such as phenyl and triphenylamine groups, are found to be effective to shift the absorption band to a longer wavelength and to decrease the cyclization quantum yield. Electron-withdrawing formyl group can increase the cyclization quantum yield, but reduce the thermal stability of the ring-closed isomer to some extent. BTT-4 bearing a triphenylamine group shows the poorest fatigue resistance among these four compounds, which is possibly due to the larger extended π-conjugation length in the ring-closed isomer. BTT-2 bearing a phenyl unit undergoes typical photochromic reaction not only in solution, but also in the PMMA thin film and in the bulky crystals with excellent fatigue resistance and thermal stability.

1 Introduction

Photochromic materials such as azobenzenes, fulgides, spiropyrans and diarylethenes (DAEs) are becoming increasingly interests in a variety of fields such as molecular data storage, logic gates, functional molecular devices as well as biological materials due to their light-trigged reversible switching abilities.[1-4] Among them, DAEs are one of the most promising families owing to their excellent thermal stability and outstanding fatigue resistance.[5] To date, many rational designs of symmetric or asymmetric DAEs have been carried out. However, the central ethene bridges which are necessary for the versatility of DAEs architectures have been mostly limited to the cyclopentene unit or its strong electron-withdrawing analogues, such as perfluorocyclopentene and maleic anhydride/imide.[6-12] Recently, several groups have demonstrated alternative ways to expand the versatility of DAE architectures by chemically tailoring the central ethene bridges. For instances, different aryl units such as thiophene,[13] thiazole,[14] imidazolium[15] and benzothiopene[16] have been employed as the central bridge. Novel DAEs containing different ethene bridges of 1,10-phenanthroline[17], thiophene derivatives[18,19] and methylimidazol derivatives[20] were exploited as functional organic ligands to prepare versatile metal organic complex toward regulation of phosphorescence, near-infrared photochromic behavior and gated photochromism.[21] Besides, DAEs with new ethene bridges including coumarin,[22] *N*-heterocyclic carbine,[23] phthalocyanine[24] and tetraazaporphyrin[25] have also been developed and applied in various areas such as live cell imaging, controllable organic catalyst, non-destructive fluorescence readout and so on. Our group has recently focused on rationally designing the central ethene bridge of DAEs by introducing a series of aryl functional groups like naphthalimide, benzothiadiazole, benzobisthiadiazole, and benzothiophene-dioxide into the DAE framework, which provide new strategies for the development of highly bistable photochromic systems.[26-29] For example, by taking advantage of the low aromaticity and nice fluorescence property of benzothiophene-dioxide unit, novel DAE derivatives based on this building block were developed, which have wide applications in molecular logic gates, gated photochromism as well as photoswitchable supramolecular systems.[30-34] On the other hand, the DAE photochromic properties can be modified by suitable functionalization of the aromatic rings with electron-donating groups or electron-withdrawing groups.[35-39] Although substitution effects of perfluorocyclopentene based DAEs have been well studied, the systematical investigation of substituent effect on the photochromic properties of DAEs based on benzothiophene-dioxide bridge is still rare.[40-42]

In the present work, substituent modulated DAEs based on benzo[*b*]thiophene-1,1-dioxide were studied (Scheme 1), which exhibit notable photochromism both in solution and in the solid state. Moreover, the substituents were found to have significant effects on the properties of DAEs such as absorption and fluorescence properties, thermal stability, fatigue resistance and quantum yield, which have been systematically

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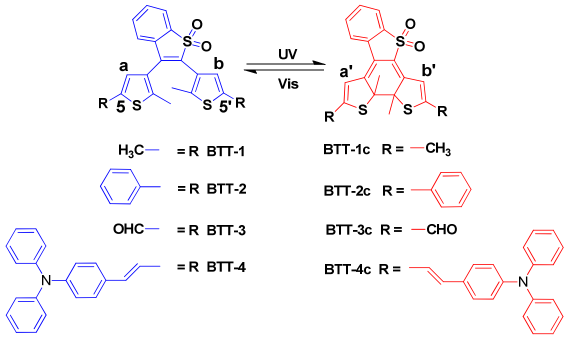
studied by optical spectra, NMR, X-ray diffraction analysis and density functional theory (DFT) calculations.



Scheme 1 Chemical structures and photochromic reactions of BTT-1 to BTT-4: four different substitutes were introduced into the 5,5′-positions of the thiophene rings: methyl (BTT-1), phenyl (BTT-2), formyl (BTT-3) and triphenylamine groups (BTT-4).

2 Experimental

2.1 Synthesis

Unless otherwise stated, all chemicals were commercially available and used without further purification. Organic solvents used were purified by standard methods prior to use. Synthetic routes for the photochromic compounds BTT-1, BTT-2, and BTT-4 were depicted in Scheme S1 in electronic supplementary information (ESI) †. CCDC1403388, 1403389 and 1403390 contain the supplementary crystallographic data for BTT-1, BTT-2 and BTT-3, which can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of BTT-1. BT-1 (0.26 g, 0.8 mmol), 2 M Na_2CO_3 (10 mL), 20 mL of THF, compound 1 (0.50 g, 3.2 mmol) and $Pd(PPh_3)_4$ (0.15 g) were added into a 50 mL bottle. Then, the resulting mixture was refluxed under the protection of nitrogen in dark for 12 h, and cooled to room temperature. After that, the mixture was poured into H_2O (50 mL) and extracted with ether for three times (15 mL × 3). The organic layer was collected and dried with Mg_2SO_4. After concentration, the crude product was purified by column chromatography on silica (petroluem: ethyl acetate, 40:1, v/v) to yield a light yellow solid (0.08 g, yield 30%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.90 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 6.58 (s, 1H, thiophene-H), 7.00 (s, 1H, thiophene-H), 7.35-7.37 (J = 8.0 Hz, m, 1H, benzothiophene-H), 7.49-7.57 (m, 2H, benzothiophene-H), 7.80-7.82 (J = 8.0 Hz, m, 1H, benzothiophene-H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.27, 14.37, 15.25, 15.29, 121.47, 122.82, 124.41, 124.77, 125.29, 127.20, 129.72, 133.29, 133.40, 133.78, 134.89, 136.26, 137.29, 137.57, 137.64, 139.84. Mass spectrometry (ESI positive ion mode for $[M + K]^+$): Calcd. for $C_{20}H_{18}O_2S_3K$, 425.0106; found, 425.0122.

Synthesis of BTT-2. A solution of compound 2 (0.76 g, 3 mmol) in dry THF (20 mL) was added into a dry Schlenk bottle, and the solution was cooled to -78 °C. After that, 1.3 mL of 2.5 M solution of butyllithium in hexane was added under nitrogen. After stirring for 15 min at that temperature, 0.45 mL trimethyl borate was added in one portion, the mixture was stirred for another 1 h. The cooling bath was removed, and the mixture was left overnight. The resulting mixture was added into a 50 mL bottle without further purification, and BT-1 (0.33 g, 1 mmol), 2 M Na_2CO_3 (10 mL), and $Pd(PPh_3)_4$ (0.16 g) were also added. The resulting mixture was refluxed under the protection of nitrogen in dark for 20 h. Then the mixture was cooled to room temperature and poured into H_2O (50 mL) and extracted with ether for three times (25 mL × 3). The crude product was purified by column chromatography on silica (petroluem: ethyl acetate, 50:1, v/v) to give a light yellow solid (0.39 g, yield 38 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.05 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 7.20 (s, 1H, thiophene-H), 7.27-7.32 (m, 2H), 7.34-7.41 (m, J = 7.6 Hz, 4H), 7.44-7.46 (m, 1H), 7.53-7.58 (d, J = 8.6 Hz, 7H), 7.86-7.88 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.64, 14.68, 121.69, 122.77, 122.99, 124.25, 125.58, 125.69, 127.65, 127.92, 128.49, 128.91, 129.09, 130.08, 132.97, 133.51, 133.6, 133.71, 134.17, 135.12, 136.42, 139.45, 141.61, 141.94, 142.4 Mass spectrometry (ESI positive ion mode for $[M + K]^+$): Calcd. for $C_{30}H_{22}O_2S_3K$, 549.0419; found, 549.0420.

Synthesis of BTT-4. BTT-4 was prepared by the similar method to synthesize BTT-2 using compound 3 instead of compound 2, and was obtained as a light yellow solid (0.18 g, yield 20 %). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 1.99 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 6.79-6.85 (m, 2H), 6.91-6.93 (d, J = 8.4 Hz, 4H), 7.03-7.09 (m, 12H), 7.17 (s, 1H), 7.24-7.35(m, 11H), 7.45-7.50 (m, 5H), 7.69-7.78 (m, 2H), 8.04 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), ppm): δ 14.79, 14.84, 119.37, 119.78, 121.64, 123.11, 123.24, 123.30, 123.44, 123.77, 124.22, 124.52, 124.58, 124.66, 125.32, 125.58, 127.20, 127.22, 128.02, 128.45, 129.31, 129.34, 130.01, 130.52, 130.88, 132.92, 133.54, 133.90, 134.88, 136.35, 138.53, 140.83, 141.00, 141.45, 147.43, 147.50, 147.65. Mass spectrometry (ESI positive ion mode for $[M + K]^+$): Calcd. for $C_{58}H_{44}N_2O_2S_3K$, 935.2202; found, 935.2216.

2.2 Instrumentation

^{1}H and ^{13}C NMR spectra were recorded on a Brucker AM-400 spectrometers with tetramethylsilane (TMS) as an internal reference. $CDCl_3$ and DMSO-d_6 were used as solvents. HRMS spectra were recorded using a Waters LCT Premier XE spectrometer using methanol or acetonitrile as solvents. Absorption and fluorescence spectra were recorded on Varian Cary 100 and Varian Cary Eclipse, respectively. The photochromic reaction was induced in situ by continuous irradiation using an Hg/Xe lamp (Hamamatsu, LC8 Lightningcu 200 W) equipped with a narrow band interference filter (Shenyang HB optical Technology) for λ_{irr} = 313 or 365 nm, a broad band interference filters (Shenyang HB optical Technology) for λ_{irr} > 450 nm. The photochromic reaction quantum yields were evaluated by the standard procedures using a BTF6 (1,2-bis(2-methylbenzo[*b*]-thiophen-3-yl)perfluorocyclopentene) derivative as the reference for photocyclization. The rates of isomerization in the initial stage of the reaction (0-5%) were compared with reference whose Φ_{o-c} (35%) in hexane are known, which brought forth 5 uncertainties on the calculations of quantum yields.[43] Absorption changes were monitored by a CCD camera mounted on a Princeton spectrometer instrument.

2.3 Computational details

We employed density functional theory (DFT) calculations to optimize the geometries of the photochromic molecules, using the hybrid B3LYP functional[44] Grimme's dispersion correction with Becke-Johnson damping was used to account for van der Waals interaction[45]. Frequency analyses were carried out to verify that the optimized geometries are true minima on the potential energy surface. At the optimized geometries, time-dependent (TD) DFT calculations were carried out using the range-separated CAM-B3LYP functional[46] and the triple-zeta basis set 6-311G+(d, p)[47] where diffuse functions are included. In TD-DFT calculations, solvent effects of ethyl acetate were taken into account by the polarizable continuum model.[48] All calculations were carried out using the Gaussian 09 program package.

2.4 Preparation of thin films of BTT-1 to BTT-4

Quartz substrates (2.5 cm × 1.0 cm) were cleaned by sequentially sonicating them with acetone, EtOH and MeOH, and drying them with clean nitrogen before spin-casting. Appropriate amounts of BTT-1 to BTT-4 (about 5% weight percentage to the polymer) and PMMA (M_n = 12 000) were dissolved in $CHCl_3$. The quartz substrates were saturated by dropwise adding the mixed solutions to them. Thin films were prepared by spin-casting using a Laurell WS-400A-6NPP/Lite spin-coater operating at 3000–4000 rpm.

3 Results and discussion

3.1 Molecular design and synthesis

In order to investigate the substitute effect on the modulation of photochromic properties, four DAE derivatives BTT-1 to BTT-4 bearing electron donating groups (methyl, phenyl, triphenylamine) or withdrawing groups (formyl) in the 5,5'-position of the side thiophene were designed and synthesized (Scheme 1). The different π-conjugation length as well as the electronic feature of substitutes would possibly lead to significant differences in the photochromic properties, providing information for the relationship between chemical structure and photochromic properties. Synthetic routes to the compounds BTT-1, BTT-2 and BTT-4 were shown in Scheme S1†. The important intermediates (1, 2 and 3) and BT-1 were prepared by the reported procedure, and were used as building blocks to synthesize the desired target molecules.[33] BTT-3 was prepared by the established method.[33] The Suzuki coupling between the corresponding boronic acids and the BT in the presence of a $[Pd(PPh_3)_4]$ catalyst in a mixture of aqueous Na_2CO_3 (2 M) and THF under reflux gave the target molecules of BTT-1, BTT-2 and BTT-4, which were fully characterized by ^1H and ^{13}C NMR spectroscopy as well as HRMS in Experimental section.

3.2 Tunable bathochromic-shift in absorption induced by different substituents

The absorption spectrum of a DAE derivative usually depends upon its chemical structure, especially in the case of the ring-closed isomer. In the present photochromic system, the tunable bathochromic-shift in absorption spectra of the ring-closed isomer was successfully achieved by introducing of different characteristic substituents into 5, 5'-position of the thiophene rings. As shown in Fig. 1, when the solutions of the ring-open isomers (BTT-1 to BTT-4) were irradiated with UV light (365 nm), new moderately intense bands appeared in the low-energy region of absorption spectra, and changed their appearance from colorless to deep color. These new absorption bands are attributed to the ring-closed isomers with extended π-conjugation produced by the specific photochromic reactions. The photocyclization reactions were also monitored by ^1H NMR. As illustrated with BTT-2 in Fig. 2, the distinct changes of ^1H NMR signals in $CDCl_3$ solution before and after UV irradiation at 365 nm light. The methyl hydrogens at the reactive carbon in BTT-2 give two single peaks at 2.05 and 2.11 ppm, respectively. Upon UV irradiation, the two new peaks appear at 2.17 and 2.18 ppm corresponding to the methyl protons of the closed isomer BTT-2c. Meanwhile, the singlet peaks at 7.20 and 7.26 ppm for BTT-2, corresponding to protons on the thiophene rings (H*a* and H*b*), shifted upfield to 7.07 and 7.10 ppm, respectively, after UV irradiation. Additionally, the proton signals on ethene bridge and benzene moiety exhibit changes after photocyclization. These changes in NMR signals are due to the great changes (extended π-delocalization) in the chemical environment. The typical color change together with NMR signal change confirms the typical photochromic properties of these DAE compounds. However, owing to the different substituent groups in each DAE derivative, the absorption bands (λ_{max}) of ring-closed isomers in the visible region were totally different, changing the color of each solution. More specifically, the colors were red for BTT-1c (λ_{max} = 495 nm), light purple for BTT-2c (λ_{max} = 564 nm), deep blue for BTT-3c (λ_{max} = 590 nm), and green for BTT-4c (λ_{max} = 634 nm). Compared with BTT-1 containing methyl group, the remarkable bathochromic-shift as large as 59, 95 and 149 nm were observed for BTT-2, BTT-3 and BTT-4, respectively. The electron-donating (phenyl, triphenylamine group) and withdrawing substituent (formyl group) both shift the absorption band of the ring-closed isomer to longer wavelengths. Such kind of substitution effect was also found in the perfluorocyclopentene based DAE derivatives.[49]

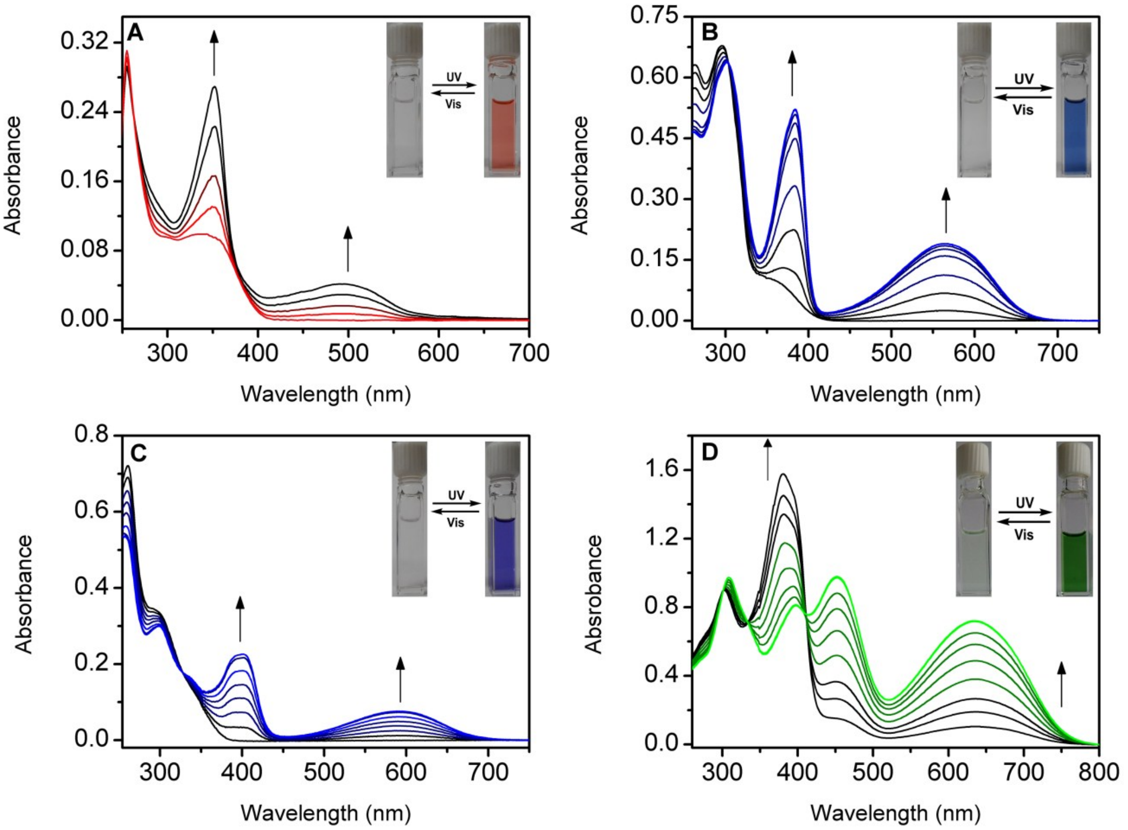


Fig. 1 Absorption changes upon irradiation at 365 nm in ethyl acetate: (A) BTT-1 (2.05 × 10^{-5} mol L^{-1}), (B) BTT-2 (2.15 × 10^{-5} mol L^{-1}), (C) BTT-3 (2.10 × 10^{-5} mol L^{-1}), and (D) BTT-4 (2.02 × 10^{-5} mol L^{-1}). Inset: the corresponding photographic images upon irradiation with UV and visible light.

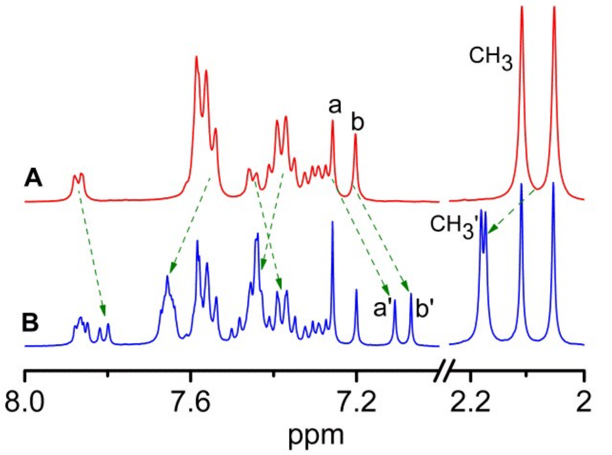


Fig. 2 ^{1}H NMR signal changes of BTT-2 in $CDCl_3$: (A) before irradiation, (B) after UV irradiation.

To gain insight into the substitution effect on their absorption, the computed absorption spectra of the four compounds were obtained by Gaussian broadening of the stick spectra from time-dependent density functional theory (TD-DFT) calculations, where the experimentally observed absorption bands are well reproduced (Fig. S1†).[50-52] The contour plots for frontier molecular orbitals of photochromic compounds BTT-1 to BTT-4 are shown in Table S1†, which exhibit similarity to some degree. In the ring-open isomers, the HOMO is usually located at the thienyl arm on the left side and the oxygen atoms of the bridging unit, while the LUMO is largely localized on the benzothiophene-dioxide bridge. The HOMO→LUMO transition of the ring-open isomer with a characteristic of intramolecular charge-transfer character (ICT), contributes to the absorption band at around 350 nm. After photocyclization, the ring-closed unit was formed, and both their HOMO and LUMO became delocalized on the central groups. In general the photochromic cyclization leads to shift in both HOMO and LUMO, and in turn narrows the HOMO-LUMO gap. Compared with the methyl group, the phenyl, formyl and triphenylamine substituents provide different extension of π-conjugation in the ring-closed DAE unit, leading to longer and different wavelengths in the absorption spectra. Noteworthy, in compound BTT-4c, the triphenylamine group contributes slightly more to the HOMO than the LUMO, resulting in a mixing of local excitation in the central DAE unit and charge-transfer excitation from triphenylamine to DAE. In compound BTT-3c, however, the direction of charge-transfer is opposite, namely from the ring-closed DAE to the carbonyl group. This is partially responsible for the larger absorption wavelength of BTT-3c with respect to BTT-2c. The calculated absorption wavelengths are in good consistency with the experimentally measured data (Table 1). The above analyses thus confirm that modulation of absorption spectra in these DAE compounds especially for the ring-closed isomers can be nicely achieved by introducing substituents with different π-conjugation into the 5, 5′-posion of the thiophene groups in the present system.

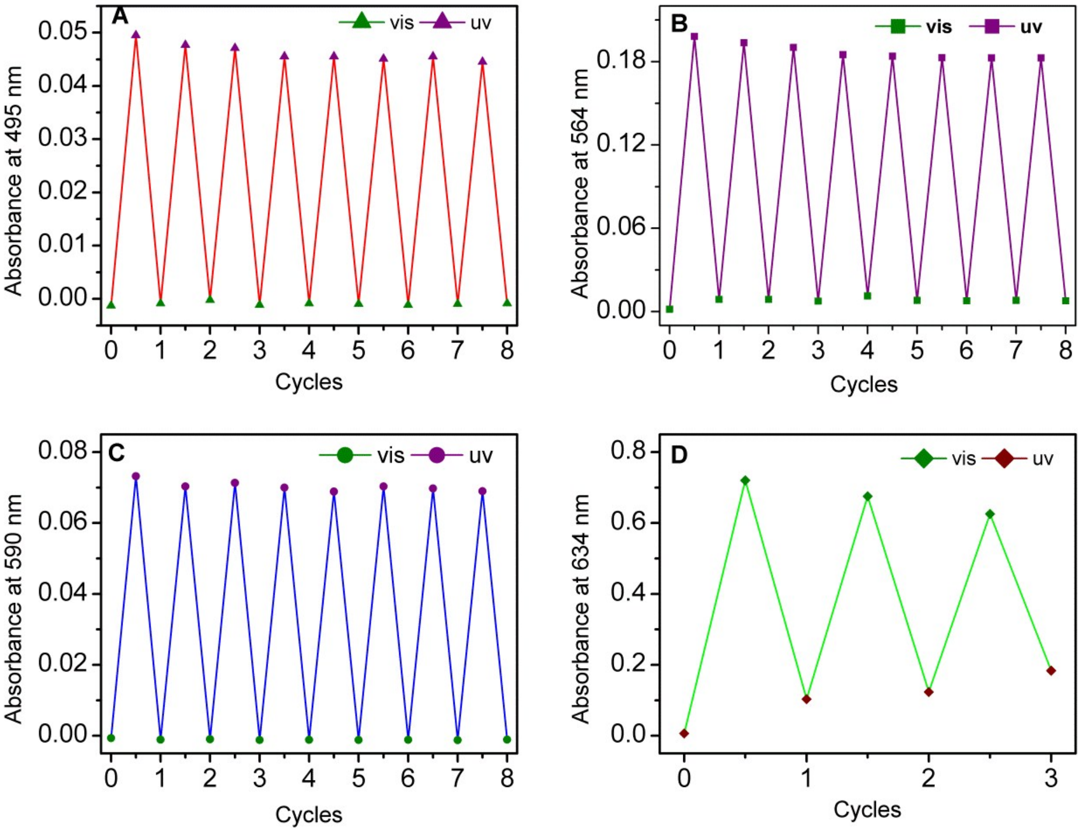


Fig. 3 Fatigue resistance upon alternating irradiation with UV (365 nm) and visible light (λ > 450 nm): (A) BTT-1, (B) BTT-2, (C) BTT-3, and (D) BTT-4.

Table 1 Absorption data, conversion yield and quantum yield of compounds BTT-1 to BTT-4

	λ_{max} (nm), exp.[a]		λ_{max} (nm), exp.[b]		α_{pss}[c]/%	$\Phi_{o\text{-}c}$[d]/%
	Open isomer	Closed isomer	Open isomer	closed isomer		
BTT-1	255	495	260	501	61.2	38.5
BTT-2	295	564	298	574	94.3	29.3
BTT-3	261	590	262	600	89.6	46.6
BTT-4	380	634	384	647	95.3	35.6
BTF6[e]	258	504	-	-	45.0	35.0

[a] Absorption spectra in ethyl acetate; [b] Absorption spectra in the film; [c] Conversion yield at photostationary state (PSS) upon irradiation with 313 nm. [d] Cyclization quantum yield (Φ o-c) was measured at 313 nm, using BTF6 as the reference. [e] BTF6 (313 nm) in hexane was taken from reference[42].

3.3 Substituents effects on fatigue resistance, thermal stability and quantum yield

For applications in the field such as optical memories, switches, and actuators, a photochromic DAE should fulfill two basic requirements: i) high fatigue resistance, and ii) good thermal stability of both isomers. Indeed, those properties are usually highly related with the substitutes on the attached aromatic rings in a DAE derivative. In the present photochromic systems, substituents were found to have significant influence on both the fatigue resistance and thermal stability for the ring-closed isomers. As shown in Fig. 3, the coloration/decoloration cycles could be well repeated in BTT-1, BTT-2 and BTT-3 by alternating UV (365 nm) and visible-light (> 450 nm) irradiation of their solution in ethyl acetate without the exclusion of oxygen. After 8 cycles, the monitored absorption spectra of BTT-3 remain intact without negligible degradations, indicative of the excellent fatigue resistance of it (Figure 3C). Besides, only small degradations were found for compound BTT-1 and BTT-2 after 8 cycles even without the exclusion of oxygen, which also suggested that BTT-1 and BTT-2 possess nice fatigue resistanc In contrast, the compound BTT-4 can only undergo photoinduced cyclization/cycloreversion reactions of less than 3 cycles in ethyl acetate without the exclusion of oxygen. The poor fatigue resistant properties may be due to the large extended π-conjugation length of the ring-closed isomer, which could be easily oxidized in the present of oxygen.[53-55]

Generally in DAE derivatives, the thermal cycloreversion often correlates with the ground-state energy differences of the open and closed isomers. When the ground-state energy difference is large, the energy barrier of the thermal cycloreversion reaction is small, leading to more probable thermal cycloreversion reaction, as reported by Irie and coworker as well as our group.[56-58] Impressively, the derivatives show nice thermal stability with the exceptions of BTT-3. The absorption spectra of the ring-closed isomers of BTT-1, BTT-2 and BTT-4 can be maintained for more than 20 h at 303 However, BTT-3 containing formyl groups exhibits obvious degradation in accordance with similar DAEs bearing perfluorocyclopentene as the ethene bridge (Fig. 4). Absorption band at 590 nm of BTT-3 decayed more than 30% after 20 h. We thus examined the thermal bistability of compounds BTT-1 t BTT-4 by calculating their energy differences between the rin open and the ring-closed isomers. Interestingly, BTT-3 show the largest energy difference of 60 kJ mol^{-1}, which is in consistent with the experimentally observed lifetime of tens of hours. This is presumably owing to electron-withdrawing ability of the aldehyde substituents, which would decrease the thermal stability of the DAE derivatives by weakening the central carbon−carbon bonds in the closed-ring isomers.[59] The other three compounds show energy differences within about 30 kJ mol^{-1}, which was half of that of BTT-3 (Table S3†). Here the smaller energy differences resulted in the better thermal stability of those three compounds.

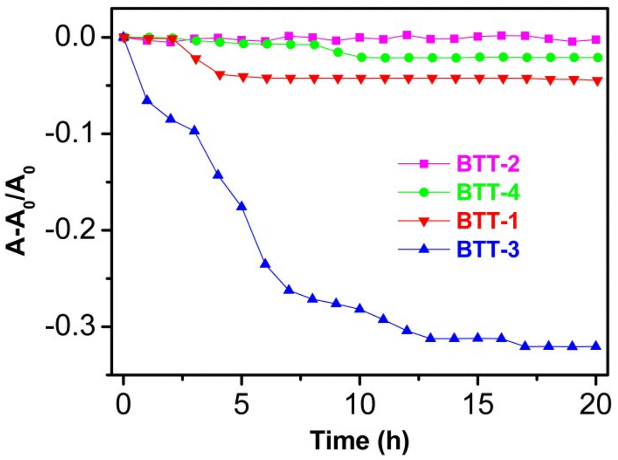


Fig. 4 Thermal bleaching behavior of BTT-1 to BTT-4 at 303 K.

By the way, the substituent effect on the cyclization quantum yield was also compared in the present photochromic DAE system. The quantum yield in the cyclization reaction of BTT-1 was determined to be 38.5%, while the yields of BTT-2 and BTT-4 were 29.3 and 35.6%. Compared with BTT-1, the incorporation of electron donating substituents (phenyl, triphenylamine) is considered to suppress the photo-cyclization reaction. In contrast, the electron-withdrawing aldehyde substituent increased the cyclization quantum yield, and a yield as high as 46.6% was observed.[49,60]

3.4 Photochromism in the crystalline phase

Among DAEs BTT-1 to BTT-4, single crystals of BTT-1, BTT-2, and BTT-3 were all grown by slow evaporation from hexane/ethyl acetate solution. The X-ray crystallographic data were collected and listed in Table S3†, and their ORTEP drawings were shown in Fig. S2†. Both BTT-1 and BTT-2 adopted a photoactive anti-parallel conformation in crystalline phase, while only the parallel conformer exists in the single crystals of BTT-3. In the single crystal state, the distances between the photoactive carbon atoms are 3.515 and 3.618 Å for BTT-1 and BTT-2, which are less than 4.2 Å, meeting the preconditions for a molecule to undergo photochromic reaction in crystalline phase.[61] Indeed, bulky crystals of BTT-1 and BTT-2 can be easily colored and decolored with the typical reversible photochromic behaviors. The color changes of crystals BTT-1 and BTT-2 upon photoirradiation are shown in Fig 5. Upon irradiation with 365 nm light, the almost colorless crystals changed into red and deep blue for BTT-1 and BTT-2 quickly. Impressively, the crystals exhibited even much better fatigue resistance and thermal stability than that in the solution state, that is, more than 100 cyclization/cycloreversion cycles can be repeated, and their colored isomers remained stable for more than one month in the dark at room temperature, exhibiting potential application for the construction of functional photo-electronic devices. In the case of BTT-3, no photochromism was observed in the crystalline phase due to the no active parallel conformation.

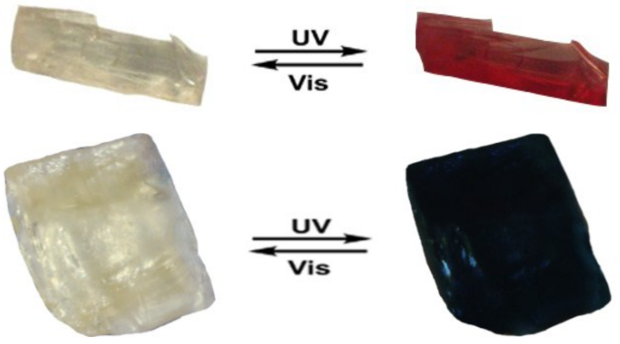


Fig. 5 Colour changes for crystals of BTT-1 and BTT-2 upon alternating irradiation with UV (365 nm) and visible light (λ > 450 nm).

3.5 Photochromism in the polymer matrix

The application of photochromic DAEs on technologies such as 3D level data storage requires the incorporation of the compounds into films that retain the operation in the practical device.[62] With this in mind, thin films of PMMA containing different DAE derivatives were prepared by spin-casting $CHCl_3$ solutions of PMMA and the corresponding photochrmomic dyes onto quartz substrates. Photochromism in PMMA films is quite similar to that in ethyl acetate (Fig. 6). Irradiation of the transparent films with UV light at 365 nm leads to the appearance of new absorption bands around 501 nm for PMMA-BTT-1, 574 nm for PMMA-BTT-2, 600 nm for PMMA-BTT-3, as well as 647 nm for PMMA-BTT-4, respectively. Also as expected, these could be bleached by irradiating with visible light (λ > 450 nm). Compared to those in ethyl acetate solution, the absorption bands of the photochromic derivatives in PMMA films show a typical bathochromic shift (Table 1), which may be due to the polar effect of the polymer matrix and the stabilization of molecular arrangement in the solid state.[63] In addition, all the thin films except the one with BTT-4 exhibit good fatigue resistance properties as observed in solution, which may have potential applications in optical storage (Fig. S3†).

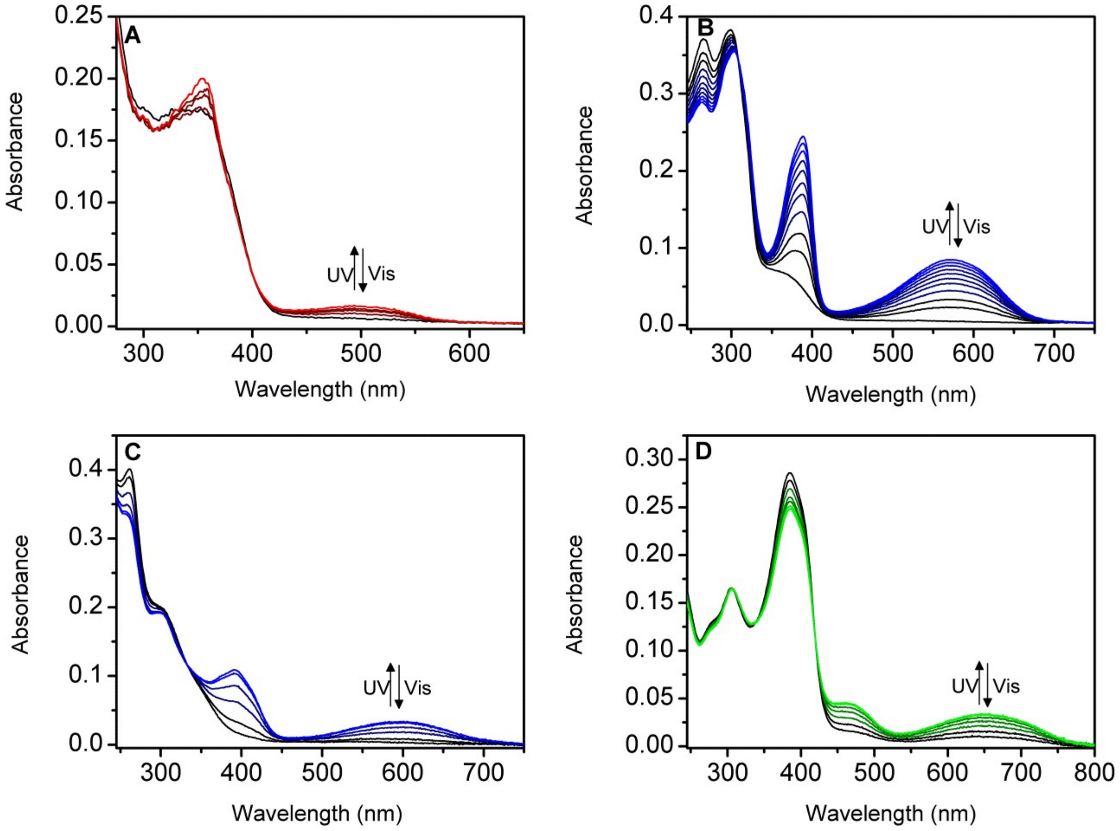


Fig. 6 Absorption spectra changes upon irradiation at 365 nm in PMMA film: (A) PMMA-BTT-1, (B) PMMA-BTT-2, (C) PMMA-BTT-3, and (D) PMMA-BTT-4.

3.6 Fluorescence modulation by photochromism

Fluorescence modulation is becoming an intriguing approach, which can be widely applied to molecular-scale optoelectronics, ion-sensors, and digital photoswitches.[64-65] When excited at the isosbestic point of 305 and 326 nm, the emission peaks of DAEs BTT-2 and BTT-3 were observed at 488 and 452 nm in ethyl acetate, respectively. Moreover, the fluorescence can be modulated with the photochromism (Fig. S4†). The fluorescence intensity of BTT-2 and BTT-3 decreased drastically by photochromic ring closure upon irradiation with 365 nm light due to the non-fluorescent closed form. The quenched fluorescence can be perfectly regained by an alternative irradiation with visible light (*λ* > 450 nm). Such good fluorescence modulation properties make them as possible candidates for application in photoswitchable devices, such as optical memory and fluorescent modulation switches.

4 Conclusions

Four photochromic DAEs bearing different substitutes on the 5,5'-position of thiophene rings were synthesized in order to investigate the substitution effect on their photochromic properties. Their absorption and fluorescence characteristics as well as photochromic properties including thermal stability, fatigue resistance and quantum yield can be well modulated by the introducing of electron-donating or electron-withdrawing substituents. Tunable bathochromic-shift in absorption induced by substituents with different extension of π-conjugation was successfully achieved. The cyclization quantum yield could be decreased by the electron-donating substituents, such as phenyl and triphenylamine groups, while increased by electron-withdrawing formyl group. Moreover, the thermal stability was found to be reduced by electron-withdrawing groups, and fatigue resistance maybe wrecked by substituents possessing large π-conjugation properties. Among the four DAE derivatives the compound containing phenyl groups (BTT-2) exhibits typical photochromism with excellent thermal stability and fatigue resistance not only in solution, but also in PMMA film and crystal state. Moreover, the reversible fluorescence controlled by photochromic reactions were also found. The wonderful photochromic properties make sample BTT-2 a promising candidate for the development of practical molecular devices.

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Notes and references

1 (*a*) H. Bouas-Laurent and H. Dürr, *Pure Appl. Chem.*, 2001, **73**,

639; (*b*) J. Zhang, Q. Zou and H. Tian, *Adv. Mater.*, 2013, **25**, 378.
2 F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327.
3 W. Szymański, J. M. Beierle, H. A. V. Kistemaker, W. A. Velema and B. L. Feringa, *Chem. Rev.*, 2013, **113**, 6114.
4 (a) G. Lv, B. Cui, H. Lan, Y. Wen, A. Sun and T. Yi, *Chem. Commun.*, 2015, **51**, 125; (*b*) M. Bälter, S. Li, J. R. Nilsson, J. Andréasson and U. Pischel, *J. Am. Chem. Soc.*, 2013, **135**, 10230.
5 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174.
6 (*a*) J. Park, D. Feng, S. Yuan and H. Zhou, *Angew. Chem., Int. Ed.*, 2015, **54**, 430; (*b*) X. Cui, J. Zhao, Y. Zhou, J. Ma and Y. Zhao, *J. Am. Chem. Soc.*, 2014, **136**, 9256.
7 (*a*) K. Higashiguchi, G. Taira, J. Kitai, T. Hirose and K. Matsuda, *J. Am. Chem. Soc.*, 2015, **137**, 2722; (*b*) T. Hirose, Y. Tsunoi, Y. Fujimori and K. Matsuda, *Chem. Eur. J.*, 2015, **21**, 1637.
8 S. Wei, M. Pan, K. Li, S. Wang, J. Zhang and C. Su, *Adv. Mater.*, 2014, **26**, 2072.
9 G. Szalóki, G. Sevez, J. Berthet, J. Pozzo and S. Delbaere, *J. Am. Chem. Soc.*, 2014, **136**, 13510.
10 M. Herder, M. Utecht, N. Manicke, L. Grubert, M. Patzel, P. Saalfrank and S. Hecht, *Chem. Sci.*, 2013, **4**, 1028.
11 A. M. Asadirad, S. Boutault, Z. Erno and N. R. Branda, *J. Am. Chem. Soc.*, 2014, **136**, 3024.
12 S. A. Díaz, F. Gillanders, E. A. Jares-Erijman and T. M. Jovin, *Nat. Commun*., 2015, **6**. 6036.
13 T. Kawai, T. Iseda and M. Irie, *Chem. Commun.*, 2004, 72.
14 S. Kawai, T. Nakashima, K. Atsumi, T. Sakai, M. Harigai, Y. Imamoto, H. Kamikubo, M. Kataoka and T. Kawai, *Chem. Mater.*, 2007, **19**, 3479.
15 T. Nakashima, M. Goto, S. Kawai and T. Kawai, *J. Am. Chem. Soc.*, 2008, **130**, 14570.
16 T. Nakashima, K. Tsuchie, R. Kanazawa, R. Li, S. Iijima, O. Galangau, H. Nakagawa, K. Mutoh, Y. Kobayashi, J. Abe and T. Kawai, *J. Am. Chem. Soc.*, 2015, **137**, 7023.
17 V. W. Yam, C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 12734.
18 C. Poon, W. H. Lam and V. W. Yam, *Chem. -Eur. J.*, 2013, **19**, 3467.
19 C. Poon, W. H. Lam and V. W. Yam, *J. Am. Chem. Soc.*, 2011, **133**, 19622.
20 P. H. Lee, C. Ko, N. Zhu and V. W. Yam, *J. Am. Chem. Soc.*, 2007, **129**, 6058.
21 C. Ko and V. Wing-Wah Yam, *J. Mater. Chem.*, 2010, **20**, 2063.
22 K. Suzuki, T. Ubukata and Y. Yokoyama, *Chem. Commun.*, 2012, **48**, 765.
23 B. M. Neilson and C. W. Bielawski, *ACS Catal.*, 2013, **3**, 1874.
24 Q. Luo, B. Chen, M. Wang and H. Tian, *Adv. Funct. Mater.*, 2003, **13**, 233.
25 H. Tian, B. Chen, H. Y. Tu and K. Müllen, *Adv. Mater.*, 2002, **14**, 918.
26 W. Li, X. Li, Y. Xie, Y. Wu, M. Li, X. Wu, W. Zhu and H. Tian, *Sci. Rep.*, 2015, **5**, 9186.
27 W. Li, C. Jiao, X. Li, Y. Xie, K. Nakatani, H. Tian and W. Zhu, *Angew. Chem., Int. Ed.*, 2014, **53**, 4603.
28 W. Zhu, L. Song, Y. Yang and H. Tian, *Chem. -Eur. J.*, 2012, **18**, 13388.
29 X. Meng, W. Zhu, Q. Zhang, Y. Feng, W. Tan and H. Tian, *J. Phys. Chem. B*, 2008, **112**, 15636.
30 S. Chen, Z. Guo, S. Zhu, W. Shi and W. Zhu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5623.
31 Y. Wu, Y. Xie, Q. Zhang, H. Tian, W. Zhu and A. D. Q. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 2090.
32 Y. Wu, S. Chen, Y. Yang, Q. Zhang, Y. Xie, H. Tian and W. Zhu, *Chem. Commun.*, 2012, **48**, 528.
33 S. Chen, Y. Yang, Y. Wu, H. Tian and W. Zhu, *J. Mater. Chem.*, 2012, **22**, 5486.
34 S. Chen, L. Chen, H. Yang, H. Tian and W. Zhu, *J. Am. Chem. Soc.*, 2012, **134**, 13596.
35 C. Bertarelli, A. Bianco, F. D'Amore, M. C. Gallazzi and G. Zerbi, *Adv. Funct. Mater.*, 2004, **14**, 357.
36 M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.*, 1995, **60**, 8305.
37 O. Galangau, T. Nakashima, F. Maurel and T. Kawai, *Chem. -Eur. J.*, 2015, **21**, 1.
38 A. Perrier, F. Maurel and J. Aubard, *J. Photoch. Photobio. A*, 2007 **189**, 167.
39 Y. Tatsumi, J. Kitai, W. Uchida, K. Ogata, S. Nakamura and K. Uchida, *J. Phy. Chem. A*, 2012, **116**, 10973.
40 S. Pu, C. Zheng, Z. Le, G. Liu and C. Fan, *Tetrahedron*, 2008, **64**, 2576.
41 H. Liu, S. Pu, G. Liu and B. Chen, *Dyes Pigm*., 2014, **102**, 159.
42 F. Gillanders, L. Giordano, S. A. Diaz, T. M. Jovin and E. A. Jares-Erijman, *Photoch. Photobio. Sci.*, 2014, **13**, 603.
43 S. Fukumoto, T. Nakashima and T. Kawai, *Angew. Chem., Int. E* 2011, **50**, 1565.
44 A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648.
45 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
46 A. Lucotti, C. Bertarelli and G. Zerbi, *Chem. Phys. Lett.*, 2004, **392**, 549.
47 R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650.
48 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **10** 2999.
49 K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi and M. Irie, *Tetrahedron*, 2001, **57**, 4559.
50 K. Yuan, J. Boixel, A. Chantzis, D. Jacquemin, V. Guerchais and H. Doucet, *Chem. -Eur. J.*, 2014, **20**, 10073.
51 K. Okuno, Y. Shigeta, R. Kishi, H. Miyasaka and M. Nakano, *J. Photoch. Photobio. A*, 2012, **235**, 29.
52 A. Perrier, F. Maurel and D. Jacquemin, *Phys. Chem. Chem. Phys.* 2011, **13**, 13791.
53 M. Herder, B. M. Schmidt, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 2738.
54 Y. Jeong, D. G. Park, I. S. Lee, S. I. Yang and K. Ahn, *J. Mater. Chem.*, 2009, **19**, 97.
55 H. Liu and Y. Chen, *New J. Chem.*, 2012, **36**, 2223.
56 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803.
57 Y. Yang, Y. Xie, Q. Zhang, K. Nakatani, H. Tian and W. Zhu, *Chem. -Eur. J.*, 2012, **18**, 11685
58 W. Zhu, Y. Yang, R. Métivier, Q. Zhang, R. Guillot, Y. Xie, H. Tian and K. Nakatani, *Angew. Chem., Int. Ed.*, 2011, **50**, 10986.
59 S. L. Gilat, S. H. Kawai and J. Lehn, *Chem. -Eur. J.*, 1995, **1**, 275.
60 G. Liu, S. Pu, X. Wang, W. Liu and T. Yang, *Dyes Pigm*., 2011, **90**, 71.
61 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
62 C. Toccafondi, L. Occhi, O. Cavalleri, A. Penco, R. Castagna, A. Bianco, C. Bertarelli, D. Comoretto and M. Canepa, *J. Mater. Chem. C*, 2014, **2**, 4692.
63 H. Zhao, U. Al-Atar, T. C. S. Pace, C. Bohne and N. R. Branda, *Photoch*. *Photobio*. *A*, 2008, **200**, 74.
64 G. Jiang, S. Wang, W. Yuan, L. Jiang, Y. Song, H. Tian and D. Zhu, *Chem*. *Mater*., 2006, **18**, 235.
65 65 S. Xia, G. Liu and S. Pu, *J. Mater*. *Chem*. *C*., 2015, **3**, 4023.

Substitution effect on photochromic properties of benzo[*b*]thiophene-1,1-dioxide based diarylethenes

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Benzo[*b*]thiophene-1,1-dioxide based DAEs, BTT-1 to BTT-4, containing methyl, phenyl, formyl and triphenylamine groups at the 5,5'-position of thiophene rings are developed for taking insight into substituent effects on the absorption properties and photochromism.