Photochromic properties of terarylene derivatives having a π-conjugation unit on central aromatic ring†

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A series of terarylenes based on 4,5-bisbenzothienylthiazole have been synthesized, and their photochromic properties are studied both in solution and in the crystalline state. The substitution effect of the central aromatic ring on the photochromic reactivity were also studied. The introduction and expansion of the π-conjugated system at the 2-position of the thiazole ring led to a red-shift of the absorption peaks for both open- and closed-ring isomers of terarylenes. 2-Hydro and 2-phenyl derivatives of 4,5-bisbenzothienylthiazoles displayed a photochromic reaction, even in the single-crystal state. X-Ray crystal analysis showed their molecular structure to have quasi-C_2 symmetry, suggesting significant CH···N and CH···S interactions. Although the 2-hydro and 2-phenyl derivatives exhibited high photocyclization reaction quantum yields over 0.5, the 2-phenylthienyl derivative showed a considerably smaller reactivity, even though it is supposed to have a similar conformation to those of the other two derivatives. Meanwhile, these molecules showed similar photocycloreversion quantum yields as high as 0.3. The relationship between their electronic structures and photochromic reactivity is also discussed by means of quantum chemical calculations.

Introduction

There has been much interest in molecular switching materials that modulate physical and chemical properties by some external stimulus from the viewpoint of developing molecular devices.[1–3] Among these materials, considerable attention has been focused on photochromic molecules, especially on photochromic diarylethenes,[4–8] which undergo reversible photoisomerization 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,[9–13] refractive index,[14,15] dielectric properties,[16] electronic conduction,[17,18] electrochemical response,[19,20] and magnetic interactions.[21] Most of these photoswitching effects are based, at least partly, on changes in the extent of π-conjugation in diarylethenes during the course of photochromic reactions. Various types of molecular electronic devices based on π-conjugation connection pathways have been designed,[22] and photon mode modulations of conjugation systems are still worthy of extensive study. In this context, we have recently proposed a new class of the hexatriene-type photochromic molecules composed of three aromatic rings in a triangular shape, so-called "terarylenes", that undergo photoinduced cyclization and cycloreversion reactions in a similar manner to diarylethenes and fulgide.[23–25] While most diarylethenes show on–off switching of the π-conjugation, terarylenes can extend their π-conjugation in multiple ways and behave as photoswitching re-routers of π-conjugation pathways.[26] The photochromic reactivity of terarylenes, both in solution and in the crystalline state, and the thermal stability of their closed-ring isomers can be systematically modulated by means of varying the aromatic units making up the terarylenes and also the substituents on the side aromatic rings connected to the central aryl unit.[23a,b] However, the effect of substituents at the central aryl unit on its photochromic properties has never been studied, even though the most fascinating advantage that differentiates terarylenes from conventional diarylethenes relies on its functionalization.[23c,d] The introduction and expansion of the π-conjugation system in the side aryl units for diarylethenes have been extensively studied, leading to a considerable decrease in their photocycloreversion quantum yields.[27,28]

In this study, the effect of the introduction and expansion of the π-conjugation system at the central aryl unit of terarylenes on their photochemical properties has been systematically investigated for a series of 2-substituted-4,5-bisbenzothienylthiazoles. The introduction of the benzothiophene unit into the molecular structure of diarylethenes is known to enhance their fatigue resistivity[29,30] because of their high oxidation potentials, giving relatively high photocycloreversion quantum yields.[31] The central thiazole unit is also expected to improve the chemical stability against oxidation, as well as photocyclization reactivity, due to the reduced steric hindrance.[23a]

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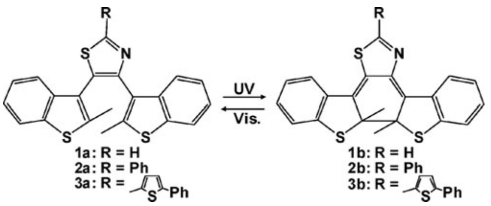
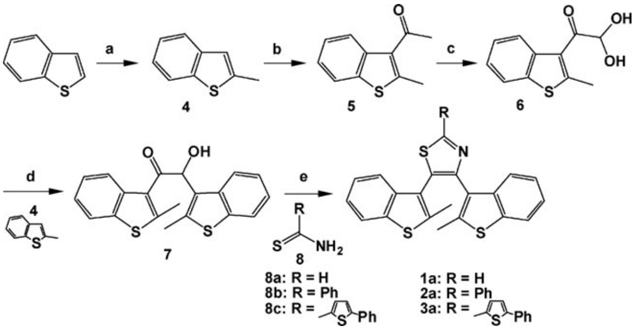
Results and discussion

A series of 2-substituted-4,5-bisbenzothienylthiazoles, **1a**, **2a** and **3a**, whose molecular structures are shown in Scheme 1, were synthesized according to Scheme 2. The thiazole ring was formed by the cyclization reactions of the corresponding α-hydroxyketones with thioamides, as reported by Krayushkin and co-workers.[25] Their chemical structures were confirmed by ^{1}H NMR, mass spectrometry and/or X-ray crystallography. Each colorless solution in hexane of **1a**, **2a** and **3a** turned red upon UV light irradiation, and the colored solutions were bleached by visible light irradiation. As typical examples, Fig. 1 shows the absorption spectral changes in the photochromic reactions of **1a** and **3a**. The reversible absorption spectral change was observed at room temperature for all compounds, and the presence of isosbestic points supports the reversible two-component photochromic reaction shown in Scheme 1. The coloration and bleaching cycles could be repeated at least 20 times without marked photodegradation. Closed-ring isomers **1b**, **2b** and **3b** were prepared by irradiation of hexane solutions of the corresponding open-ring isomers **1a**, **2a** and **3a** with UV light, and were isolated from the colored solutions by normal-phase HPLC with hexane/ethyl acetate as the eluent or reversed-phase HPLC with acetonitrile as the eluent. The conversion ratios between **1a** and **1b**, and between **3a** and **3b**, at their photostationary states, achieved by irradiation with UV light (λ = 313 nm), were estimated to be 54 and 32%, respectively. The values of $\lambda_{\max}$ and molecular extinction coefficient ε of each compound are summarized in Table 1 with the photochromic reaction quantum yields, which were evaluated by a standard procedure using 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene in hexane[29,31] as a standard. The absorption peak positions for both bleached and colored states showed a clear relationship with the substituent at 2-position of the central thiazole ring. The expansion of the π-conjugation system of the central unit led to a red-shift of the absorbance peak. Relatively high photochemical cyclization quantum yields, as high as 50%, were found for **1a** and **2a**. On the other hand, **3a**, having a 2-phenylthienyl thiazole unit, showed a considerably lower cyclization quantum yield than those of the **1a** and 2-phenyl-substituted **2a**. Similar to diarylethenes, the photocyclization quantum yield of terarylenes is expected to show a considerable dependence on the conformation of their open-ring isomer in the ground state.[23a] Compounds **1**, **2** and **3** are expected to have a similar conformation around the reaction center because the photoreactive hexatriene structure for each molecule is composed of same aromatic unit. Consequently, the low quantum yield of **3a** might be attributable to its electronic structure, derived from its expanded π-electron system. The fact that compound **3** shows fluorescence emission with a quantum yield of 7.8% may also decrease the



Scheme 1 The photochromic reactions of terarylenes **1–3**.



Scheme 2 The syntheses of photochromic terarylenes **1a**, **2a** and **3a**. Conditions a: (i) nBuLi, (ii) iodomethane; b: AcCl, AlCl$_3$; c: SeO$_2$/H$_2$O, 1,4-dioxane; d: SnCl$_4$/toluene; e: TFA.

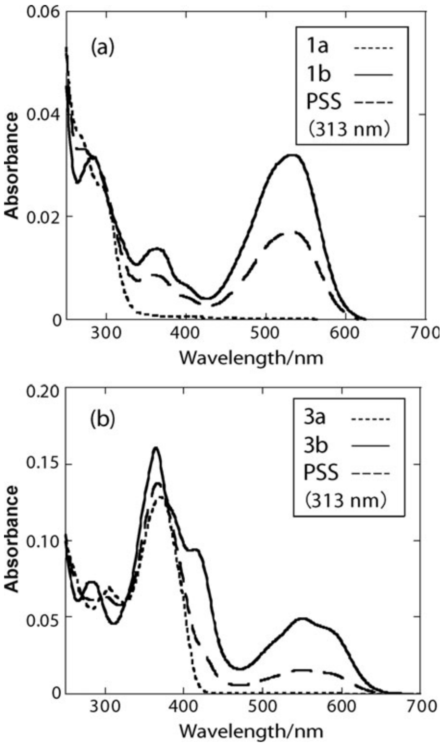


Fig. 1 Absorption spectral changes of (a) **1** and (b) **3** in hexane: open-form **a** (· · ·), closed-form **b** (—) and photostationary state under irradiation with 313 nm light (--). The concentrations of **1** and **3** were 2.9 × 10^{-6} and 4.9 × 10^{-6} M, respectively.

Table 1 Absorption maxima and molecular extinction coefficients of the open- and closed-ring isomers of **1**, **2** and **3**, together with their quantum yields in hexane

	$\lambda_{\max}$/nm (ε/10^4 M^{-1} cm^{-1})	$\lambda_{\max}$/nm (calc.)	$\phi_{a\to b}$	$\phi_{b\to a}$
1a	295 (1.1)	325.6	0.56	—
1b	534 (1.4)	564.4	—	0.30
2a	329 (1.3)	369.5	0.58	—
2b	539 (1.2), 556 (1.2)	601.8	—	0.45
3a	370 (2.6)	404.2	0.078	—
3b	550 (1.0), 590 (0.82)	654.5	—	0.29

photochemical reaction quantum yield. On the other hand, the cycloreversion quantum yield showed no systematic decrease upon expanding the π-conjugation system, which is specifically different from the case of the cycloreversion reactivity of diarylethenes.[27]

Interestingly, compounds **1a** and **2a** showed photochromic coloration and bleaching reactions, even in their crystalline states, whereas the corresponding diarylethene, 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene, doesn't exhibit photochromism in its crystalline state. Fig. 2 shows the photoinduced coloration and bleaching behavior of a single-crystal of **1a** under a polarizing microscope. Under this polarizing microscope, the source and detection polarizers were set in parallel, and the crystal was colored in red at a certain polarization angle (0°) and was colorless with the rotation angle of the polarizer set at 90°. The peak absorption wavelength of the colored state was observed at 550 nm, as shown in Fig. 3. This wavelength was slightly longer than that in hexane solution (534 nm). When the polarizer was rotated by 90° under the microscope, the red color weaken and the optical density decreased, as also shown in Fig. 3. The changes in optical density seen upon rotating the polarizer indicate that the closed-ring isomers are partially oriented in one direction in the crystal and that the photochromic reaction takes place in the crystal lattice. As shown in Fig. 4, the ORTEP drawing of **1a** indicates two different conformations that are packed alternately in the crystal.[32] These two structures are quite similar, and the distances between the reacting carbon atoms, C5···C14 and C26···C35 in Fig. 4, for example, were evaluated to be 0.358 and 0.369 nm, respectively. Both distances are short enough for the photochromic ring cyclization reaction to take place in a topochemical manner.[33,34] Each conformation has a central hexatriene moiety with a quasi-C_2 symmetric structure, which is favorable for the photochromic cyclization reaction with a contra-rotatory mechanism.[35] We thus expect that both conformers will have similar photochromic reactivities. Kobatake *et al.* have reported that diarylethene derivatives possessing a distance between the reacting carbon atoms shorter than 0.4 nm should show a similar photochromic reactivity in the single-crystal state.[34] The distances between the sulfur atoms in the thiazole rings and the 4-H positions in the benzothienyl units of the two conformers, S1···H5 and S4···H20, were estimated to be 0.277 and 0.295 nm, respectively, which are appreciably shorter than the sum of the van der Waals radii of S (0.185 nm) and H (0.120 nm). Similarly, the distances between the nitrogen atoms in the thiazole rings and the 4-H′ positions in the benzothienyl units of the two conformers, N1···H12 and N2···H27, are estimated to be 0.264 and 0.254 nm, respectively. These distances are again shorter than the sum of the van der Waals radii of N (0.150 nm) and H (0.120 nm). The specific photoactive antiparallel-type conformation of compound **1a** would be stabilized by these weak hydrogen bonding interactions, resulting in the reversible photochromic reactivity of **1a** in the crystalline state, unlike the corresponding diarylethene. Similar structural features were also observed in the results of the X-ray crystallographic analysis of compound **2a**, which will be reported elsewhere.[36]

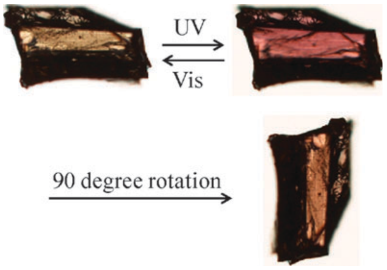


Fig. 2 Photographs of single-crystal **1a** with light irradiation and rotation.

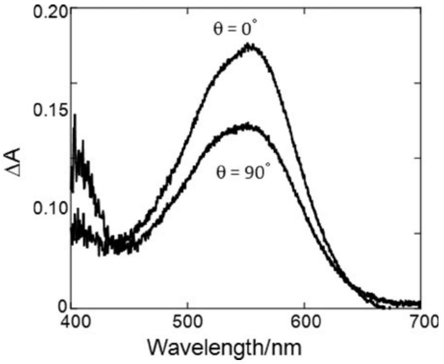


Fig. 3 Polarized absorption spectra of the photogenerated colored crystal of **1a**.

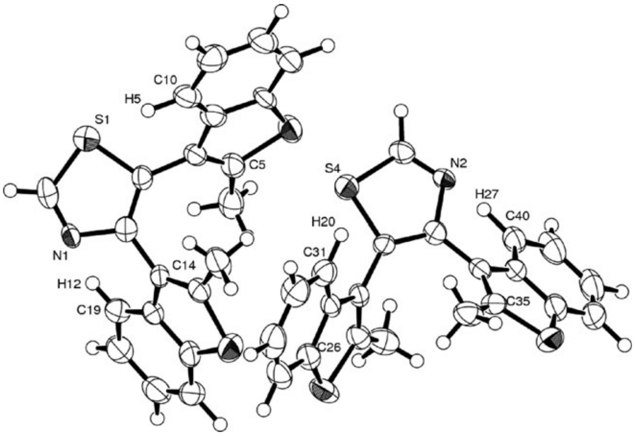


Fig. 4 An ORTEP drawing, showing 50% probability displacement ellipsoids, of open-ring isomer **1a** in the crystal. Two different alternately-packed conformations exist for **1a** in the single-crystalline phase.

We further investigated the electronic structures of **1a** and **3a**, and **1b** and **3b** using time dependent density functional theory (TDDFT)[37] calculations at the B3LYP/6-311G^{++}*[38] level. These calculated absorption peaks are summarized in Table 1. Characteristic red-shifts in the absorption band of both open- and closed-ring isomers were reproduced with the expansion of the π-conjugated system. Fig. 5 shows the spatial profile of the most stable structure, and selected frontier molecular orbitals of **1** and **3** in their open- and the closed-ring forms. The most stable structure of **1a** was calculated to be in good agreement with the result of our X-ray crystallographic analysis. Both the HOMO and LUMO of **1a** expand

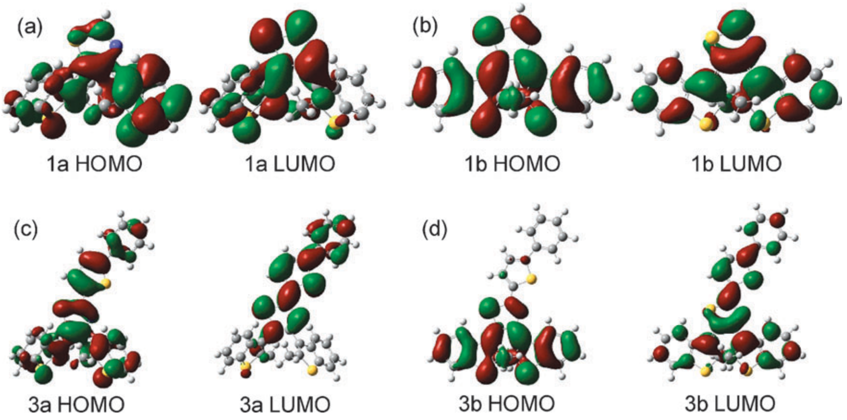


Fig. 5 Spatial plots of selected TDDFT frontier molecular orbitals of (a) **1a**, (b) **1b**, (c) **3a** and (d) **3b**.

over the whole molecule, and both carbon atoms of the photochemical reaction centers contribute considerably to these frontier orbitals. On the other hand, the frontier LUMO of **3a** is rather localized on the phenylthienyl moiety, and the contribution of these two reactive carbon atoms seems to be considerably small. This excited state nature of **3a** might be responsible for the decreased photochemical quantum yields of the cyclization reaction of **3a** to **3b**, regardless of its photochromic reactive quasi-C_2 symmetry conformation. Meanwhile, the HOMO and LUMO around the 1,2-cyclohexadiene moieties of both **1b** and **3b** are almost identical and moderately distributed across the reactive center, which may result in their similarly high photocycloreversion quantum yields. The spatial overlap of the HOMO and LUMO of **1b** is considerably larger than that of **3b**, and this confined nature of **1b** may be responsible for its larger extinction coefficient than that of **3b**.

Conclusions

We have designed and synthesized new terarylene derivatives based on 4,5-bisbenzothienylthiazole and studied the effect of expanding their π-conjugation system at the 2-position of the thiazole ring. The wavelength of their optical absorption peaks shift to longer wavelengths by introducing the π-conjugation unit. Compound **3a**, having phenylthienyl units, showed a significantly lower photocyclization quantum yield than those of **1a** and **2a**, whereas the photocycloreversion quantum yield was comparable. Terarylene derivatives **1** and **2** exhibited reversible photochromism in the crystalline phase, whereas the corresponding diarylethene does not. The difference in the photochromic reactivity in the crystalline state was attributed to the specific interactions between the heteroatoms of the central thiazole unit and the 4-H hydrogen atoms of both sides of the benzothiophene units, stabilizing the photoreactive antiparallel conformation in the crystalline state. Quantum chemical calculations explained the decrease of the photocyclization quantum yield and unchanged photocycloreversion reactivity of **3** with its expanded π-system. The authors believe the present study provides a guiding principle for designing future photoswitching molecules, accompanied by expanded π-electron systems for controlling their nature.

Experimental section

General

Organic chemicals were purchased from Nacalai, Wako and TCI, and were used as received. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a JEOL AL-300 spectrometer. Mass spectra were measured using a JEOL JMS-T100LC AccuTOF mass spectrometer. Purification by high-performance liquid chromatography (HPLC) and gel permeation chromatography (GPC) was performed using HPLC (JASCO PU-2080, UV-2075) and GPC (JASCO PU-2080, UV-2086) systems with appropriate columns. UV-vis absorption spectra were recorded on a JASCO V-550 spectrophotometer. An ultra-high pressure Hg lamp (500 W) and a Hg–Xe lamp (150 W) were used as light sources for steady-state measurements. Monochromic light was obtained by passing the light through a monochromator (Shimadzu SPG-120S, 120 mm, f = 3.5). Absorption spectra in the single-crystalline phase were measured using an Olympus BX-51 polarizing microscope connected to a Hamamatsu PMA-11 photodetector with an optical fiber. The polarizer and analyzer were set in parallel to each other. X-Ray crystallographic analyses were carried out using a Rigaku R-AXIS RAPID/s imaging plate diffractometer with Mo-K$_\alpha$ radiation at 296 K.

Syntheses

2-Methylbenzo[*b*]thiophene (4). A hexane solution of butyl lithium (120 ml, 1.6 M in hexane, 0.19 mol) was added to a stirred solution of benzo[*b*]thiophene (25 g, 0.19 mol) in dry THF (150 ml) at −78 °C under a nitrogen atmosphere. After 30 min, MeI (12 ml, 0.19 mol) was added and the mixture allowed to warm up to room temperature. After 4 h, the reaction mixture was quenched by adding water, followed by extraction with diethyl ether. The organic layer was washed with a saturated NaCl solution, dried with anhydrous $MgSO_4$ and the drying agent filtered off. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel using hexane as the eluent to give **4** (27 g, 97%). ^{1}H NMR (300 MHz, acetone-d_6): δ 2.56 (3H, s), 7.06 (1H, s), 7.21–7.32 (2H, m), 7.67–7.69 (1H, d) and 7.78–7.81 (1H, d).

1-(2-Methylbenzo[*b*]thiophen-3-yl)ethanone (5). A mixture of 2-methylbenzo[*b*]thiophene (**4**) (11 g, 73 mmol), acetyl chloride (5.5 ml, 73 mmol) and anhydrous aluminum chloride (12 g, 73 mmol) in dry DCM (200 ml) was stirred overnight. After removing the DCM, an equal amount of water and ethyl acetate was added. The organic layer was separated and washed with a saturated NaCl solution, dried with anhydrous $MgSO_4$ and the drying agent filtered off. After removing the solvent *in vacuo*, the residue was purified by column chromatography on silica gel using chloroform/hexane (30–40%) as the eluent to give **5** as a colorless solid (11 g, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.66 (3H, s), 2.79 (3H, s), 7.37 (2H, m), 7.75 (1H, d) and 8.19 (1H, d).

2,2-Dihydroxy-1-(2-methylbenzo[*b*]thiophen-3-yl)ethanone (6). To a solution of selenium dioxide (3.4 g, 30 mmol) in dioxane (25 ml) and water (1.0 ml) at 60 °C was added **5** (5.7 g, 30 mmol). The mixture was refluxed for 8 h, filtered (removal of Se) and the filtrate evaporated under reduced pressure. The oily residue thus obtained was crystallized from water. The precipitate was removed by filtration and washed with a small amount of water, affording colorless crystals of **6** (5.8 g, 87%). ^1H NMR (300 MHz, DMSO-d_6): δ 2.77 (3H, s), 5.59 (1H, t), 6.67 (2H, d), 7.38 (2H, d), 7.93 (1H, d) and 8.15 (1H, d).

2-Hydroxy-1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)ethanone (7). A solution of tin tetrachloride (0.58 ml, 5.0 mmol) in toluene (10 ml) was added drop-wise to a stirred solution of **6** (1.1 g, 5.0 mmol) and **4** (0.82 g, 5.5 mmol) in toluene (25 ml). The reaction mixture was stirred for 9 h at room temperature. The solution was then carefully poured into water (20 ml) and extracted with diethyl ether. The organic layer was separated, washed with a saturated NaCl solution, dried over $MgSO_4$ and evaporated. The crude product was used without further purification.

Thioformamide (8a). To a cooled (0–5 °C) solution of formamide (3.1 ml, 76 mmol) in 100 ml diethyl ether was added phosphorus pentasulfide (8.9 g, 19 mmol) in small portions. The reaction mixture was allowed warm to ambient temperature, stirred for 2 h, filtered and concentrated under vacuum to afford **8a** as a pungent yellow oil that was used without purification (0.8 g, 17%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.28 (1H, t), 7.98 (1H, t) and 9.46 (1H, dd).

5-Phenylthiophene-2-carbothioamide (8c). A suspension of potassium carbonate (5.5 g, 40 mmol), tetra-*n*-butylammonium bromide (5.2 g, 16 mmol) and palladium acetate (0.18 g, 0.80 mmol) in an acetonitrile/water mixture (3.7/0.4 ml) was stirred under nitrogen for 5 min. 2-Cyanothiophene (3.0 g, 32 mmol) and iodobenzene (1.8 g, 16 mmol) were then successively added, and the mixture heated at 80 °C for 5 h. After cooling to room temperature, water and diethyl ether were added, the organic phase washed with water and dried over $MgSO_4$. After removal of the solvent under vacuum, the residue was crystallized from hexane. The precipitate was removed by filtration and washed with a small amount of hexane, affording yellow crystals of 5-phenylthiophene-2-carbonitrile (1.555 g, 50%). Subsequently, to a slurry of 70% sodium hydrosulfide hydrate (1.8 g, 20 mmol) and magnesium chloride hexahydrate (2.0 g, 10 mmol) in 20 ml of DMF, was added 5-phenylthiophene-2-carbonitrile (1.6 g, 8.0 mmol) in one portion, and the mixture stirred at room temperature for 2 h. The resulting green slurry was poured into 20 ml of water, resuspended in 1N HCl, stirred for 20 min, and then filtered and washed with water to give pure **8c** (0.72 g, 41%). ^1H NMR (300 MHz, acetone-d_6): δ 7.35–7.50 (4H, m), 7.66–7.74 (3H, m) and 8.87–8.80 (2H, d)

4,5-Bis(2-methylbenzo[*b*]thiophen-3-yl)thiazole (1a). Crude **7** was added to a solution of **8a** (0.80 g, 13 mmol) in 3.0 ml of TFA, and the mixture kept for 24 h at room temperature, diluted with diethyl ether and neutralized with an aqueous solution of sodium hydroxide. The aqueous phase was extracted with diethyl ether, the extracts washed in succession with water, a 20% solution of sodium hydroxide and water again, dried over $MgSO_4$ and evaporated (yield 1.3 g, 68%). ^1H NMR (300 MHz, DMSO-d_6): δ 1.97 (s, 3H), 2.00 (s, 3H), 7.30–7.23 (m, 4H), 7.49 (br, 2H), 7.89–7.82 (m, 2H) and 9.51 (s, 1H). EI-HRMS (*m*/*z*) calc. for $C_{27}H_{19}NS_3^+$ (M^+): 378.0445; found: 378.0450. Anal. calc. for $C_{27}H_{19}NS_3$: C, 66.81; H, 4.00; N, 3.71; found: C, 66.57; H, 3.69; N, 3.76%.

4,5-Bis(2-methylbenzo[*b*]thiophen-3-yl)-2-phenylthiazole (2a). This compound was prepared by the same procedure as that used to prepare **1a** (yield 0.15 g, 6.7%). ^1H NMR (300 MHz, CD_3CN): δ 2.14 (s, 6H), 7.28–7.20 (m, 4H), 7.56–7.50 (m, 3H), 7.64–7.57 (m, 2H), 7.79–7.74 (m, 2H) and 8.09–8.05 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 14.9, 15.0, 122.6, 122.8, 122.9, 123.7, 123.8, 124.8, 125.0, 125.2, 125.6, 127.2, 128.3, 128.7, 130.1, 131.3, 134.5, 138.6, 138.7, 140.2, 140.3, 140.5, 141.3, 149.5 and 168.0. EI-HRMS (*m*/*z*) calc. for $C_{27}H_{19}NS_3^+$ (M^+): 453.0680; found: 453.0685. Anal. calc. for $C_{27}H_{19}NS_3$: C, 71.49; H, 4.22; N, 3.09; found: C, 71.36; H, 4.13; N, 3.05%.

4,5-Bis(2-methylbenzo[*b*]thiophen-3-yl)-2-(5-phenylthiophen-2-yl)thiazole (3a). This compound was prepared by the same procedure as that used to prepare **1a** (yield 0.15 g, 5.6%). ^1H NMR (300 MHz, DMSO-d_6): δ 2.04 (s, 3H), 2.06 (s, 3H), 7.39–7.27 (m, 5H), 7.48–7.43 (m, 2H), 7.68–7.61 (m, 3H), 7.78–7.76 (m, 2H) and 7.91–7.84 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.9, 15.0, 121.6, 121.9, 122.0, 122.6, 122.9, 123.7, 123.8, 124.2, 124.3, 124.6, 125.9, 126.6, 127.0, 127.6, 128.2, 129.0, 133.7, 136.3, 137.9, 138.0, 139.5, 139.6, 139.9, 140.7, 146.8, 148.3 and 161.1. EI-HRMS (*m*/*z*) calc. for $C_{31}H_{21}NS_4^+$ (M^+): 535.0557; found: 535.0560. Anal. calc. for $C_{31}H_{21}NS_4$: C, 69.50; H, 3.95; N, 2.61; found: C, 69.30; H, 4.00; N, 2.62%.

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