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Photochromism of Thiazole-Containing Triangle Terarylenes

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Triangle terarylene derivatives based on the 4,5-diarylthiazole structure have been synthesized and their photochromic properties have been studied both in solution and in the crystalline state. The thiazolyl-substituted terarylenes displayed reversible photochromism in solution, with photocyclization quantum yields as high as 60 %, while a 4,5-dithienylthiazole derivative underwent photochromic reaction even in the single-crystal state, although a 4,5-dithiazolylthiazole (terthiazole) showed no photochromic reaction in the crystalline phase. The difference in photochromic reactivity between the 4,5-dithienylthiazole and the 4,5-dithiazolylthiazole was found by X-ray crystallographic analyses to originate from conformational differences in the crystalline state. The thermal cycloreversion activation energies in the solution phase were measured for thiazolyl-substituted terarylenes and for a corresponding terthiophene derivative. The activation energy for the transition from photogenerated closed-ring isomer to open-ring isomer increased with the number of substitutions of thiazole unit for thiophene. The lower aromatic stabilization energy of thiazole in relation to that of thiophene was considered to be responsible for the thermal stability of the closed-ring isomers of thiazolyl-substituted terarylenes.

Introduction

There is much interest in molecular switching materials that modulate a given physical property through the action of some external trigger, with the goal of the development of molecular devices.[1–3] Among these materials, considerable attention has focused on photochromic molecules,[4–7] especially on photochromic diarylethenes,[8,9] which undergo reversible photoisomerizations between pairs of bistable isomers with different absorption spectra upon irradiation at appropriate wavelengths. Photoswitching effects in diarylethenes have been extensively studied for controlling various chemical and physical properties such as fluorescence intensity and wavelength,[10–14] refractive index,[15,16] dielectric properties,[17] electronic conduction,[18,19] electrochemical response,[20,21] magnetic interactions,[22] and self-assembling behavior.[23,24] Most of these photoswitching effects are based, at least partly, on changes in the extent of π-conjugation in the diarylethenes in the course of photochromic reactions. While various types of molecular electronic devices based on π-conjugation connection pathways have been designed,[25] photon mode modulations of conjugation systems are worthy of extensive study. In this context we have recently reported on photochromic triangle terthiophene derivatives, which behave as photoswitching two-way rerouters of π-conjugation expansion.[26] These molecules include hexatriene components in their molecular structures and undergo photoinduced cyclization and cycloreversion reactions in a similar manner to diarylethenes. Tian et al. also proposed a similar very easily prepared photochromic triangle terthiophene while this work was in progress.[27] These terthiophene derivatives have thus been put forward as a novel category of photochromic molecules, the so-called “triangle terarylenes”. In terms of aromatic stabilization energies, however, the closed-ring form of triangle terthiophene seems to be less stable than that of dithienylethene because three aromatic units collapse simultaneously with the photocyclization. As in diarylethenes, the aryl group aromaticity might suppress the thermal stability of the closed-ring isomers of terarylenes.[28]

Here we describe the photochromic triangle terarylenes **1** and **2**, containing one and three thiazole substituent(s), respectively. The aromatic stabilization energy of thiazole was calculated to be 21.3 kcal mol^{-1} whereas that of thiophene was 22.4 kcal mol^{-1},[29] and the lower aromaticity of thiazole was expected to reduce the energy difference between the open- and closed-ring isomers of terarylenes, giving thermally bistable isomers. In addition to the energetic aspect mentioned above, the introduction of the thiazole group may be advantageous for the cyclization reaction because of its low steric hindrance. The diarylthiazole struc-

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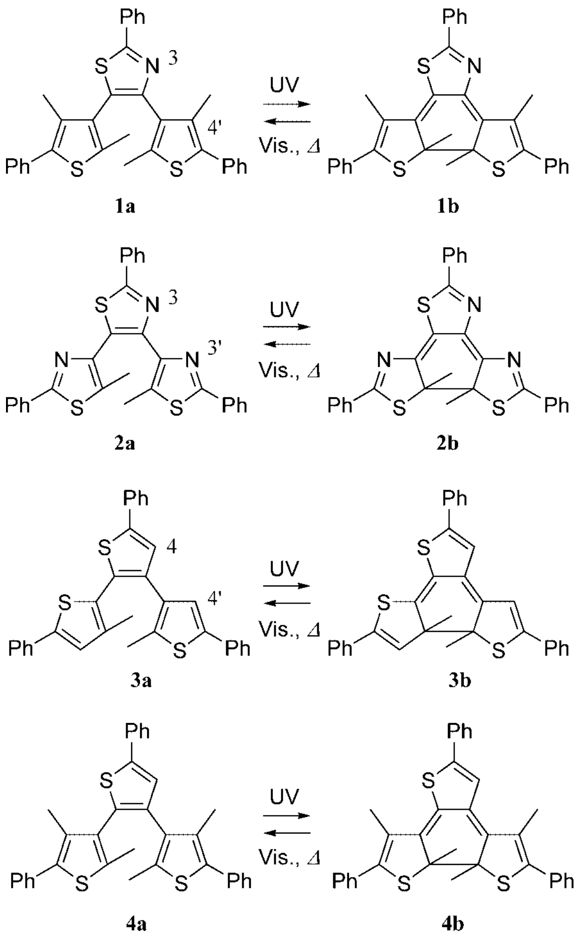
ture might offer considerable advantages, as the steric hindrance between the 3(N)- and the 4′-methyl positions in **1** and between the 3(N)- and the 3′(N)- positions in **2** (Scheme 1) should be suppressed in relation to that in the terthiophene derivatives **3**[26] and **4** [between 4-H and 4′-H (or methyl) positions]. From the perspective of the development of photofunctional molecular materials, these molecules should act as switching modules connecting the π-conjugation pathways in multiple ways. In their open-ring forms, compounds **1** and **2** each consist of three aromatic π-conjugation units. Upon photochromic reaction the three aromatic rings collapse simultaneously and the two expanded π-conjugation systems are formed: one is extended throughout the molecule and the other is extended between the central and "right-hand side" phenyl groups. Since the expansion of π-conjugating connection markedly affects the optical and electrical properties of organic molecules and polymers, these photochromic molecules might be expected to function as active materials for future molecular devices based on nonlinear optical materials and conducting polymers.



Scheme 1. Photochemical and thermal interconversion of terarylenes **1**–**4**.

In the development of photochromic hexatriene compounds, some diarylethene derivatives incorporating expanded π-conjugation systems such as quinone,[30] phenanthroline,[31] and tetraazaporphyrin[32] on the central ethene group have been proposed. Functions such as fluorescence and electrochemical activity dependent on the central π-conjugated group were modulated through photochromic reactions. These molecules also represent a stimulating possibility for the development of novel photofunctional molecular materials, but no-one has yet made detailed studies of the photochromic reactivities and thermal stabilities of the closed-ring forms of this new class of photochromic compounds. A guiding principal for designing future photofunctional molecular materials relating to the photochromic triangle terarylenes is proposed for the first time.

Results and Discussion

Compounds **1a** and **2a** were synthesized by conventional cross-coupling reactions of arylene derivatives and their chemical structures were confirmed by ^{1}H NMR, mass spectrometry, and X-ray crystallography. The ring-closed isomers **1b** and **2b** were prepared by irradiation of hexane solutions of the corresponding open-ring isomers **1a** and **2a** with UV light and were isolated from the colored solutions by reversed-phase HPLC with methanol as the eluent. The formation of the ring-closed isomers **1b** and **2b** was confirmed by ^{1}H NMR spectroscopy in $CDCl_3$ solution.[33]

Colorless solutions of the open-ring isomers **1a** and **2a** were observed to turn blue upon irradiation with UV light (λ = 313 nm), while the colored solutions were bleached by visible light irradiation ($\lambda > 400$ nm). As shown in Figure 1 (a), **1a** had no absorption band in the visible range, but a new absorption band at 610 nm appeared upon irradiation with UV light. An isosbestic point appeared at 340 nm, supporting the two-component photochromic reaction as shown in Scheme 1. The colored solution could be completely bleached upon irradiation with visible light, producing an absorption spectrum identical with that of the initial solution of **1a**, and the coloration and bleaching cycles could be repeated at least twenty times without any photodegradation. Similar photochromic behavior was also observed for **2** (Figure 1, b). The conversion ratios between **1a** and **1b** and between **2a** and **2b** at their photostationary states, achieved by irradiation with UV light (λ = 313 nm) were estimated to be 90 and 93%, respectively. The values of λ_{max} and ε in **1** and **2** are summarized in Table 1 with photochromic reaction quantum yields evaluated by the standard procedure with 1,2-bis[5-(2,4-diphenylphenyl)-2,4-dimethyl-3-thienyl]perfluorocyclopentene in hexane[16] as a standard. Relatively high quantum yields were found for compounds **1** and **2** in their cyclization reactions, the values being not less than those observed for well established diarylethenes.[8b] On the other hand, the previously reported triangle terthiophene derivative **3a** showed a low cyclization quantum yield ($\phi_{a\text{–}b}$ = 0.04).[26] Part of the enhancement in the photocyclization quantum yields may therefore presumably be attributed to the reduced steric hindrance due to the substitution of thiazole for thiophene. The trisubstituted terthiazole **2** showed a lower cyclization quantum yield than the monothiazolyl-substituted **1**, and the difference in the population ratios of the conformations in solution is presumed to be responsible for the difference in the cyclization quantum yields of **1a** and of **2a**. Briefly, as in the case of diarylethene, terarylenes may have two conformations – photochemically inactive parallel and active antiparallel[34] – and they interconvert in solution at room temperature. The photocyclization quantum yields should, in general, depend on the population ratios of the two conformations,[8b] so the lower cyclization quantum yield of dithiazolylthiazole **2** in relation to dithienylthiazole **1** might be attributable to the lower population ratio of the photochemically active conformation in solution. The crystal structure study discussed in the following paragraphs does not contradict this explanation. Meanwhile, the low photocycloreversion reaction quantum yields observed in **1b** and **2b** are characteristic of closed-ring diarylethenes with extended π-conjugation systems.[8b]

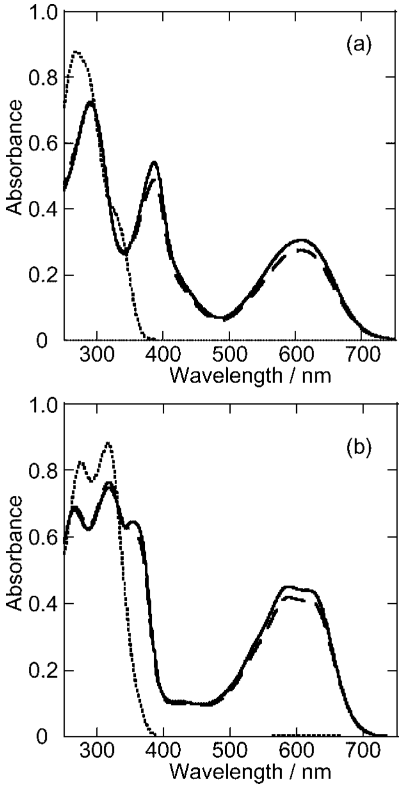


Figure 1. Absorption spectral changes of **1**(a) and **2**(b) in hexane: open-form **a** (dotted lines), closed-form **b** (solid lines) and photostationary state under irradiation with 313 nm light (dashed lines). The concentrations of **1** and **2** were 2.5×10^{-5} and 2.9×10^{-5} M, respectively.

Table 1. Absorption maxima and coefficients of the open- and closed-ring isomers of **1** and **2**, together with the quantum yields in hexane.

	λ_{max} [nm] ε [10^4 M^{-1}cm^{-1}]	ϕ_{a-b}	ϕ_{b-a}
1a	269 (3.5)	0.6	–
1b	610 (0.94)	–	0.07
2a	315 (3.0)	0.4	–
2b	587 (1.6)	–	0.03

Compounds **1a** and **2a** both formed plate-shaped colorless crystals on recrystallization from their hexane solutions. The single crystal of **1a** turned blue upon irradiation with UV light ($330 < \lambda < 385$ nm) and the blue color disappeared upon irradiation with visible light ($\lambda > 500$ nm) (Figure 2). In the absence of light, the coloration of the single crystal was maintained for days at room temperature. Terarylene **1** is thus one of the few examples[35] – with the exception of diarylethenes based on hexafluorocyclopentene[36] – of a compound that will undergo thermally irreversible and photochemically reversible photochromic reactions in the crystalline phase. Under a polarized microscope, with the source and the detection polarizers set in parallel, the crystal was colored blue at a certain angle (0°). As shown in Figure 2(c), the peak absorption wavelength of the colored state was 640 nm, slightly longer than that observed in hexane solution. When the crystal was rotated by 90° under the microscope, the blue color was bleached and the optical density decreased. The changes in optical density seen on rotating the crystal sample indicate that the closed-ring isomers are macroscopically oriented in the crystal and that the photochromic reaction takes place in the crystal lattice. No spectral shift was observed in the absorption band of the colored state even when the coloration and bleaching cycles in the single crystal were repeated many times.

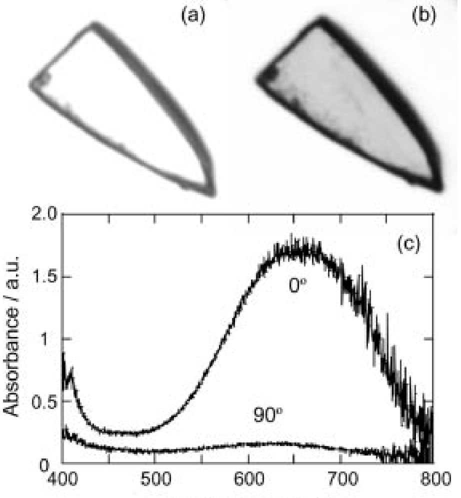


Figure 2. Photographs of crystal **1** before (a) and after (b) irradiation with UV light. c) Polarized absorption spectra of the photogenerated blue crystal of **1**.

Unlike **1a**, compound **2a** showed no photochromic performance in the crystalline phase. To investigate the difference in photochromic reactivity between 4,5-dithienylthiazole **1a** and ter-thiazole **2a**, we then performed X-ray crystallographic analyses.[37] The ORTEP drawing of **1a** indicates two different conformations packed alternately in the crystal, as shown in Figure 3(a). The two structures are quite similar: the distances between the reacting carbon atoms – C11–C23 and C44–C56 in Figure 3 (a), for example – were evaluated to be 0.364 nm and 0.366 nm, respectively. Both of them are very close and short enough for the photochromic ring-cyclization reaction.[38,39] The two conformations each have a central hexatriene moiety with a quasi-C_2 symmetric structure, which is favorable for the photochromic reaction with a contrarotational cyclization mechanism.[34] Although we do not have further evidence, it is speculated that the two conformations should have similar photochromic reactivity. Kobatake et al. have reported that the diarylethene derivatives possessing C–C distances shorter than 0.4 nm between the reacting carbon atoms show similar photochromic reactivity in the single-crystal state.[39]

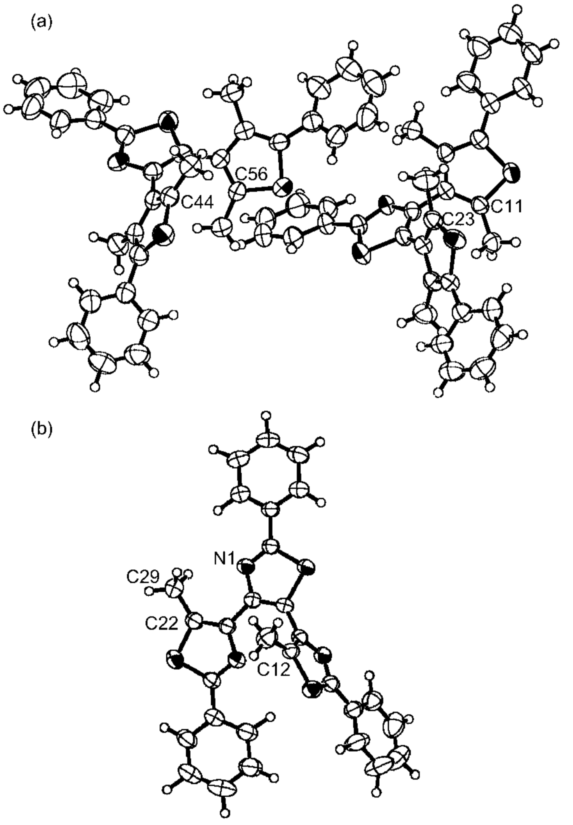


Figure 3. ORTEP drawings of open-ring isomer in crystal **1a** (a) and in crystal **2a** (b), showing 50% probability displacement ellipsoids. Two different alternately packed conformations existed for **1a** in the single-crystalline phase.

On the other hand, as shown in Figure 3 (b), the packed structure of **2a** is very different from that of **1a**. The distance between the two carbon atoms C12 and C22 is evaluated as 0.492 nm, which might be too long for the photocyclization reaction.[39] This specific conformation may be stabilized by the weak CH/N hydrogen bonding interaction between N1 and C29-H.[40] The distance between N1 and C29-H was estimated to be 0.257 nm, which is appreciably shorter than the sum of the van der Waals radii of (C–)H (0.155 nm) and N (0.12 nm). A similar interaction may stabilize and enrich the photoinactive conformation even in solution, resulting in a lower photocyclization quantum yield in solution for **2a** (0.4) than for **1a** (0.6).

In order to investigate the effect of thiazolyl substitution on the thermal stability of the closed-ring isomers **1b** and **2b**, the thermal cycloreversion kinetics of **1b** and **2b** were examined at various temperatures. Toluene was used as solvent in these measurements in order to avoid changes in concentration caused by the evaporation of solvent upon heating. The corresponding terthiophene derivative **4** was also used as a reference. The absorption spectrum of the colored state was measured at elevated temperature and the bleaching of the visible absorption band was monitored over several hours. All spectra were recorded at the elevated temperature and absorbance change (A/A_0) is plotted logarithmically as a function of time. Figure 4 shows the decay lines of the absorbance of the ring-closed isomers at several temperatures. The decay lines followed first-order kinetics. In these experiments, the thermal fading due to the decomposition of the colored isomer was negligible, because the absorption spectra of the thermally bleached solutions after photocoloration/thermal bleaching cycles remained the same in shape and intensity as the initial spectra of the ring-open isomers. The thermal bleaching of the visible absorption band is thus attributed only to the thermal cycloreversion to the open-ring isomer.

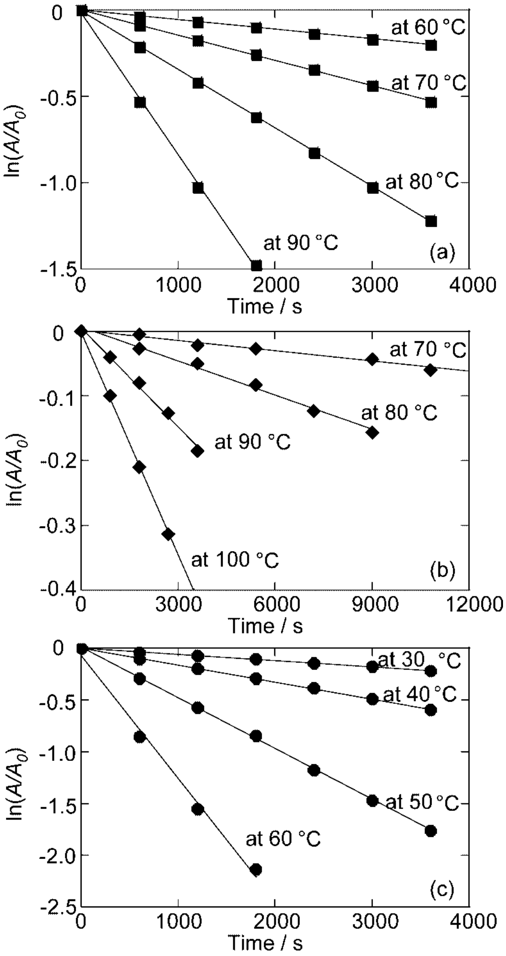


Figure 4. Decay lines of peak absorbance by thermal cycloreversion reactions of **1b** (a), **2b** (b), and **4b** (c) at various temperatures in toluene.

The first-order thermal cycloreversion reaction rate constants (k) at various temperatures were evaluated from Figure 4 and their temperature dependences are illustrated in Figure 5. The activation energy (E_a) and frequency factor (A) of the thermal cycloreversion reaction of each compound are estimated from the linear regression lines and are summarized in Table 2. The values of E_a increased in a manner depending on the number of substituted thiazole rings, giving the order of thermal bleaching rate of **2b** < **1b** < **4b**. Extrapolation of the temperature dependence indicates that the half-lifetimes of the closed-ring isomer at 20 °C are 11 h, 14 d, and 3.3 years for **4b**, **1b**, and **2b**, respectively. This result strongly suggests that the thermal stabilities of the ring-closed isomers could be controlled, like those of dithiazolylethenes,[41,42] through the aromatic stabilization energies of the aryl groups that make up photochromic terarylenes.

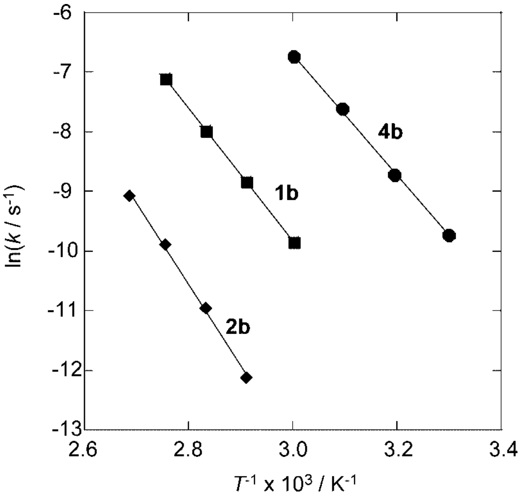


Figure 5. Temperature dependence of the thermal fading rates of **1b**, **2b**, and **4b** in toluene.

Table 2. Arrhenius parameters of thermal cycloreversion and half-lifetimes from the closed- to the open- ring isomers in toluene.

	E_a [kJ mol^{-1}]	A [s^{-1}]	$t_{1/2}$ (20 °C)
1b	92	1.6×10^{10}	14 d
2b	112	7.1×10^{11}	3.3 years
4b	84	2.0×10^{10}	11 h

Conclusions

We have designed and synthesized triangle terarylenes with the substitution of one or three thiazole groups as aryl units. The thiazole-containing compounds **1** and **2** show relatively high photocyclization quantum yields, comparable with those seen in the well established diarylethenes. Interestingly, the monothiazolyl-substituted terarylene **1** exhibited reversible photochromism even in the crystalline phase, whereas terthiazole **2** did not. This difference was explained in terms of conformational differences in the crystalline phase as revealed by X-ray crystallographic analyses. The thermal stabilities of the ring-closed isomers were greatly enhanced by the introduction of the thiazole group, which possesses a smaller aromatic stabilization energy than that of thiophene. Monothiazolyl-substituted **1** and trisubstituted **2** had half-lifetimes 30 times and 2600 times longer, respectively, than that of trithiophene-substituted **4**. We expect these thermal stable terarylene derivatives to play a considerable roll in photoswitched molecular devices.

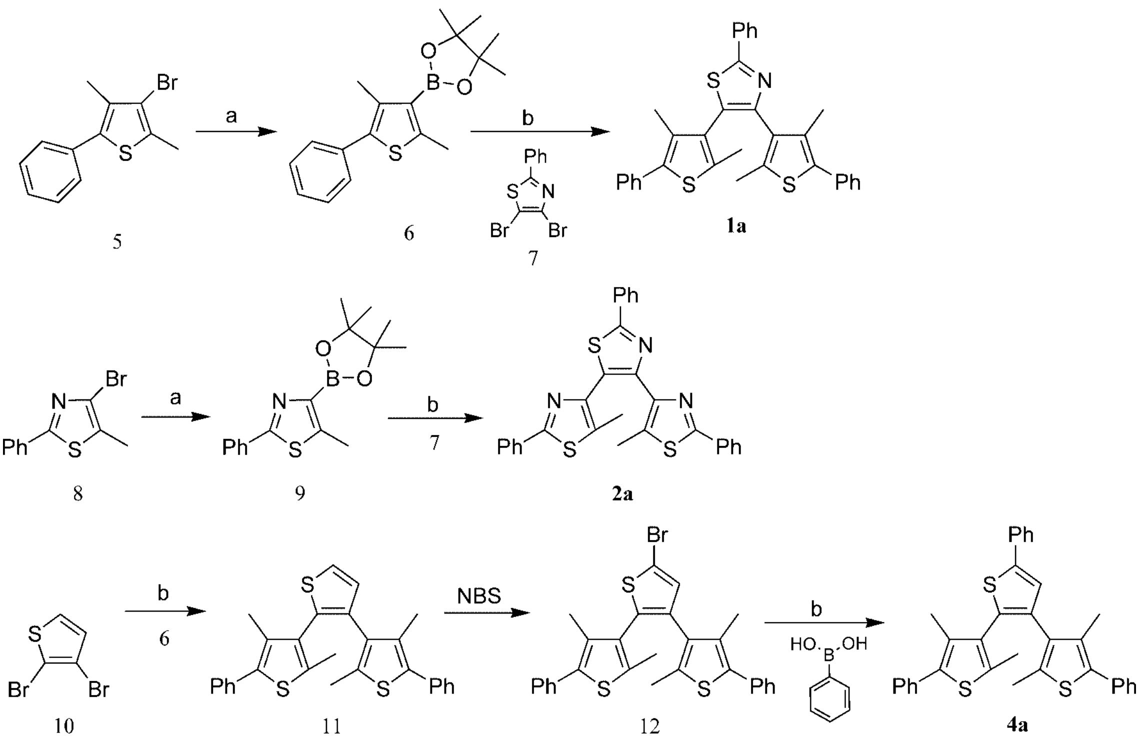
Experimental Section

General: ^{1}H NMR spectra were recorded on a JEOL AL-300 spectrometer (300 MHz). Separative HPLC was performed on a HITACHI LaChrom ELITE HPLC system and a JASCO LC-2000 Plus Series. Mass spectra were measured with a JEOL JMS-T100LC AccuTOF mass spectrometer. Absorption spectra in solution were studied with JASCO V-550 and V-670 spectrophotometers with a temperature control unit. Photoirradiation was carried out with an USHIO 500-W ultra-high-pressure mercury lamp or a Panasonic Aicure UV curing system (LED, λ = 365 nm) as the exciting light source. Monochromic light was obtained by passing the light through a monochromator (Shimadzu SPG-120S, 120 mm, f = 3.5). Absorption spectra in the single-crystal phase were measured with an Olympus BX-51 polarizing microscope connected to a Hamamatsu PMA-11 photodetector through an optical fiber. Polarizer and analyzer were set in parallel to each other. X-ray crystallographic analyses were carried out with a Rigaku R-AXIS RAPID/s Imaging Plate diffractometer with Mo-K_α radiation at 296 K.

2-(2,4-Dimethyl-5-phenylthiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6): *n*BuLi (1.6 M in hexane, 5.6 mL, 9.0 mmol) was added slowly under Ar at –78 °C to a solution of 3-bromo-2,4-dimethyl-5-phenylthiophene (**5**, 2.1 g, 8.2 mmol) in dry THF (60 mL), and the mixture was stirred for 1 h at that temperature (Scheme 2). 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 mL, 9.9 mmol) was then added in a dropwise fashion and the system was stirred for another 1 h. The reaction mixture was allowed to warm to room temperature. Methanol was added to the reaction mixture, which was extracted with ethyl acetate. The combined organic fraction was washed with water, dried with anhydrous magnesium sulfate, and concentrated to give 2.7 g (99%) of **6** as colorless powder. The obtained powder was used without further purification.

4,5-Bis(2,4-dimethyl-5-phenylthiophen-3-yl)-2-phenylthiazole (1a): A 100 mL four-necked flask was charged with **6** (1.9 g, 5.9 mmol), 4,5-dibromo-2-phenylthiazole (**7**,[43] 0.9 g, 2.8 mmol), triphenylphosphane (0.10 g, 0.38 mmol), Pd(PPh$_3$)$_4$ (0.15 g, 0.13 mmol), and K$_3$PO$_4$ (2 M) in water/1,4-dioxane (10 mL/70 mL) solution. The mixture was then stirred at 110 °C under N$_2$. After having been stirred for three days the reaction mixture was extracted with ethyl acetate and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/ethyl acetate 19:1) and reversed phase HPLC (methanol) afforded **1a** (0.18 g, 12%) as a colorless solid. ^{1}H NMR (300 MHz, CDCl$_3$/TMS): δ = 2.08 (s, 3 H), 2.13 (s, 3 H), 2.15 (s, 3 H), 2.20 (s, 3 H), 7.28–7.49 (m, 15 H) ppm. ESI HRMS (m/z) [M + H]$^+$ calcd. for $C_{33}H_{28}NS_3^+$: 534.1378; found: 534.1304.

5-Methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thiazole (9): This compound was prepared by the same procedure as had been used as for **6**, except that **5** was replaced by **8**. From **8** (1.1 g, 4.3 mmol) in dry ether (40 mL), *n*BuLi (1.6 M in hexane, 3.0 mL, 4.9 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-di-



Scheme 2. Synthesis of photochromic terarylenes **1a**, **2a**, and **4a**. Conditions: a; 1) *n*BuLi, 2) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. b; K_3PO_4, $Pd(PPh_3)_4/H_2O$, 1,4-dioxane.

oxaborolane (1.5 mL, 9.9 mmol), **9** (1.3 g, 97%) was obtained as a colorless powder.

4,5-Bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole (2a): This compound was prepared by the same procedure as had been used as for **1a**, except that **6** was replaced by **9**. From **9** (1.3 g, 4.1 mmol), **7** (0.53 g, 1.7 mmol), triphenylphosphane (0.075 g, 0.30 mmol), $Pd(PPh_3)_4$ (0.075 g, 0.13 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (15 mL/15 mL) solution, **2a** (50 mg, 6%) was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 2.11 (s, 3 H), 2.52 (s, 3 H), 7.33 (m, 3 H), 7.43 (m, 6 H), 7.80 (m, 2 H), 7.93 (m, 2 H), 8.07 (m, 2 H) ppm. ESI HRMS (*m*/*z*) [M + H]$^+$ calcd. for $C_{29}H_{22}N_3S_3^+$, 508.0970; found: 508.0974.

2,3-Bis(2,4-dimethyl-5-phenylthiophen-3-yl)thiophene (11): This compound was prepared by the same procedure as had been used as for **1a**, except that **7** was replaced by **10**. From **4** (2.0 g, 6.3 mmol), **10** (0.65 g, 2.7 mmol), triphenylphosphane (0.10 g, 0.38 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (10 mL/40 mL) solution, **11** (0.42 g, 34%) was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.93 (s, 3 H), 1.98 (s, 3 H), 2.06 (s, 3 H), 2.10 (s, 3 H), 2.15 (s, 3 H), 2.28 (s, 3 H), 7.31 (m, 4 H), 7.43 (m, 8 H) ppm.

2-Bromo-4,5-bis(2,4-dimethyl-5-phenylthiophen-3-yl)thiophene (12): *N*-Bromosuccinimide (0.21 g, 1.2 mmol) and a trace amount of $ZnCl_2$ were added to a solution of **11** (0.42 g, 0.92 mmol) in THF (10 mL). The mixture was stirred at room temperature for 2 d and then extracted with ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue (0.47 g, 95%) was used without further purification.

2,3-Bis(2,4-dimethyl-5-phenylthiophen-3-yl)-5-phenylthiophene (4a): This compound was prepared by the same procedure as had been used as for **1a**, except that **6** and **7** were replaced by phenylboronic acid and **12**, respectively. From **12** (0.77 g, 1.4 mmol), phenylboronic acid (0.18 g, 1.5 mmol), triphenylphosphane (0.10 g, 0.38 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol), and K_3PO_4 (2 M) in water/1,4-dioxane (10 mL/40 mL) solution, **4a** (41 mg, 5%) was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$/TMS): δ = 1.99 (s, 3 H), 2.11 (s, 3 H), 2.15 (s, 3 H), 2.33 (s, 3 H), 7.31 (m, 3 H), 7.40 (m, 11 H), 7.66 (m, 2 H) ppm. The comformational isomer[40] of **4a** was also found by ^{1}H NMR; conformer A: δ = 2.03 (s, 3 H), 2.11 (s, 3 H), 2.15 (s, 3 H), 2.20 (s, 3 H), 7.31 (m, 3 H), 7.40 (m, 11 H), 7.66 (m, 2 H), conformer B: δ = 1.99 (s, 3 H), 2.11 (s, 3 H), 2.15 (s, 3 H), 2.33 (s, 3 H), 7.31 (m, 3 H), 7.40 (m, 11 H), 7.66 (m, 2 H) ppm, the ratio of conformer estimated from the ^{1}H NMR spectrum was 7:8. ESI HRMS (*m*/*z*) [M + H]$^+$ calcd. for $C_{34}H_{29}S_3^+$: 533.1431; found: 533.1437.

Supporting Information (see also the footnote on the first page of this article): ^{1}H NMR spectra and ESI HRMS charts of **1a**, **2a** and **3a**.

Acknowledgments

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[33] ^{1}H NMR spectroscopic data for **1b**: (300 MHz, $CDCl_3$/TMS): δ = 2.12 (s, 3 H), 2.29 (s, 3 H), 2.31 (s, 3 H), 2.41 (s, 3 H), 7.32–7.48 (m, 15 H) ppm; for **2b**: (300 MHz, $CDCl_3$/TMS): δ = 2.10 (s, 3 H), 2.12 (s, 3 H), 7.50 (m, 9 H), 7.92 (m, 2 H), 8.05 (m, 4 H) ppm.

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[37] Crystallographic data for **1a**: $C_{33}H_{27}NS_3$, a = 11.156(4), b = 12.220(5), c = 20.683(9) Å, α = 84.218(15), β = 85.607(13), γ = 9.841(13)°, triclinic, space group P-1, Z = 4, V = 2756.5(19) Å^3, $\rho_{\text{calcd.}}$ = 1.286 g cm^{-3}. Of 27074 reflections up to 2θ = 55.0°, 12 410 were independent (R_{int} = 0.064) and 5208 with $I > 2\sigma(I)$. The structure was solved by direct methods and refined with full-matrix against all F^2 data. Hydrogen atoms were calculated in riding positions. wR = 0.1016, R = 0.064; for **2a**: $C_{29}H_{21}N_3S_3$, a = 9.486(4), b = 11.994(5), c = 12.546(6) Å, α = 113.333(17), β = 102.908(15), γ = 95.732(15)°, triclinic, space group P-1, Z = 2, V = 1249.0(9) Å^3, $\rho_{\text{calcd.}}$ = 1.350 g cm^{-3}. Of 12405 reflections up to 2θ = 55.0°, 5674 were independent (R_{int} = 0.023) and 3604 with $I > 2\sigma(I)$. The structure was solved and refined in an analogous manner to **1a**. wR = 0.1943, R = 0.057. CCDC-621390 (for **1a**) and -621391 (for **2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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