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Tunable Luminescence of New Photochromic Bisthienylethenes Containing Triphenylamine

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Two new photochromic 1,2-bisthienylethenes containing triphenylamine were conveniently prepared; large cyclization quantum yields and obvious fluorescent changes regulated by the photoisomerization were observed. The substitution effect on the photochromic process is discussed based on these systems.

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Introduction

Recently, there has been increasing interest in the synthesis, design, and investigation of organic photochromic material as a potential technological application for the optical recording for storage of information and optical switching.[1–4] Practical applications are also well established, such as in optical transmission or in holography. Among these photochromic molecules 1,2-bisthiophenylethenes (BTEs)[5] have become promising candidates[6–14] because these compounds combine many favourable properties, namely thermal irreversibility, high resistant fatigue, and large changes in absorption wavelength between the two isomers.[5,15,16] Moreover, the photochemical and photophysical properties of BTEs could be selectively controlled by substitution and by electronic coupling of the two switching units.[17,18] Photoregulated emission is also possible using photochromic compounds when there is a discriminating interaction between the excited state of the fluorescent dye and the ground state of one of the photochromic isomers. This interaction can be through photo-induced energy or electron-transfer processes.[19–21] By choosing a suitable combination of a fluorescent dye and a photochromic compound, complete on–off switching of fluorescence could be realized. The switching characteristics are well controlled by changing the concentration of the photochromic compound.[22] Since the ring-opened form of diarylethene has parallel and anti-parallel conformations, the balance between the two conformations limits the maximum cyclization quantum yield to 0.5,[5a] which consequently limits the switching efficiency for various potential applications. By increasing the ratio of the anti-parallel conformation by inclusion of a photochromic diarylethene in a cyclodextrin cavity, Takeshita and Choi[23] reported enhancement of the photocyclization yield. It was also reported that some bulky substituents attached to the 4- or 4′-position of the thiophene rings could increase the coloration quantum yields.[24] In addition, introduction of triphenylamine at both positions in the thiophene ring resulted in photochromic amorphous materials.[25]

It is well known that the incorporation of bulky and heavy substituents makes glass formation easier, leading to enhanced stability of the resulting amorphous glass. Triphenylamine is the substitute most often chosen for this modification.[25] The substituents introduced in the 2,2′-positions of BTEs strongly influence the distribution between the parallel (*p*) and antiparallel (*ap*) conformers (active form for electrocyclization) present in diarylethene derivatives.[26] In this paper, the substituted triphenylamines, whose the *n*-butyl substitutes can remarkably increase the solubility of the title compound, were introduced to the 5- or 5′-position of the thiophene rings to provide two new photochromic 1,2-dicyanobisthienylethenes. As might be expected, their cyclization quantum yields have been drastically improved. In addition, the different number (one or two) of fluorescent chromophores of triphenylamine anchored to the bisthienylethenes can lead to quite different reversible luminescence changes in their photochromic processes.

Results and Discussion

Compounds **1** and **2** were prepared by the reaction of boric acid **3** and 1,2-bis(5-bromo-2-methyl-3-thienyl)-1,2-dicyanoethene **4** with $Pd(PPh_3)_4$ as catalyst in THF as shown in Scheme 1. The ^1H NMR (500 MHz, $CDCl_3$) spectra of compounds **1** and **2** are shown in Fig. 1. For compound **1**, the signals of the two methyl protons at the 2- and 2′-positions of the two thiophene rings appeared at 2.09 and 2.27 ppm, respectively. The thienyl protons at the 4- and 4′-positions appeared at 7.03 and 6.78 ppm. The doublet signals at 6.95, 7.00, 7.14, and 7.20 ppm could be assigned to the phenyl

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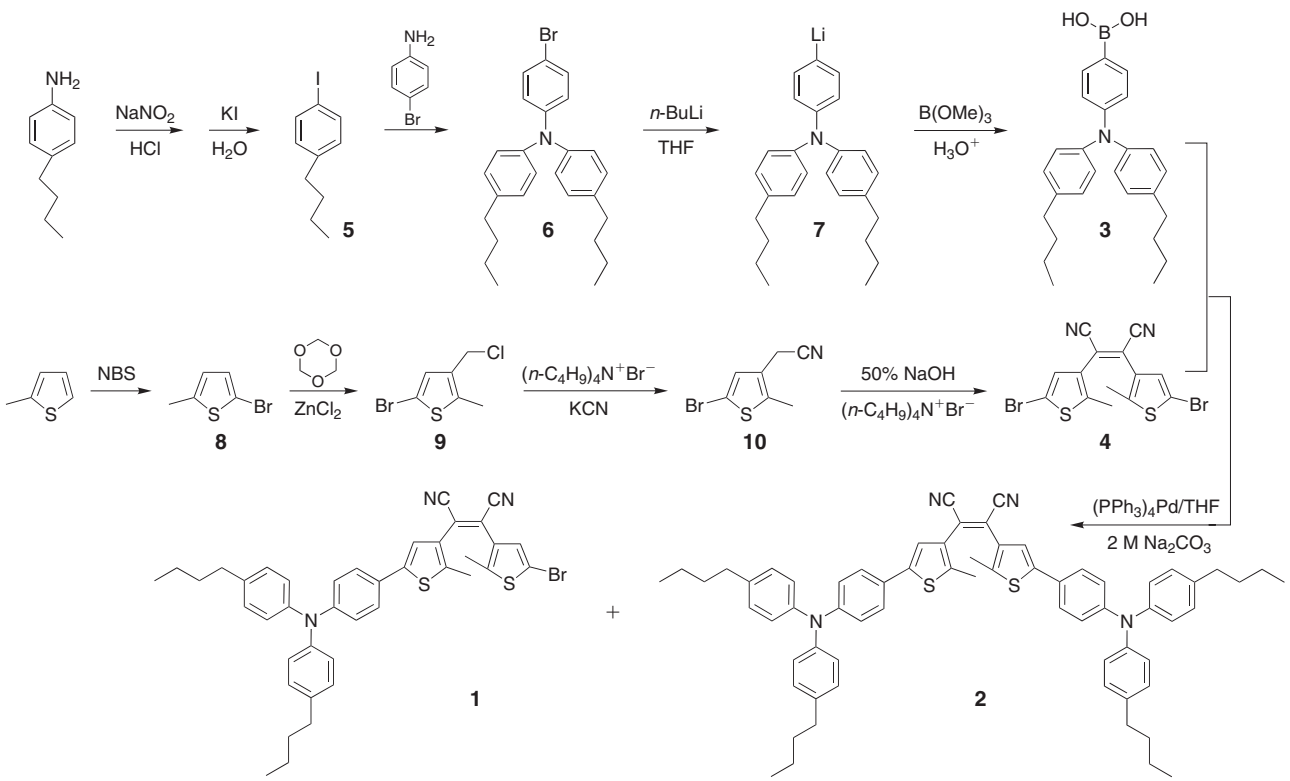


Scheme 1. The synthesis of compounds **1** and **2**.

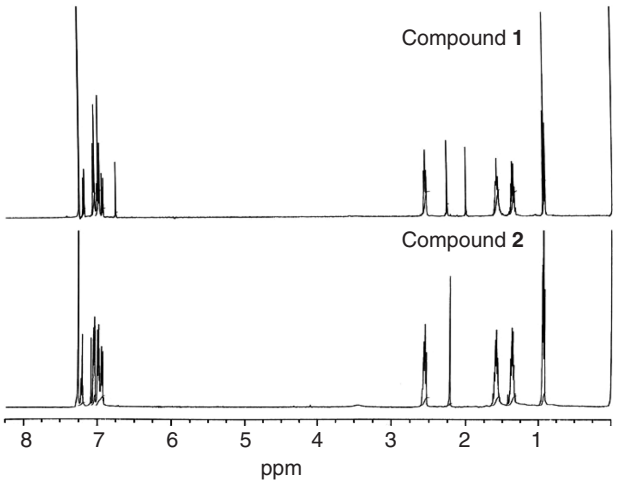


Fig. 1. The ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compounds **1** and **2**.

protons of the substituted triphenylamine. Although there are also two methyl groups in the two thiophenes of compound **2**, the symmetry of the molecule placed them in the same chemical and magnetic environment. Therefore, the methyl protons are considered chemically equivalent and appeared at 2.24 ppm, while the thienyl protons appeared at 7.09 ppm. The phenyl proton signals of the triphenylamine were observed at 6.93, 6.99, 7.05, and 7.22 ppm.

The photochromic properties of compounds **1** and **2** in CH_2Cl_2 are shown in Fig. 2. Compound **1** (open form) has the absorption bands at 304 and 358 nm. The introduction of triphenylamine groups that absorb strongly in the UV region considerably increases the extinction coefficient of the photochromic systems at the wavelength of irradiation, as shown in Fig. 2. Upon irradiation of the solution of compound **1** with 365 nm light, the absorption peaks at 304 and 358 nm gradually decreased, and a new absorption band with a maximum at around 600 nm appeared. During the photochromism there exists an isosbestic point owing to the formation of the closed form of compound **1** by photocyclization. The colour of **1** in CH_2Cl_2 changed from yellow to green. The system finally reached a photostationary state after irradiation for 160 s. Irradiation of the ring-closed isomer of **1** with 600 nm light induced a rapid ring-opening photoreaction, and the original absorption spectrum corresponding to the ring-opened form recovered (Scheme 2). Compound **2** exhibited similar photochromism to compound **1**, as shown in Fig. 2. Compound **2** (ring-opened form) has an absorption maximum at 356 nm in CH_2Cl_2. When this compound was irradiated by 365 nm light, a new absorption peak appeared at 620 nm. The absorption maximum shifts to longer wavelength by comparison with its opened form (shown in Fig. 2 and Scheme 2). Upon exposure of the closed form (green solution) to visible light (600 nm), the solution again became yellow and the initial absorption was restored. For compound **2**, the time taken to reach the chromic photostationary state was only 18 s.

The cyclization quantum yields and the coefficients of the compounds **1** and **2** were measured in CH_2Cl_2 at 25°C (shown in Table 1). As listed in Table 1, the coefficients are relatively large in the UV region, and the quantum yields are more than 40%. This may be due to the substituent effect at the

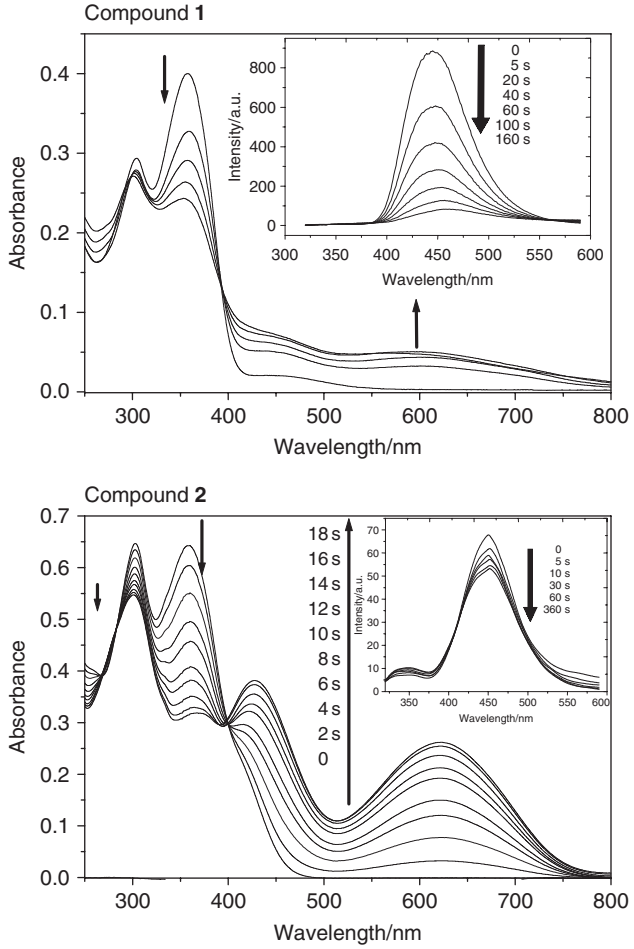
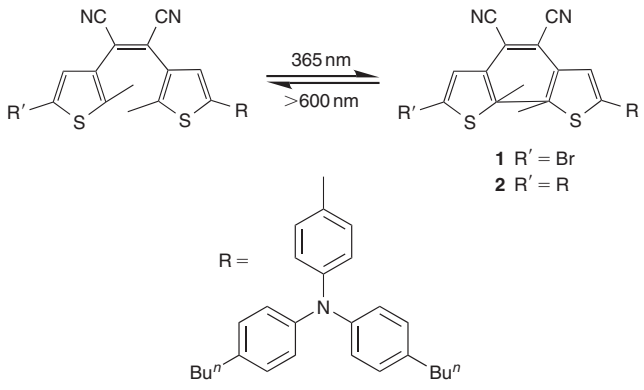


Fig. 2. The absorption changes of **1** and **2** in CH_2Cl_2 using different irradiation times at 365 nm. The inset shows the emission spectra (excited at 303 nm) changes of **1** and **2** in CH_2Cl_2 (1.2×10^{-5} mol L^{-1}) with different irradiation times at 365 nm.



Scheme 2. The interconversion of the ring-closed and ring-opened forms of **1** and **2**.

5,5′-position of the thiophene rings. Owing to the introduction of bulky substituents (such as triphenylamine) and heavy atoms (Br) at the 5,5′-position of the thiophene rings, the population of the anti-parallel conformation might increase, increasing the quantum yields in turn.[5a,27] The systems display well defined isosbestic points. Thus, one can calculate the relative conversion of the photocyclization reaction, α_{ps}, following the expressions based on the absorbance of the two

Table 1. Absorption maximum and coefficients of the ring-closed form, and the cyclization quantum yields of 1 and 2 in CH_2Cl_2

Compound	λ_{max} [nm] (ring-closed)	ε [10^4 $M^{-1}cm^{-1}$]	A_{ps} (Φ_{o-c})[A] ([%])
1	598	1.2 (358 nm)	0.05 (41.2)
2	620	5.4 (303 nm)	0.26 (48.9)

[A] A_{ps} is the longer wavelength absorption maximum of the photostationary state under irradiation with 365 nm light.[28] Φ_{o-c} is the quantum yield for the photocyclization of the open form to the closed form, calculated by a comparable method.[29]

forms.[21] The conversion of the photocyclization reaction, α_{ps}, at the photostationary state can be determined as 0.21 and 0.55 for compounds **1** and **2**, respectively. The enhancement in the conversion can be explained by active participation of the bulky substituents in the photochromic process. However, the quantum yields for the ring-opening reactions of related compounds with extended π-conjugation are generally very small.

Both compounds **1** and **2** emit luminescence with varying intensity when excited at 303 nm. It is interesting to note that the fluorescence intensity greatly depends on the photochromic reactions of compounds **1** and **2** (insets in Fig. 2). In the open form, compound **1** displays significant fluorescence intensity at around 455 nm, which is the emission character of triphenylamine group.[25] Irradiation of this compound with 365 nm light produced the ring-closed form, and the fluorescence intensity was reduced to less than 5% of the initial value for approx. 3 min. The greater-than-95% fluorescence quenching of the triphenylamine group by the ring-closed form might result from one main pathway for energy loss, namely the efficient energy transfer from the excited triphenylamine to the ring-closed form of bisthienylethene (Förster or photochromic fluorescence resonance energy transfer, pcFRET).[21,30] The irradiation by light of 600 nm regenerates the ring-opened form of compound **1**, stops the energy transfer mentioned above, and then restore the original emission spectrum. Therefore, efficient fluorescent switching can take place between the *on* and *off* states by irradiation with 365 and 600 nm light. FRET can be activated and deactivated reversibly by switching on and off the closed form of the bisthienylethenes, as demonstrated by the synchronous change in absorbance of the closed form and donor fluorescence intensity induced by the UV-vis irradiation cycles. Compared with that for compound **1**, the fluorescence decay of compound **2** is not so significant (only about 20% of the initial value). In theory, the efficient pcFRET from the excited triphenylamine to the ring-closed bisthienylethene is due to overlapping of the emission band of its opened form and the absorption spectra of the ring-closed form.[21] The overlapping for compound **1** is more efficient than that for compound **2**, and the fluorescence quenching of compound **1** is more significant than compound **2**. However, the quite large differences between **1** and **2** could not be explained satisfactorily by pcFRET only.

Since the photochromic bisthienylethene unit studied here contains cyano groups and bromine for compound **1**, it

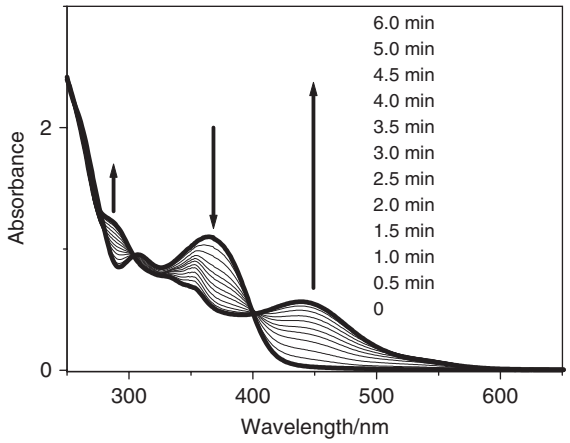


Fig. 3. Absorption changes of compound **4** in CH_2Cl_2 upon irradiation at 365 nm.

acts as a strong electron acceptor. The luminescence of triphenylamine in both compounds is effectively regulated by photochromic processes of the BTE subunit, attributed to another pathway, namely the change in photo-induced electron transfer (PET) between triphenylamine and each form of BTE subunit.[19,31] Obviously, the BTE subunit containing bromine in compound **1** has stronger electron-accepting ability than that for compound **2**, where both ends of the BTE subunit are anchored the same electron donor triphenylamine groups. Therefore, more than 95% of the fluorescence quenching of compound **1** by the photochromic process results from two pathways, namely the efficient energy transfer (Förster or pcFRET) and PET from the excited triphenylamine to the ring-closed form of bisthienylethene. In other words, the photochromic process for compound **1** is assisted by a FRET effect and PET.[26] Although the conversion efficiency of compound **1** is relative small, the quantum yield is more than 40%. This is another explanation for the high quantum yields, besides the substituent effect at the 5,5′-position of the thiophene rings.

In addition, the intermediate product, compound **4** shown in Scheme 1, also exhibited good photochromism properties (Fig. 3). When compound **4** was irradiated at 365 nm, a new absorption band appeared at 440 nm. Fig. 3 shows a typical change in absorption of diarylethene derivatives in solvents. From this figure, it can also be clearly seen that an isosbestic point appeared at 400 nm, the same wavelength of the isosbestic point in compounds **1** and **2**. Moreover, compared to most of the known diarylethene derivatives, the absorption maximum of the closed form for compound **4** was in the region of shorter wavelength (yellow), which may be useful in photon-mode full colour tuning and rewritable full colour print.[32,33]

Conclusions

In summary, new photochromic bisthienylethenes (BTEs) bearing triphenylamine units have been conveniently prepared. They undergo open-to-closed and closed-to-open ring photochromism in relative large quantum yields by alternate irradiation with light of 365 and 600 nm. The introduction of a fluorescent chromophore on the thiophene rings was shown to lead to excellent photo-switchable luminescence in differing degrees, which has potential applications in the areas of fluorescent probes and optical readouts for erasable memory media.

Experimental

Materials and General Procedures

CH_2Cl_2 was distilled over calcium hydride under argon. All other solvents were used as received. All other reagents and starting materials were purchased from Acros. Solvents for NMR analysis (purchased from Aldrich) were used as received.

^{1}H NMR spectra were obtained with a Brucker AM-500 spectrometer. Mass spectra were determined on a Hitachi-80 spectrometer. UV-Visible spectra were determined with a Varian Cary 500 spectrometer. Fluorescent spectra were recorded on a Varian Cary Eclipse spectrometer.

*Preparation of Compounds **1** and **2***

*1-Butyl-4-iodobenzene **5***

Concentrated HCl (300 mL), 4-butylaniline (150 g), and sodium nitrite (80 g) were agitated by a mechanical stirrer at below 5°C. An aqueous solution of potassium iodide (170 g) was added, and the reaction mixture was allowed to stir overnight. After completion of the reaction, the mother liquor was distilled under reduced pressure and then steam-distilled to give the pure product.

N-*(4-Bromophenyl)*-N,N-*bis(4-butylphenyl)benzenamine **6***

In a 250 mL round-bottomed flask were placed *o*-dichlorobenzene (150 mL), 1-butyl-4-iodobenzene (35 g, 0.135 mol), *p*-bromoaniline (8.6 g, 0.05 mol), potassium carbonate (30 g, 0.22 mol), bronze powder (2.2 g), and polyethylene glycol (1 g). The mixture was stirred at reflux overnight under nitrogen, then cooled to room temperature, and filtered. The mother liquor was distilled under reduced pressure to remove dichlorobenzene. Compound **6** was isolated in 40% yield by column chromatography on silica gel. δ_H (500 MHz, $CDCl_3$) 0.93 (t, 6H, CH_3), 1.36 (m, 4H, CH_2), 1.58 (m, 4H, CH_2), 2.56 (t, 4H, CH_2), 6.89 (d, 2H, *J* 7.02), 6.97 (d, 4H, *J* 8.41), 7.03 (d, 4H, *J* 8.41), 7.26 (d, 2H, *J* 7.02). *m*/*z* 435.2 (M^+, 96%), 437.2 ($M^+ + 2$, 92), 392.1 ($M - C_3H_7$, 100), 394.1 ($M + 2 - C_3H_7$, 97).

*4-[Bis(4-butylphenyl)amino]phenylboronic Acid **3***

A 100 mL, two-necked, round-bottomed flask was flushed with dry nitrogen and filled with dry tetrahydrofuran (50 mL). Compound **6** (7.08 g, 16 mmol) was added and the solution was cooled to −78°C in a liquid nitrogen bath. *n*-BuLi (10 mL) was added dropwise with stirring. After 30 min, methyl borate (3 mL) was added and, on completion of the reaction, the mixture was allowed to warm to room temperature (overnight) with stirring. HCl (10 M, 10 mL) was then added until the layers separated, the mixture was stirred for 5 h, and then poured into water. The THF layer was separated and the aqueous layer extracted three times with ether. The organic phases were combined and the mixture was distilled under reduced pressure. Finally, silica gel column chromatography [CH_2Cl_2/petroleum (1 : 1)] yielded the pure product (34%), mp 158–160°C. δ_H [500 MHz, $(CD_3)_2SO$] 0.91 (t, 6H, CH_3), 1.32 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 2.53 (t, 4H, CH_2), 6.81 (d, 2H, *J* 8.30), 6.93 (d, 4H, *J* 8.15), 7.12 (d, 4H, *J* 8.15), 7.63 (d, 2H, *J* 8.30), 7.82 (s, 2H, OH). *m*/*z* 435.2 (M^+, 96%), 437.2 ($M^+ + 2$, 92).

*2-Bromo-5-methylthiophene **8***

In the absence of light, 2-methylthiophene (49 g, 0.5 mol) was added to *N*-bromosuccinimide (95 g, 0.53 mol) in chloroform/glacial acetic acid [500 mL of a 50 : 50 (v/v) mixture], and the resulting solution mildly heated to reflux for approx. 1 h. The mixture was then allowed to warm to room temperature and poured into aqueous NaOH (3 M, 500 mL). The organic layer was separated and washed with H_2O. The oily crude product was distilled under reduced pressure (66–68°C/13 mmHg), and

2-bromo-5-methylthiophene was obtained (74.3 g, 84%). δ_H (500 MHz, $CDCl_3$) 2.42 (s, 3H), 6.51 (d, 1H, *J* 3.63), 6.82 (d, 1H, *J* 3.63).

5-Bromo-3-chloromethyl-2-methylthiophene ***9***

A stream of dry HCl gas was purged into a vessel containing a vigorously stirred mixture of 2-bromo-5-methylthiophene (54 g, 0.3 mol), trioxane (15 mol), and anhydrous zinc chloride in CCl_4 (150 mL) for 1 h at room temperature, and for another 4 h at 45°C. The resulting solution was poured into water; the organic layer was separated and washed with H_2O and saturated $NaHCO_3$. After the solvent was removed, distillation of the resulting oil under reduced pressure (132–134°C/13 mmHg) gave a yellow oily liquid (64%). δ_H (500 MHz, $CDCl_3$) 2.39 (s, 3H), 4.46 (s, 2H), 6.93 (s, 1H). *m/z* 225.9 (M^+, 42%), 223.9 ($M^+ - 2$, 31), 191 (M − Cl, 92), 189 (M − Cl − 2, 100).

2-(5-Bromo-2-methylthiophen-3-yl)acetonitrile ***10***

KCN (10 g, 0.15 mol) and $(n\text{-Bu})_4N^+Br^-$ (2.5 g) were dissolved in water (50 mL) at room temperature. To this solution was added compound **9** (22.4, 0.1 mol) and benzene (50 mL), and the resulting solution was stirred at reflux for 4 h. After being cooled to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2. The solvent was removed by distillation, and the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10 : 1) as eluent. δ_H (500 MHz, $CDCl_3$) 2.35 (s, 3H), 3.54 (s, 2H), 6.91 (s, 1H). *m/z* 217 ($M^+ + 2$, 61%), 215 (M^+, 61), 190 (M − CN + 1, 100), 188 (M − CN − 1, 97).

2,3-Bis(5-bromo-2-methylthiophen-3-yl)maleonitrile ***4***

Aqueous NaOH solution (50%, 30 mL) containing $(n\text{-Bu})_4N^+Br^-$ (0.42 g, 2 mmol) was added to a mixture of compound **10** and CCl_4 (120 mL) at 40°C, and the resulting solution was stirred for 1.5 h. The reaction mixture was poured into water, and the product extracted with ether and chloroform. After the solvent was removed, chromatography (petroleum ether/CH_2Cl_2, 2 : 1) gave pure *trans*- and *cis*-product.

Cis-form (R_F 0.2), yellow solid, mp 123–125°C. δ_H (500 MHz, $CDCl_3$) 2.20 (s, 6H, CH_3), 6.63 (s, 2H, CH). *m/z* 430.9 (M^+, 63%), 432.9 (M^+, 27).

Trans-form (R_F 0.6), yellow powder, mp 147–149°C. δ_H (500 MHz, $CDCl_3$) 2.54 (s, 3H, CH_3), 2.55(s, 3H, CH_3), 7.16 (s, 2H, CH). *m/z* 430.9 (M^+), 432.9 (M^+).

2-(5-{4-[Bis(4-butylphenyl)amino]phenyl}-2-methylthiophen-3-yl)-3-(5- bromo-2-methylthiophen-3-yl)maleonitrile ***1*** *and 2,3-Bis(5-{4-[bis(4-butylphenyl)amino]phenyl}-2-methylthiophen-3-yl)maleonitrile* ***2***

The resulting boric acid (1.5 g, 3.5 mmol) was added to a mixture of aqueous Na_2CO_3 (2 M, 10 mL) and THF (30 mL). 2,3-Bis(5-bromo-2-methylthiophen-3-yl)maleonitrile (0.52 g, 1.3 mmol) and $Pd(PPh_3)_4$ catalyst were then added. The reaction mixture was stirred at reflux under nitrogen overnight. After completion of the reaction, the mixture was poured into water, the organic layer separated, and the aqueous layer extracted with ether three times. The combined organic phases were concentrated under reduced pressure, subjected to column chromatography (CH_2Cl_2/petroleum ether, 1 : 3), and the products (**1** and **2**, shown in Scheme 1) were obtained.

Compound **1** was obtained as an orange solid (0.22 g, 24%), R_F 0.22 (Calc. for $C_{40}H_{38}BrN_3S_2$: C 68.2, H 5.4, N 6.0. Found: C 68.3, H 5.4, N 6.0%). δ_H (500 MHz, $CDCl_3$) 0.94 (t, 6H, CH_3), 1.37 (m, 4H, CH_2), 1.59 (m, 4H, CH_2), 2.57 (t, 4H, CH_2), 2.09 (s, 3H, thiophene CH_3), 2.27 (s, 3H, thiophene CH_3), 6.78 (s, 1H, thiophene H), 7.03 (s, 1H, thiophene H), 6.95 (d, 2H, *J* 8.6, Ar–H), 7.00 (d, 4H, *J* 8.31, Ar–H), 7.14 (d, 4H, *J* 8.31, Ar–H), 7.20 (d, 2H, *J* 8.6, Ar–H). *m/z* 703 (M^+), 704 ($M^+ + 1$).

Compound **2** was obtained as a yellow solid (0.14 g, 12.4%), R_F 0.45, mp 61–63°C (Calc. for $C_{66}H_{68}N_4S_2$: C 80.8, H 7.0, N 5.7. Found: C 80.6, H 7.0, N 5.8%). δ_H (500 MHz, $CDCl_3$) 0.94 (t, 12H, CH_3), 1.37 (m, 8H, CH_2), 1.60 (m, 8H, CH_2), 2.57 (t, 8H, CH_2), 2.22 (s, 6H, thiophene CH_3), 7.09 (s, 2H, thiophene H), 6.93 (d, 4H, *J* 8.41, Ar–H), 6.99 (d, 8H, *J* 8.42, Ar–H), 7.05 (d, 8H, *J* 8.54, Ar–H), 7.22 (d, 4H, *J* 8.54, Ar–H). *m/z* 980.6 (M^+).

Acknowledgments

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