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Synthesis and characterization of new planar butterfly-shaped fused oligothiophenes

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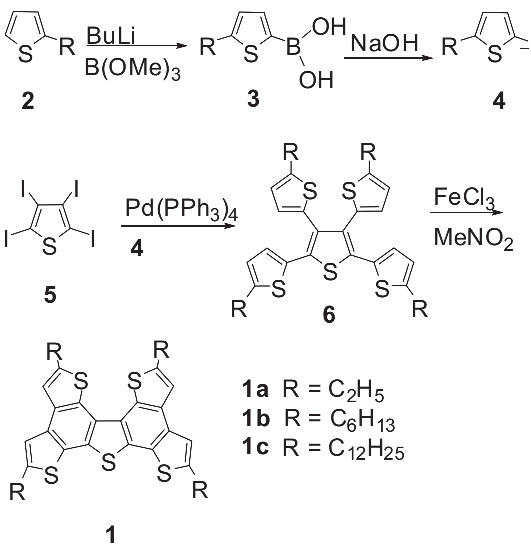
ABSTRACT

A simple oxidative cyclization reaction was used to construct new seven-ring-fused butterfly-shaped oligothiophene backbone: dibenzothieno[1,2-*b*:4,3-*b*′:6,7-*b*″:9,8-*b*‴]tetrathiophene. The new materials show high stability and strong solid state fluorescence. X-ray crystallography results reveal that they exist in 2-D stacked structures in their crystals.

1. Introduction

Owing to the growing interests in the field of organic semiconductors (OSCs), conjugated oligomers and fused aromatics have attracted intense attentions for their potential applications in organic field-effect transistors (OFETs) and organic light emitting diodes (OLEDs). Among these materials, linear acenes and oligothiophenes are the two most studied classes of OSCs to date.[1–4] Linear acenes, such as pentacene[5,6] are common benchmarks in the field of organic electronics with very high mobility. But pentacene and other higher acenes generally suffer from low environmental stability and poor solubility in common organic solvents, which limits their practical applications.[7,8] At the same time, fused thiophene oligomers seem to enjoy an increased stability in comparison with linearly linked structures, together with a more efficient conjugation.[9–12] Bis(dithienobenzene) represents one of the earliest reports of an air-stable organic semiconductor, which exhibited reasonable thin-film mobility (0.04 $cm^2 V^{-1} s^{-1}$).[13] Despite some work already invested in synthesis and device studies of fused thienothiophene and benzothiophene derivatives, the design of new OSCs continues to be an important area of materials research.

In our search for superior semiconductors for OFETs, we focused our attention on fused thiophenes. In this paper, we report the design and synthesis of a new seven-ring-fused dibenzothieno[1,2-*b*:4,3-*b*′:6,7-*b*″:9,8-*b*‴]tetrathiophene backbone, which can be functionalized by different alkyl substituents in a simple way (Scheme 1). The molecules can be described as a symmetric ‘butterfly’ shape.



Scheme 1. Synthesis of compounds **1a**–**c**.

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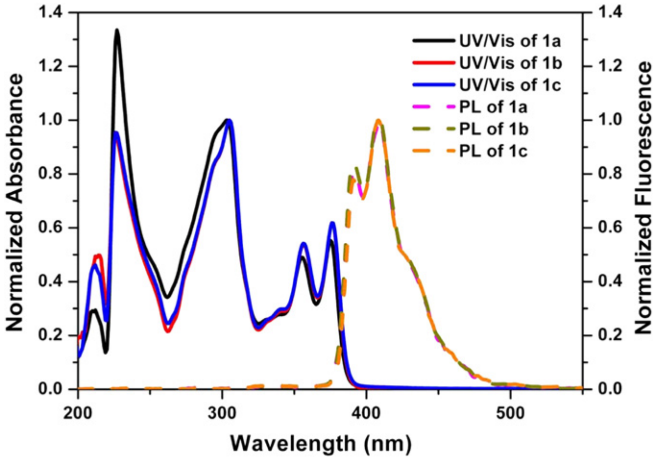

Fig. 1. Normalized UV–vis absorption (solid lines) and photoluminescence (dashed lines) spectra of **1a**–**c** recorded in DCM.

2. Results and discussion

2.1. Synthesis

The synthesis of compounds **1a**–**c** was presented in Scheme 1. Compounds **4a** and **4c** were synthesized by a similar process to that reported for compound **4b**.[14] The starting compounds, tetraiodothiophene (**5**) was prepared according to literature methods.[15] The 2,3,4,5-tetra(5-alkylthiophen-2-yl)thiophene (**6**) was obtained by Suzuki cross-coupling reaction between tetraiodothiophene (**5**) and trihydroxyboronate salt (**4**). The $FeCl_3$ oxidative cyclization protocol was then utilized to construct the dibenzothieno[1,2-*b*:4,3-*b*′:6,7-*b*″:9,8-*b*‴]tetrathiophene skeleton via thienyl–thienyl carbon–carbon bond formation.[16,17] The oxidative cyclization reaction using ferric chloride, which is an effective way to construct polycyclic aromatic hydrocarbons, was accomplished within 30 min under a mild condition to afford **1a**, **1b** and **1c** in 60%, 50% and 45% yields, respectively.

Compounds **1a**–**c** are pale yellow solids, which are readily dissolved in common organic solvents, such as $CHCl_3$, CH_2Cl_2, THF and toluene. So they were purified conveniently by flash column chromatography rather than vacuum sublimation usually used for the purification of insoluble organic semiconductors. ^1H and ^{13}C NMR spectra and MS associated with elemental analysis were employed to confirm the structure and purity of all new compounds.

2.2. Optical properties

UV–vis and fluorescence spectra of compounds **1a**–**c** are shown in Fig. 1, and the optical data are collected in Table 1. The solution-based absorption and emission measurements were carried out at very low concentrations ($<10^{-5}$ M) in DCM. All compounds showed similar absorption pattern with the peaks at 225, 305, 356 and 377 nm (Table 1). This result indicated that the different length of *n*-alkyl groups had little influence on the molecular π-system, which is as expected.[18] As shown in Fig. 2, the photophysical properties of drop-cast films of compounds **1a**–**c** were also measured and were compared with that in solution. The thin-film absorptions were red shifted and broadened compared to those recorded in solution, apparently due to the increased electronic interactions in the film.[19]

All three compounds show strong blue photoluminance (PL) in solution, but emit yellow light in the solid state (Fig. 3). The normalized PL spectra of compounds **1a**–**c** in thin-film are shown in Fig. 2. The PL spectra of the three compounds were virtually identical, consisting of a maximum emission at 409 nm in solution and 516 nm in thin-film, indicated that the different *n*-alkyl groups had little influence on the excited-state energies of the parent backbone. Emission maxima (λ_{max}) and fluorescence quantum yields (Φ_F) are presented in Table 1. All three compounds show very small Stoke's shift (5–25 nm) in solution and much larger Stoke's shift (131 nm) in thin-film. In thin-film state, the fluorescence of compounds **1a**–**c** is comparably weak (absolute $\Phi_F \approx 2.5\%$).

The photo-stabilities of compounds **1a**–**c** were investigated by monitoring the reduction in the absorbance at λ_{max} in an air-saturated 1.0×10^{-4} M toluene solution under ambient light at 27 °C (Fig. 4). There was comparatively little change (less than 15%) in the absorption of compounds **1a**–**c** even after 8 days of ambient light illumination. The new materials are substantially more stable than pentacene, which is known to deteriorated in a few minutes.[8,20] The observed stability order is: **1a**>**1c**>**1b**. By using the density functional theory (DFT) calculation, the HOMO energies for **1a**–**c** are found at −5.14, −5.09 and −5.07 eV (vs vacuum) (Table 1), which are lower than that of pentacene.[21] The band gap estimated from lowest-energy absorption edges of their solid state absorption onset was found to be 3.01, 3.02 and 2.94 eV for **1a**–**c**, respectively. The relatively low HOMO level and larger band gap of **1** may be the

Table 1
Optical absorption wavelength (λ), fluorescence emission wavelength (E), band gap (E_g), fluorescence quantum yields (Φ_F), half-life time, decomposition temperatures and DFT-MO theoretical calculation for compounds **1a**–**c**

Compound	λ (nm)		E_{em} (nm)	E_{em} (nm)	E_g (eV)[a]	E_g (eV)[a]	Φ_F	Φ_F	Half-life time (day)	Dec temp (°C)[b]	Theoretical calculation[c]	
	Soln	Film	Soln	Film	Soln	Film	Soln	Film			E_{LUMO} (eV)	E_{HOMO} (eV)
1a	223	227										
	308	303	390	516	3.22	3.01	5.9	2.9	52.7	255	−1.44	−5.14
	363	355	409									
	385	375										
1b	227	225										
	310	305	390	516	3.22	3.02	4.5	2.8	35.0	415	−1.39	−5.09
	363	356	409									
	385	377										
	223	225										
1c	306	305	390	516	3.22	2.94	3.3	2.1	51.0	320	−1.37	−5.07
	365	356	409									
	386	377										

[a] Optical HOMO–LUMO gaps determined from the onset of lowest-energy visible absorption band. The onset is defined as the intersection between the baseline and a tangent line that touches the point of inflection.

[b] The decomposition point is listed as the temperature at which 10% of the mass is lost as determined by a TGA experiment (10 °C min^{-1}) run at atmospheric pressure and under nitrogen.

[c] HOMO and LUMO levels and energy gap were obtained by DFT calculation at B3LYP/6-31G (d) level using Gaussian 03 package.

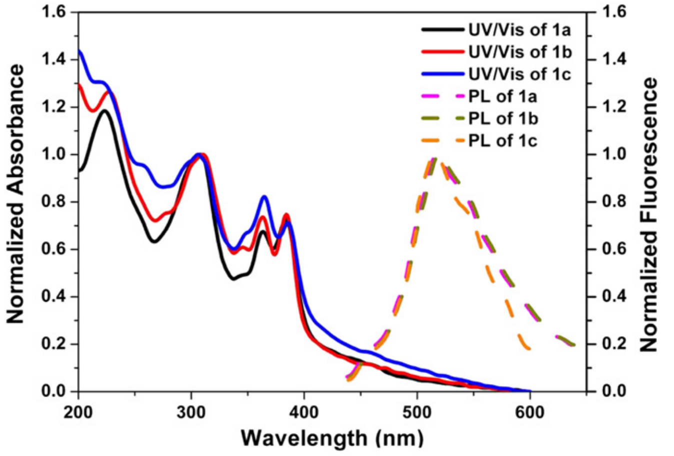

Fig. 2. Thin-film UV–vis absorption (solid lines) and photoluminescence (dashed lines) spectra of **1a**–**c**.

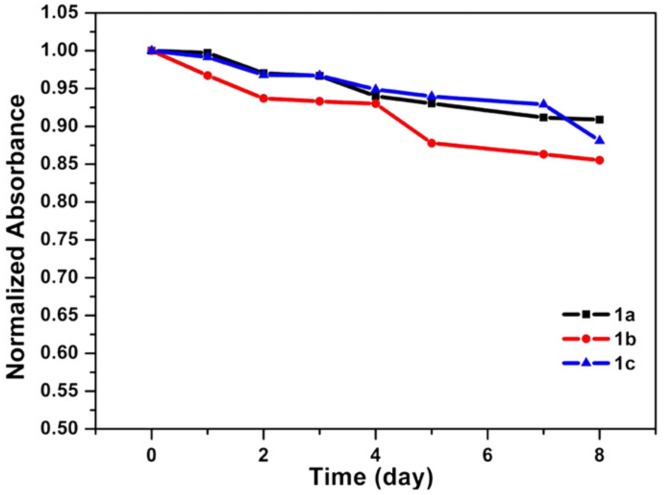

Fig. 4. Photo-stability of **1a**–**c** monitored through decrease in their absorption in toluene solution upon exposure to ambient light and air at 27 °C.

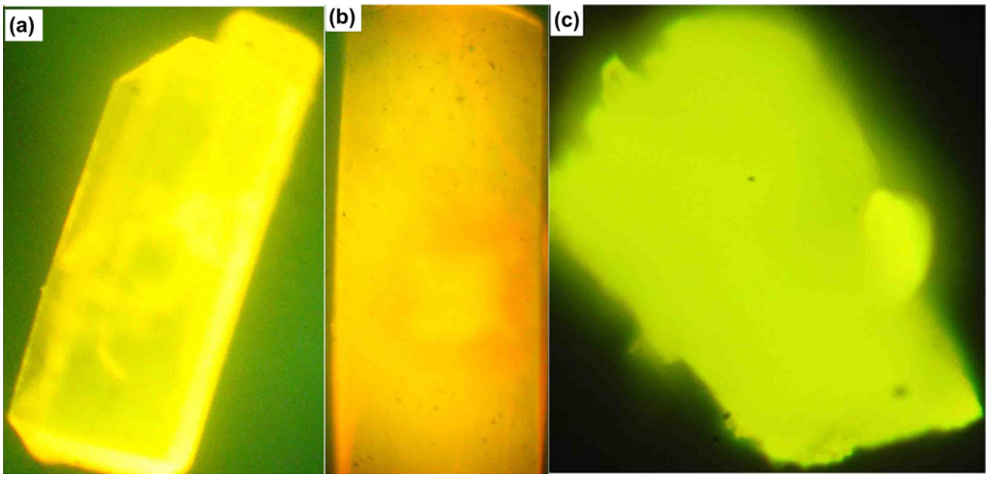

Fig. 3. Solid fluorescence of compounds **1a**–**c**.

reason that they are more stable than pentacene. The theoretical calculation results indicate that the lengthening of *n*-alkyl chains results in an increase of the HOMO, LUMO energies.

2.3. Thermal properties

The thermal properties of compounds **1a**–**c** were investigated by thermogravimetric analysis (TGA) (Table 1). The new materials show very high decomposition temperatures. The observed thermal stability order is: **1b**>**1c**>**1a** (Fig. 5). The TGA results demonstrated that the new conjugated backbone is thermally stable. The stronger π–π interactions between stacks of **1b** as evidenced by X-ray (Fig. 6) may be the reason for it high stability. Such a remarkable stability is particularly important for application of these compounds in OTFTs, where the stability of organic semiconductors is still a major limitation.

2.4. X-ray single crystal analysis

Single crystals of compounds **1a** and **1b**, which were successfully obtained by slow evaporation of solution in a chloroform/ethanol mixture, have been analyzed by X-ray diffraction to elucidate its molecular structure and packing characteristics. Compounds **1a** and **1b** crystallize in triclinic crystal system with P–1 space group and all form a slipped face-to-face π-stacking motif in the crystals. X-ray analyses display that the size of substituents has an effect on molecular solid-state packing.

Compound **1a** is slightly twisty. As shown in Fig. 6a, the fourth and fifth thiophene rings and ethyl moieties lie on either side of the five-ring-fused π-system plane, which contains the first to the third

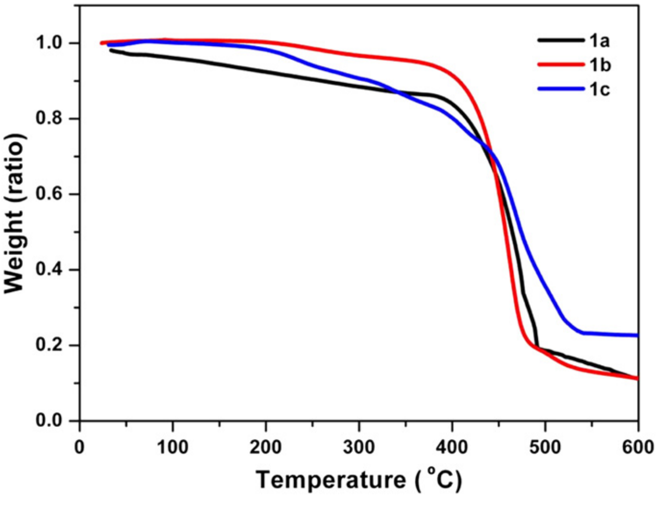

Fig. 5. TGA plots of **1a**–**c** with a heating rate of 10 °C min^{-1} under N_2.

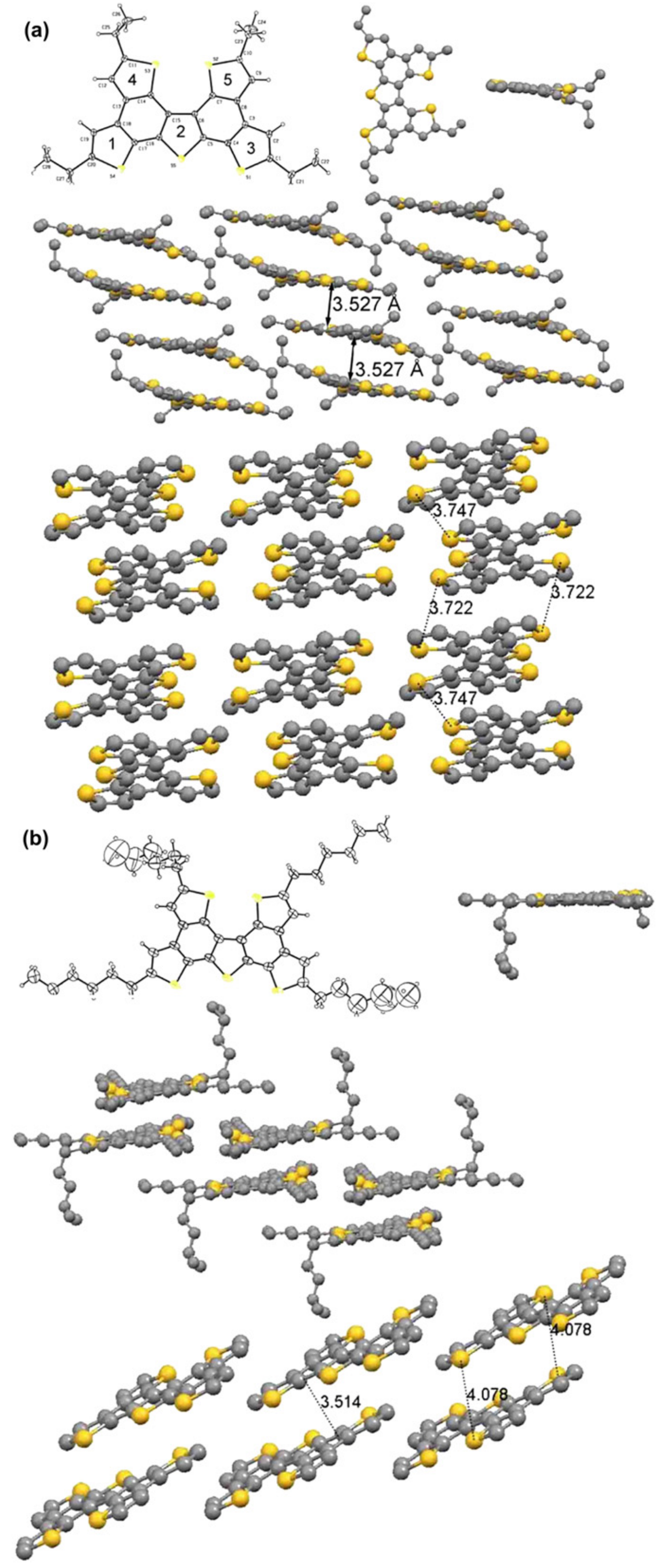

Fig. 6. (a) X-ray crystal structure of compound **1a**. (b) X-ray crystal structure of compound **1b**. (Yellow spheres depict S atoms and gray spheres C. Alkyl groups have been omitted.)

thiophene rings and two phenyl rings. The dihedral angles between the five-ring-fused π-system plane of the fourth and fifth thiophene rings are 10.6° and 7.5°, respectively. One molecule, which has ethyl group above the five-ring-fused π-system plane, and the other molecule, which has ethyl group below the five-ring-fused π-system plane form the unit of molecular packing in the crystal. The interplanar distance is 3.527 Å. The short distances of S···S are 3.722 Å and 3.747 Å, respectively.

While the seven fused rings, compound **1b** forms planar structure. There are two n-hexyl groups at amorphous state, and the exact structures of two n-hexyl groups were not defined. One molecule, which has n-hexyl group above the five-ring-fused π-system plane, and the other molecule, which has n-hexyl group below the five-ring-fused π-system plane form the unit of molecular packing in the crystal. The interplanar distance is 3.514 Å and the shortest distance of S···S is 4.078 Å. Both interplanar distances of **1a** and **1b** are lower than the sum of van der Waals radii of sulfur (3.68 Å),[22] indicating strong π–π interactions between stacks (Fig. 6).

3. Conclusion

A series of new planar seven-ring-fused oligothiophenes derivatives were successfully synthesized by four steps reactions. The new molecule can be described as a butterfly-like shape. These molecules exhibit high photo and thermal stability, along with strong solid state fluorescence making them good candidates for applications in organic optoelectronics.

4. Experimental section

4.1. General materials and methods

All chemicals and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer and calibrated to the residual protonated solvent at δ 0.00 ppm for deuterated chloroform ($CDCl_3$). ^{13}C NMR experiments were carried out in $CDCl_3$ and calibrated at δ 77.00. UV–vis absorption spectra were recorded using a T6 UV–vis spectrometer. IR spectra were obtained as KBr discs on a Bruker V70 FT-IR spectrometer. Elemental analyses were obtained at the UBC Microanalytical facility. Fluorescence measurements were made using an LS55 fluorescence spectrometer. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA7. A heating rate of 10 °C min^{-1} under flowing N_2 was used with runs being conducted from room temperature to high temperature.

4.2. Synthesis of compounds

*4.2.1. Synthesis of **4a**–**c**.* The synthesis of compound **4a** serves as an illustrative example. Compound **4c** was synthesized in a similar manner. Compound **4b** was synthesized by literature method.[14]

*4.2.1.1. Sodium(5-ethylthiophen-2-yl)trihydroxyborate (**4a**).* 2-Ethylthiophene (1.40 g, 12.50 mmol) was dissolved in dry THF (20 mL) and the solution was stirred at −78 °C under argon. n-BuLi (6 mL, 15.00 mmol, 2.5 M solution in hexane) was added dropwise to the solution over a period of 30 min, after which the reaction mixture was allowed to warm to room temperature and stirred for a further 1.5 h. The mixture was then slowly added over a period of 1 h to a solution of trimethylborate (2.58 g, 25.00 mmol) in dry THF (15 mL), which had been pre-cooled to −78 °C. The resulting mixture was allowed to slowly warm to room temperature and left stirring overnight. Dilute hydrochloric acid (5 mL, 2 M) was added and the mixture was extracted with diethyl ether (3×10 mL). The combined organic layers were dried, filtered, and the solvent was removed under vacuum. The residue was dissolved in a minimum amount of warm toluene under stirring and the solution allowed cooling to room temperature. Saturated NaOH solution was added dropwise until no further precipitate formed. The mixture was allowed to stir for 30 min. The precipitate obtained was filtered off, washed with toluene and petroleum ether and dried under vacuum to give the compound as a white amorphous solid, which was used for next step without further purification. Mp >300 °C ^{1}H NMR (400 MHz, D_2O) δ: 6.78 (d, J=3.6 Hz, 1H), 6.65 (d, J=3.6 Hz, 1H), 2.75 (q, J=7.6 Hz, 2H), 1.32 (t, J=7.6 Hz, 3H). IR (KBr): 3414, 2958, 1443, 1229, 936, 530 cm^{-1}.

*4.2.1.2. Sodium(5-dodecylthiophen-2-yl) trihydroxyborate (**4c**).* Compound **4c** was prepared from **2c** (3.15 g, 12.50 mmol) and get a white amorphous solid, which was used for next step without further purification. Mp >300 °C ^{1}H NMR (400 MHz, D_2O) δ: 6.76 (d, J=3.6 Hz, 1H), 6.40 (d, J=3.6 Hz, 1H), 2.70 (t, J=7.6 Hz, 2H), 1.56–1.63 (m, 2H), 1.20–1.32 (m, 18H), 0.84 (t, J=6.8 Hz, 3H). IR (KBr): 3371, 2920, 1465, 1441, 1237, 931, 524 cm^{-1}.

*4.2.2. Synthesis of **6a**–**c**.* The synthesis of compound **6a** serves as an illustrative example. Compounds **6b** and **6c** were synthesized in a similar manner.

*4.2.2.1. 2,3,4,5-Tetra(5-ethylthiophen-2-yl)thiophene (**6a**).* The aryl trihydroxyboronate salt **4a** (2.45 g, 12.50 mmol), aryl halide **5** (735 mg, 1.25 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) and a saturated aqueous solution of $NaHCO_3$ (1.05 g, 12.50 mmol) were placed in a flame flask under argon. Freshly distilled and de-gassed THF (25 mL) was added and the mixture was heated and stirred at reflux for 48 h. After cooling to room temperature the mixture was poured into a saturated solution of NH_4Cl, and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with saturated brine and dried over Na_2SO_4. The solution was then filtered, the solvents removed and the residue purified by column chromatography, using hexane as the eluent to yield a yellow oil (197 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88 (d, J=3.6 Hz, 2H), 6.68 (d, J=3.6 Hz, 2H), 6.62 (t, ^{1}J=4.8 Hz, ^{2}J=3.6 Hz, 4H), 2.79 (q, ^{1}J=7.6 Hz, ^{2}J=4.8 Hz, 4H), 2.74 (q, ^{1}J=7.6 Hz, ^{2}J=4.8 Hz, 4H), 1.25 (t, J=7.6 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.12, 148.34, 133.24, 133.09, 132.81, 132.23, 128.86, 125.81, 123.25, 122.93, 23.47, 23.37, 15.98, 15.65. MS (EI): m/z=524. Calcd for $C_{28}H_{28}S_5$: C, 64.08; H, 5.38; S, 30.54. Found: C, 64.15; H, 5.30; S, 30.55.

*4.2.2.2. 2,3,4,5-Tetra(5-hexylthiophen-2-yl)thiophene (**6b**).* Compound **6b** was prepared by coupling of compound **4b** (3.15 g, 12.50 mmol) with **5** (735 mg, 1.25 mmol) and purified by column chromatography, using hexane as the eluent to yield a yellow oil (374 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88 (d, J=3.6 Hz, 2H), 6.66 (d, J=3.6 Hz, 2H), 6.59 (t, ^{1}J=4.0 Hz, ^{2}J=3.6 Hz, 4H), 2.68–2.75 (m, 8H), 1.60 (t, ^{1}J=7.2 Hz, ^{2}J=6.8 Hz, 8H), 1.25–1.34 (m, 24H), 0.88 (t, J=6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.45, 146.84, 133.33, 133.18, 132.74, 132.24, 128.80, 125.69, 123.83, 123.70, 31.58, 31.55, 31.53, 31.41, 30.07, 30.06, 28.75, 28.49, 22.60, 22.55, 14.09, 14.06. LRMS (APCI) 748. Found: 749 $[M+H^{+\cdot}]$. Calcd for $C_{44}H_{60}S_5$: C, 70.53; H, 8.07; S, 21.40. Found: C, 70.60; H, 8.05; S, 21.35.

*4.2.2.3. 2,3,4,5-Tetra(5-dodecylthiophen-2-yl)thiophene (**6c**).* Compound **6c** was prepared by coupling of compound **4c** (4.20 g, 12.50 mmol) with **5** (735 mg, 1.25 mmol) and purified by column chromatography, using hexane as the eluent to yield a yellow solid (474 mg, 35% yield). Mp 42–44 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88 (d, J=3.6 Hz, 2H), 6.66 (d, J=3.6 Hz, 2H), 6.59 (t, ^{1}J=4.0 Hz, ^{2}J=3.6 Hz, 4H), 2.67–2.75 (m, 8H), 1.60 (t, ^{1}J=6.8 Hz, ^{2}J=6.4 Hz, 8H), 1.26–1.35 (m, 72H), 0.88 (t, J=6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.46, 146.84, 133.33, 133.17, 132.73, 132.22, 128.80, 125.67, 123.82, 123.69, 31.93, 31.66, 31.46, 30.07, 29.73, 29.68, 29.65, 29.57, 29.39, 29.36, 29.14, 28.86, 22.70, 14.13. LRMS (APCI) 1084. Found: 1085 $[M+H^{+\cdot}]$. Calcd for $C_{68}H_{108}S_5$: C, 75.21; H, 10.02; S, 14.77. Found: C, 75.22; H, 9.99; S, 14.79.

*4.2.3. Synthesis of **1a**–**c**.* The synthesis of compound **1a** serves as an illustrative example. Compounds **1b** and **c** were synthesized in a similar manner.

*4.2.3.1. 2,5,9,12-Tetraethyldibenzothieno[1,2-b:4,3-b′:6,7-b″:9,8-b‴]tetrathiophene (**1a**).* To a vigorously stirred solution of compound **6a** (105 mg, 0.20 mmol) in dichloromethane (20 mL) was added dropwise a solution of $FeCl_3$ (195 mg, 1.20 mmol) in $MeNO_2$ (3 mL) at 0 °C. Anhydrous MeOH was added after 30 min and stirred for another 60 min. The mixture was washed with brine, 2 M aqueous NaOH and NH_4Cl solution, respectively, and dried over Na_2SO_4. The solution was then filtered, the solvents removed and the residue purified by column chromatography, using hexane as the eluent to give the desired product as a yellow solid (62 mg, 60% yield). Mp 180–182 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (s, 2H), 7.36 (s, 2H), 3.12 (q, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 3.04 (q, J=7.6 Hz, 4H), 1.52 (t, J=7.6 Hz, 6H), 1.46 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 148.08, 145.72, 134.05, 133.65, 130.14, 130.04, 128.57, 126.72, 118.73, 117.95, 24.23, 23.76, 15.72, 15.65. IR (KBr): 3435, 2955, 2856, 1460, 1370, 718, 500 cm^{-1}. MS (EI): m/z=520. Calcd for $C_{28}H_{24}S_5$: C, 64.57; H, 4.64; S, 30.79. Found: C, 64.65; H, 4.67; S, 30.68.

*4.2.3.2. 2,5,9,12-Tetrahexyldibenzothieno[1,2-b:4,3-b′:6,7-b″:9,8-b‴]tetrathiophene (**1b**).* Compound **1b** was prepared from compound **6b** (150 mg, 0.20 mmol) and purified by column chromatography, using hexane as the eluent to yield a yellow solid (74 mg, 50% yield). Mp 79–80 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (s, 2H), 7.38 (s, 2H), 3.09 (t, J=7.6 Hz, 4H), 3.01 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 1.90 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 1.83 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 1.36–1.54 (m, 24H), 0.91 (t, J=6.8 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.71, 144.34, 134.04, 133.64, 130.24, 130.16, 128.57, 126.76, 119.49, 118.69, 31.66, 31.61, 31.42, 31.37, 30.92, 30.46, 28.94, 28.83, 22.64, 22.59, 14.12, 14.10. IR (KBr): 3432, 2952, 2852, 1461, 1375, 730, 505 cm^{-1}. LRMS (APCI) 744. Found: 745 $[M+H^{+\cdot}]$. Calcd for $C_{44}H_{56}S_5$: C, 70.91; H, 7.57; S, 21.52. Found: C, 70.95; H, 7.57; S, 21.48.

*4.2.3.3. 2,5,9,12-Tetradodecyldibenzothieno[1,2-b:4,3-b′:6,7-b″:9,8-b‴]tetrathiophene (**1c**).* Compound **1c** was prepared from compound **6c** (217 mg, 0.20 mmol) and purified by column chromatography, using hexane as the eluent to yield a yellow solid (97 mg, 45% yield). Mp 42–44 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (s, 2H), 7.36 (s, 2H), 3.07 (t, J=7.6 Hz, 4H), 2.99 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 1.89 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 1.82 (t, ^{1}J=7.6 Hz, ^{2}J=7.2 Hz, 4H), 1.36–1.54 (m, 72H), 0.87 (t, J=7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.66, 144.29, 134.01, 133.60, 130.21, 130.12, 128.54, 126.72, 119.46, 118.65, 31.93, 31.44, 31.39, 30.90, 30.45, 29.68, 29.66, 29.56, 29.47, 29.41, 29.37, 29.28, 29.16, 22.69, 14.12. IR (KBr): 3437, 2953, 2852, 1465, 1377, 721, 506 cm^{-1}. LRMS (APCI) 1080. Found: 1081 $[M+H^{+\cdot}]$. Calcd for $C_{68}H_{104}S_5$: C, 75.49; H, 9.69; S, 14.82. Found: C, 75.53; H, 9.65; S, 14.82.

4.3. Crystal data for compounds 1a and 1b[23]

Single crystal X-ray diffraction measurements were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å) at 296(2) K.

*4.3.1. Compound **1a**.* CCDC reference number 751387. $C_{28}H_{24}S_5$, M=520.77, triclinic, space group: $P-1$, a=10.7535(4) Å, α=64.898(2)°, b=11.2604(4) Å, β=69.859(2)°, c=11.9865(5) Å, γ=85.849(2)°, V=1229.33(8) Å^{3}, Z=2, D_x=1.407 Mg/m^{3}.

*4.3.2. Compound **1b**.* CCDC reference number 751388. $C_{44}H_{56}S_5$, M=745.19, triclinic, space group: $P-1$, a=10.1471(4) Å, α=104.485

(2)°, b=11.6413(4) Å, β=96.393(2)°, c=18.6557(7) Å, γ=98.156(2)°, V=2087.15 (13) $Å^3$, Z=2, D_x=1.186 Mg/m^3.

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Supplementary data

^{1}H and ^{13}C spectra for all the new compounds. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.11.061.

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23. All crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.