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End-capping of conjugated thiophene–benzene aromatic systems

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ABSTRACT

The synthesis of end-capped thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene was achieved from thiophene and 2,5-thiophenedicarboxaldehyde. Specifically, hexyl and dodecyl end-capping groups conferred reversible redox behavior as evidenced by cyclic voltammetry with oxidation potentials of 0.73 V versus Fc/Fc^+ couple. An extensive spectrophotometric analysis is reported.

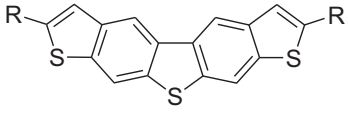
1. Introduction

Conjugated polycyclic aromatic systems are excellent candidates for optoelectronic device applications and specifically are an important resource of semiconducting materials in the development of organic field-effect transistors (OFET).[1–5] Conjugated organic materials are attractive targets because they can be synthesized on large scale, synthetically tailored to the desired HOMO and/or LUMO level and processed at low temperature by wet and dry methods. These properties make them suitable for application on flexible, plastic substrates, and would potentially lower the production costs over traditional, silicon-based FETs.[6] OFETs find application in displays, RFID tags and other modern electronic devices.[7] The development criteria for plastic electronics in OFET applications are a high material stability under operating conditions and good signal-to-noise ratio, as well as low turn-on voltages and high charge-carrier mobility. Previously, we reported the effective four-step synthesis of two regioisomers of thieno[*f*:*f*′]bis[1]benzothiophene (TBBT)[8,9] comprising ring systems of alternating benzene and thiophene units. These materials have shown promising properties in organic field-effect transistor applications,[10] with excellent stability in air up to 340 °C and a good on–off current ratio of $>10^5$.[11] The *syn* isomer, thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene TBBTs **1**, exhibited a high charge-carrier mobility of up to 0.12 $cm^2/V\,s$; however, displayed a strong hysteresis in the reverse sweep as observed in the output characteristic during device operation coupled with a high threshold-voltage.[11] One possible source of the observed hysteresis and threshold-voltage shift is irreversible oxidation and possible polymerization of the material during device operation.

2. Results and discussions

To improve the material's properties, we have end-capped parent compound **1** at the susceptible alpha-positions[12] of the terminal thiophene rings, since we attribute the undesired behavior in device configuration during device operation to polymerization of the material **1** at the labile alpha carbons next to sulfur on the terminal thiophene rings.[11] The target compounds **1a** and **1b** are depicted in Figure 1. The target compounds carry alkyl chains on both alpha-positions of the terminal thiophene units. The alkyl groups are hexyl (**1a**) and dodecyl (**1b**). The synthetic approach for the hexyl derivative **1a** is outlined below and requires the inclusion of the alkyl groups into the starting building blocks **2a**. Compound **1b** was synthesized in a similar approach. Both compounds, 2,3-dibromo-5-hexylthiophene (**1a**) and 2,3-dibromo-5-dodeylthiophene (**1b**) are new compounds.

The synthesis of **1a** from 2,3-dibromo-5-hexylthiophene (**2a**) is depicted in Scheme 1 and is based on the synthetic approach of the



1 R = H
1a R = C_6H_{13}
1b R = $C_{12}H_{25}$

Fig. 1. Structure of parent **1** and target compounds **1a** and **1b**.

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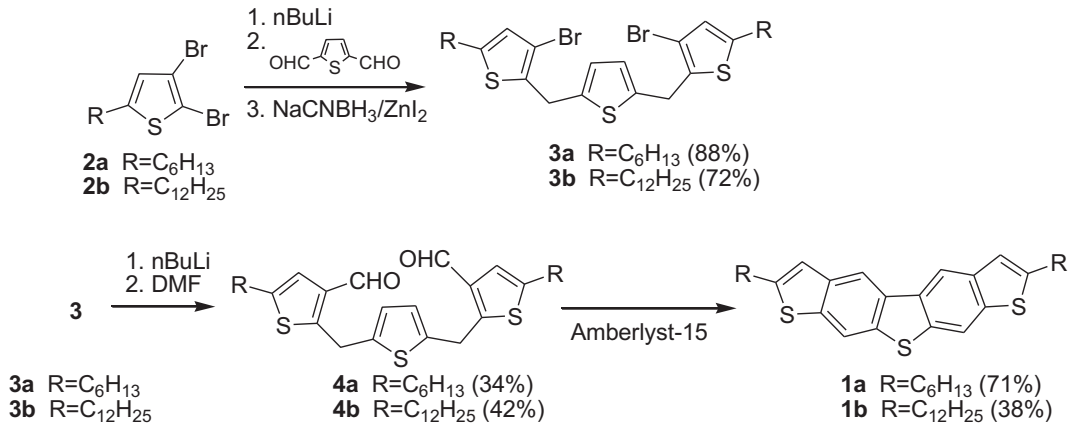


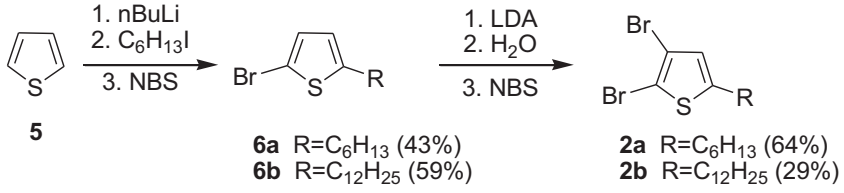
Scheme 1. Synthesis of target compounds **1a** and **1b**.

parent molecule **1**.[8,9] Compound **2a** underwent selective lithium–halogen exchange on position 2 followed by reaction with 2,5-thiophenedicarboxaldehyde to yield a dicarbinol, which was immediately reduced using sodium cyanoboronhydride and zinc iodide to yield **3a**. A double-lithium–halogen exchange followed by treatment with dry DMF furnished the dialdehyde **4a**. A Bradsher reaction[13] catalyzed by Amberlyst-15 in benzene under Dean–Stark conditions yielded the target compound **1a** in 15% overall yield. Target compound **1b** was synthesized in a similar fashion starting from 2,3-dibromo-5-dodecylthiophene (**2b**). Due to the extended alkyl chains, i.e., dodecyl, the lithiation reactions leading up to target compound **1b** were carried out in pure THF due to the low solubility of the intermediates in chilled, dry ether. The target compounds were purified by column chromatography, characterized and passed elemental analysis. 2,5-Thiophenedicarboxaldehyde is commercially available, whereas the 2,3-dibromo-5-alkylthiophenes were synthesized in an effective approach starting from thiophene (Scheme 2). Compounds **1a** and **1b** showed marked solubility of 3 mg/mL in chlorobenzene, a common solvent for the wet processing of materials via spin coating.

341 °C in aerobic atmosphere, therefore only the dodecyl groups have increased the stability of the material toward thermal decomposition.[8] The DSC and powder XRD measurements of **1a** and **1b** showed the absence of mesophase behavior in **1a** and **1b**.

Except a slight alteration in the peak positions, the absorption spectra of **1a** look similar in both polar (ethanol) and nonpolar (cyclcohexane) environment providing three different peaks at around 265 nm, 282 nm, and 293 nm, respectively, and a small hump at around 328 nm as shown in Figure 4. In comparison to the parent thieno[3,2-*f*:4,5-*f*′]bis[1]benzothiophene **1**, a concentration dependence study of **1a** did not show any major change in the spectra except a linear increase in absorbance with concentration. Absorption spectra of **1b** also showed a similar trend in various solvent environments indicating the increase in chain length from hexyl to dodecyl did not result in any change in the absorption spectra.

The fluorescence excitation spectra of **1a** and **1b** provided in Figure 5 look similar to absorption spectra suggesting that both S_0 (ground state singlet) and S_1 (first excited state singlet) have similar electronic state and vibrational levels. The fluorescence spectra of



Scheme 2. Synthesis of 2,3-dibromo-5-alkylthiophene (**2a**, **2b**).

The oxidation potential of compounds **1a** and **1b** was determined in dichlorobenzene using tetrabutylammonium tetrafluoroborate as electrolyte, platinum electrodes as working and reference electrode, and ferrocene/ferrocenium (Fc/Fc^+) couple as internal standard. The observed oxidation potential is 0.732 (0.728) V versus Fc/Fc^+ couple for **1a** (**1b**). The substitution of the parent compound **1** with alkyl chains has therefore resulted in a potential change of ~0.1 V. The oxidation reactions of both **1a** and **1b** are reversible and no polymerization on the electrode was observed, Figure 2. Thermogravimetric analysis in an aerobic atmosphere of the compounds revealed a high thermal stability up to 326 °C for **1a** and 367 °C for **1b**, observed at 5% decomposition, respectively (Fig. 3). Parent compound **1** shows onset of decomposition at

these compounds in various solvent environments mirror the excitation spectra, but as expected positioned in the shorter energy (longer wavelength) ranges, Figure 6. Variation of chain length also did not change appreciably the fluorescence spectra of **1a** or **1b**. Estimation of the Stokes shift was done by taking the difference between the maxima of the absorption and emission spectra.[14] Absorption maxima, emission maxima, and Stokes shifts in various polar and nonpolar solvent environments for **1a** and **1b** are estimated[15] and summarized in Table 1. Spectral shifts can be generally interpreted in terms of the solvents' identity by the Lippert–Mataga equation, which shows the relationship between the Stokes shift of the compound in each solvent and the change in the dipole moment of the fluorescence moiety upon excitation, and on

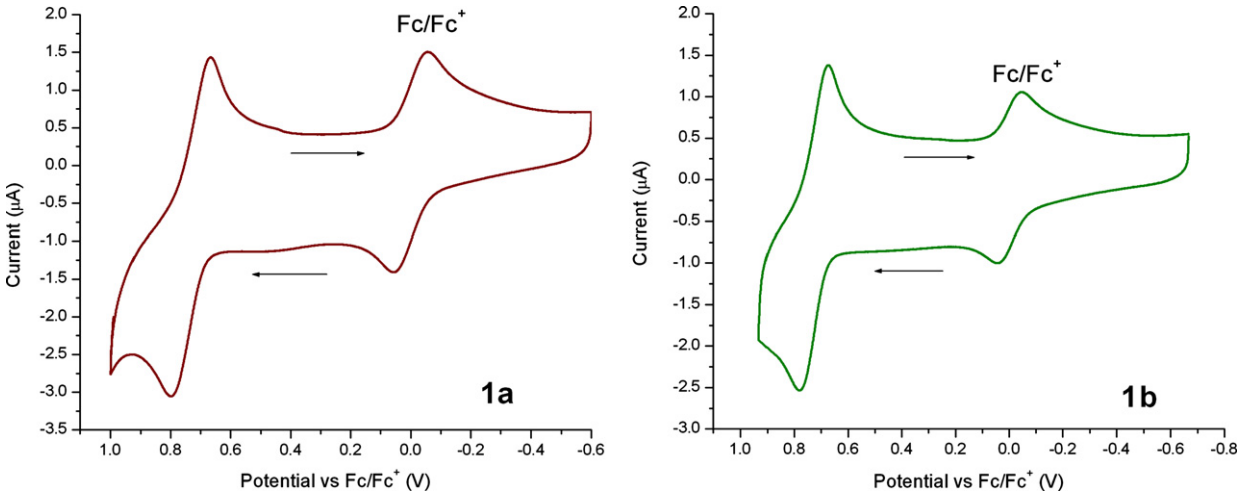


Fig. 2. Cyclic voltammogram of **1a** (left) and **1b** (right).

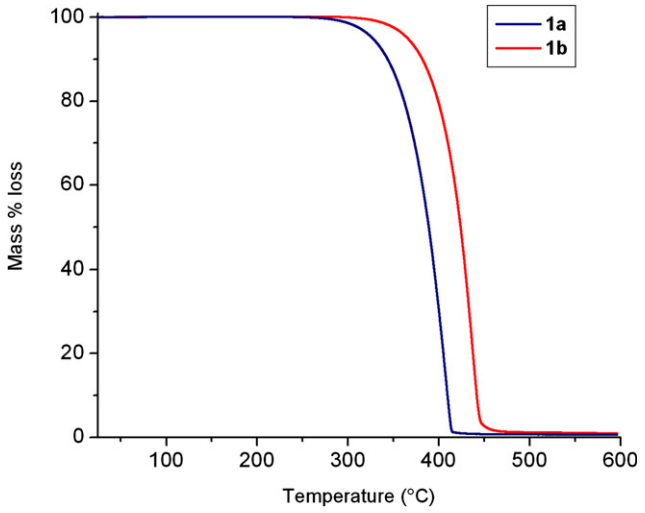


Fig. 3. TGA of **1a** and **1b**.

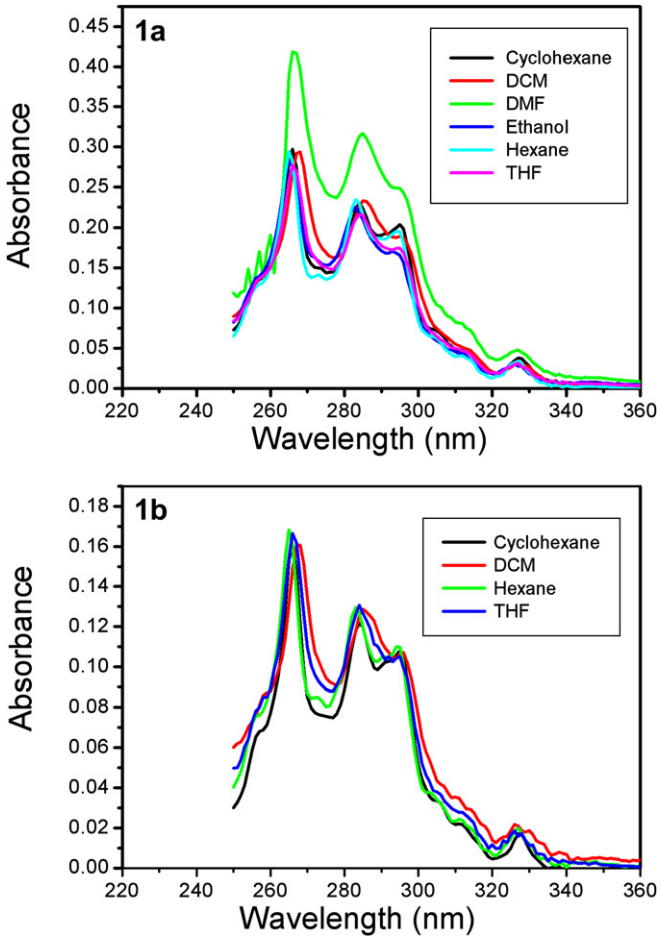


Fig. 4. Absorption spectra of **1a** and **1b** in various solvents.

the other hand, the dependence of the energy of the dipole moment on the dielectric constant and refractive index of the solvents being used.[15–22] The Lippert–Mataga equation can be expressed as follows:

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)\frac{(\mu_E-\mu_G)^2}{a^3} + \text{Constant}$$

where $\bar{\nu}_A$ and $\bar{\nu}_F$ are the wavenumbers (cm^{-1}) of the absorbance and fluorescence emission, respectively, which both determine the Stokes shift, h is the Planck's constant, c is the speed of light in vacuum, a is the radius of the cavity in which the fluorophore resides, μ_E and μ_G are the dipole moments in the excited and ground states, respectively, ε and n are the dielectric constant and the index of refraction of the solvents, respectively.

The Lippert–Mataga plot can be obtained by plotting the Stokes shift versus the term in the brackets in the above equation, referred to as the orientation polarizability (Δf) of the solvent, which is the result of both the mobility of the electrons in the solvent, and the dipole moment of the solvent.

$$\Delta f = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}$$

In the case of charge transfer in a molecule, the gross solvent polarity indicator scale such as E_T30 is more applicable.[23,24] Plots of Stokes shift versus the orientation polarizability (Δf) and E_T30 values of the solvents used for **1a** and **1b** are shown in Figures 7 and 8, respectively. The Stokes shift varies with both orientation polarizability (Δf) and solvent polarity (E_T30) in a rather systematic linear fashion except for E_T30 values of **1a** giving the plots a scattered appearance.

The fluorescence lifetimes, fluorescence quantum yield, and radiative and nonradiative constants are also given in Table 2. The

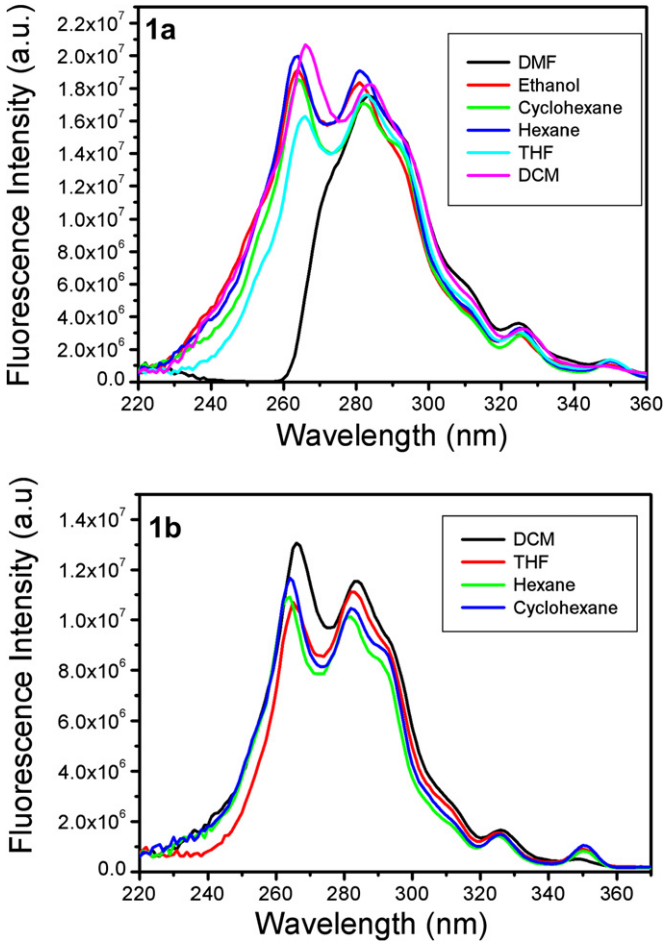


Fig. 5. Fluorescence excitation spectra of **1a** and **1b** in various solvents.

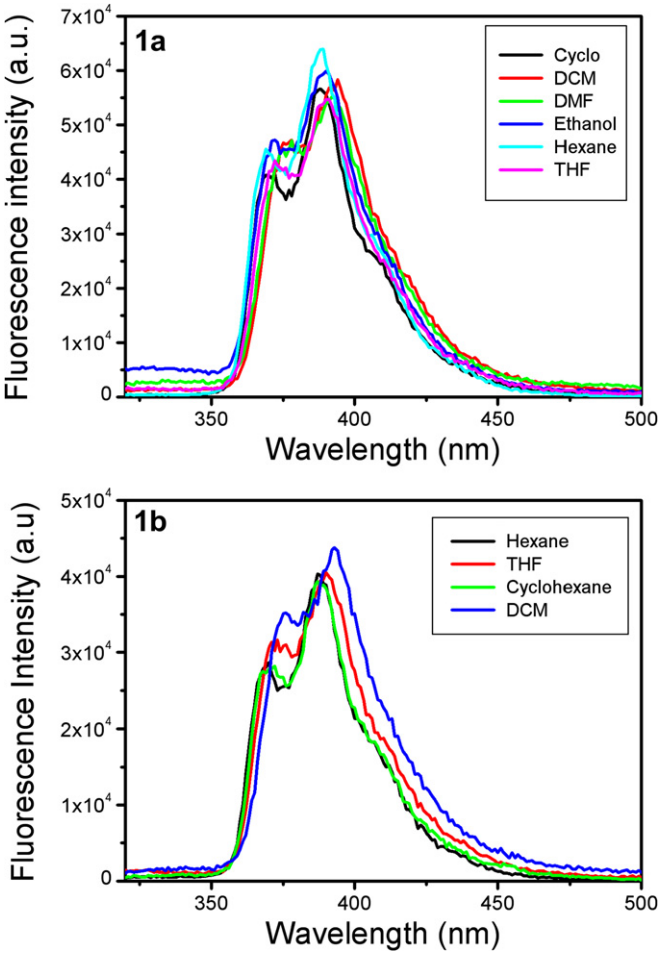


Fig. 6. Fluorescence emission spectra of **1a** and **1b** in various solvents.

fluorescence lifetime studies for the **1a** and **1b** showed biexponential decays, one of them is a short one in picoseconds with a higher population whereas the other one has a much longer lifetime in the nanosecond time scale with a lower population. The average fluorescence lifetime was calculated by taking the average of shorter and longer components. There was no correlation of average fluorescence lifetime with the polarity of the solvent for these two compounds. The chain length also did not influence the average fluorescence lifetime in a regular manner. The fluorescence quantum yield was determined as stated in the Experimental section. The fluorescence quantum yield was, in general, found to be very poor and in most cases it was obtained as ~0.01 for both **1a** and **1b**, similar to the nonalkylated parent compound.[25] The radiative rate constant was calculated by the equation.[15]

$$\kappa_r = \phi_f/\tau_f$$

where k_r is the radiative rate constant, ϕ_f is the fluorescence quantum yield, and τ_f is the fluorescence lifetime, and the nonradiative rate constant is evaluated as[15]

$$\kappa_{nr} = \left(1/\tau_f\right) - \kappa_f$$

The calculated radiative rate constant is in the order of $10^6\ s^{-1}$ compared to $10^7\ s^{-1}$ for the parent, nonalkylated molecule,[25] while the nonradiative rate constants (Table 2) are in the order of $10^8\ s^{-1}$, similar to the parent, nonalkylated molecule.[25]

In summary, we report the preparation, electronic and spectroscopic characterization of two new materials for potential use in organic field-effect transistor applications.

Table 1
Absorption maxima, emission maxima, and Stokes shift **1a** and **1b** in various solvents

Compound	Solvent	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Stokes shift (cm^{-1})
1a	Cyclohexane	266	387	11,754
	Dichloromethane	268	394	11,933
	Hexane	265	388	11,963
	Tetrahydrofuran	266	390	11,953
	Dimethylformamide	266	392	12,084
	Ethanol	265	390	12,095
1b	Cyclohexane	257	387	11,754
	Dichloromethane	266	393	12,149
	Hexane	268	387	11,474
	Tetrahydrofuran	267	390	11,812

3. Experimental

3.1. General information

Chemicals and solvents were purchased from Acros and Aldrich. Standard grade silica gel (60 Å, 32–63 μm) and silica gel plates (200 μm) were purchased from Sorbent Technologies. Reactions that required anhydrous conditions were carried out under argon in oven-dried glassware. A Bruker spectrometer was used to record the NMR spectra. $CDCl_3$ was the solvent for NMR and chemical shifts relative to TMS at 0.00 ppm are reported in parts per million (ppm) on the δ scale. Elemental analyses were performed at

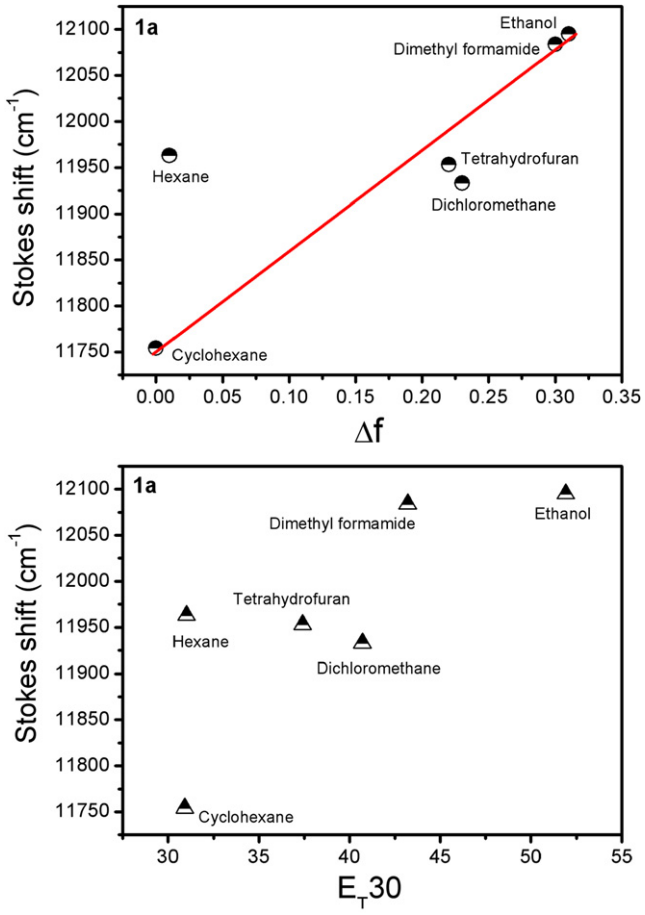


Fig. 7. Stokes shift versus solvent polarity scale (orientation polarizability, Δ*f* (top); E_T30 scale (bottom)) for **1a**.

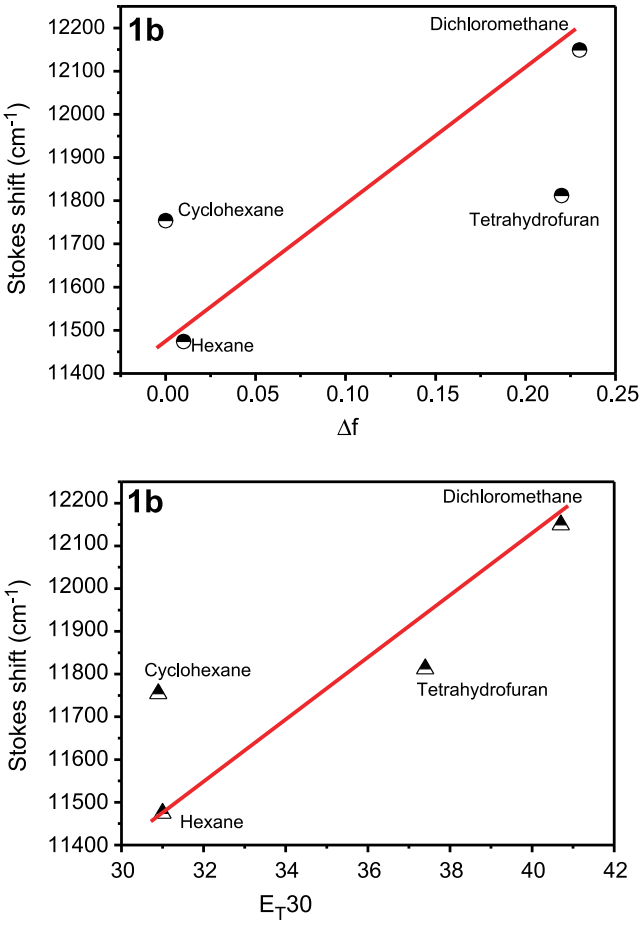


Fig. 8. Stokes shift versus solvent polarity scale (orientation polarizability, Δ*f* (top); E_T30 scale (bottom)) for **1b**.

Table 2
Fluorescence lifetime, average fluorescence lifetime, fluorescence quantum yield, radiative and nonradiative rate constants of **1a** and **1b** in various solvents at 25 °C

Compound	Solvent	τ_1 (B_1) in ns	τ_2 (B_2) in ns	χ^2	τ_{av} in ns	ϕ	$\kappa_r/10^6$ s^{-1}	$\kappa_{nr}/10^8$ s^{-1}
1a	Cyclohexane	0.474 (79%)	3.58 (21%)	1.70	2.03	~0.01	4.93	4.88
	Dichloromethane	2.59 (13%)	10.53 (87%)	1.25	6.56	~0.01	1.52	1.51
	Hexane	0.758 (77%)	3.68 (23%)	1.83	2.22	~0.01	4.51	4.46
	Tetrahydrofuran	0.341 (79%)	2.93 (21%)	1.96	1.64	~0.01	6.11	6.05
	Dimethylformamide	0.371 (72%)	3.48 (28%)	1.97	1.93	—	—	—
	Ethanol	0.933 (81%)	3.42 (19%)	1.60	2.18	—	—	—
1b	Cyclohexane	1.00 (83%)	5.44 (17%)	1.94	3.22	~0.01	3.11	3.07
	Dichloromethane	0.667 (83%)	2.24 (17%)	1.63	1.45	~0.02	13.76	6.74
	Hexane	0.612 (83%)	2.07 (17%)	1.94	1.34	~0.01	7.46	7.38
	Tetrahydrofuran	0.652 (86%)	2.27 (14%)	1.82	1.46	~0.01	6.84	6.78

Atlantic Microlab Inc., Norcross, GA. Diisopropylamine was freshly distilled from NaH before use.

3.2. Synthesis

3.2.1. 2-Hexylthiophene. Synthesized according to a literature procedure.[26] Yield: 70% (lit.[26] 96%) of a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (3H, t, *J*=4.8 Hz), 1.30 (6H, m), 1.67 (2H, m), 2.82 (2H, t, *J*=7.2 Hz), 6.77 (1H, m), 6.90 (1H, dd, *J*=5.2, 3.6 Hz), 7.09 (1H, dd, *J*=5.2, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.6, 28.8, 29.9, 31.6, 31.8, 122.7, 123.9, 126.6, 145.9.

3.2.2. 2-Bromo-5-hexylthiophene ***6a****.* Synthesized according to a literature procedure.[26] Yield: 61% (lit.[26] 80%) of a clear oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (3H, t, *J*=6.9 Hz), 1.62 (2H, m), 1.30 (6H, m), 2.76 (2H, t, *J*=7.8 Hz), 6.52 (1H, d, *J*=3.6 Hz), 6.83 (1H, d, *J*=3.6 Hz).

3.2.3. 4-Bromo-2-hexylthiophene. Synthesized according to a modified literature procedure.[27] Diisopropylamine (16.88 mL, 120.14 mmol) was cooled to −78 °C in a solution of THF (70 mL). ^{n}BuLi (50 mL, 120.12 mmol) was dropwise added and the reaction mixture stirred for 5 min. The thus generated LDA was transferred via cannula to a solution of 2-bromo-5-hexylthiophene in THF (100 mL) at −78 °C. The reaction mixture was stirred for 30 min and then water was added at the same temperature. After warming to room temperature, THF was removed under vacuum and the aqueous phase extracted with ether (2×200 mL). The organic layer

is then washed with brine (50 mL) and water (50 mL), before drying over $MgSO_4$ (anhyd). Purification using vacuum distillation yielded 24.12 g (89%) (lit.[27] 64%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (3H, t, J=6.9 Hz), 1.31 (6H, m), 1.64 (2H, m), 2.77 (2H, t, J=7.7 Hz), 6.69 (1H; d, J=1.5 Hz), 7.00 (1H, d, J=1.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.6, 28.7, 30.0, 31.3, 31.5, 108.9, 120.0, 126.7, 147.2.

3.2.4. 2,3-Dibromo-5-hexylthiophene ***2a***. 4-Bromo-2-hexylthiophene (24.10 g, 97.49 mmol) was dissolved in DMF and cooled to 0 °C. A solution of NBS (17.49 g, 98.27 mmol) in DMF was dropwise added under darkness. The icebath was removed and the reaction mixture stirred until GC showed complete conversion (7 h). Then, the reaction mixture was poured on water containing few crystals of sodium thiosulfate and the aqueous layer extracted with $CHCl_3$. The organic layer was twice washed with water and dried over Na_2SO_4 (anhyd). After removal of the solvent, a dark oil remained, which yielded 22.98 g (72%) (lit.[29] 93%) of a yellow oil after vacuum distillation. Bp 130–134 °C/2 Torr. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.89 (3H, t, J=6.9 Hz), 1.30 (6H, m), 1.62 (2H, m), 2.71 (2H, t, J=7.7 Hz), 6.60 (1H, t, J=0.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.5, 28.6, 30.5, 31.0, 31.5, 107.4, 112.8, 126.9, 147.3. Anal. Calcd C, 36.83; H, 4.33. Found: C, 37.22; H, 4.40.

3.2.5. 2-Dodecylthiophene[29]. Synthesized in a similar fashion as 2-hexylthiophene. Bp 134 °C/2 Torr (lit.[28] 178–182 °C/13 Torr). Yield: 64% (lit.[29] 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (3H, t, J=6.9 Hz), 1.26 (18H, m), 1.67 (2H, m), 2.82 (2H, t, J=8.1 Hz), 6.77 (1H, m), 6.90 (1H, dd, J=5.1, 3.3 Hz), 7.09 (1H, dd, J=5.1, 1.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 29.1, 29.4, 29.6, 29.7, 29.9, 31.8, 31.9, 122.7, 123.9, 126.6, 145.9.

3.2.6. 2-Bromo-5-dodecylthiophene ***6b***[29]. Synthesized in similar fashion as 2-bromo-5-hexylthiophene. Yield: 92% (lit.[29] 87%). Bp 162 °C/2 Torr (lit.[29] 120–125 °C/0.001 Torr). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (3H, t, J=6.9 Hz), 1.26 (18H, m), 1.62 (2H, m), 2.73 (2H, t, J=7.5 Hz), 6.53 (1H, m), 6.83 (1H, d, J=3.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 29.0, 29.3, 29.5, 29.6, 30.3, 31.4, 31.9, 108.5, 124.3, 129.4, 147.7.

3.2.7. 4-Bromo-2-dodecylthiophene[28]. Synthesized in similar fashion as 4-bromo-2-hexylthiophene. Product was used in next step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (3H, t, J=6.9 Hz), 1.26 (18H, m), 1.64 (2H, m), 2.77 (2H, m), 6.69 (1H, m), 7.00 (1H, d, J=1.2 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 29.0, 29.3, 29.5, 29.6, 30.0, 31.33, 31.9, 108.9, 120.0, 126.7, 147.2. Anal. Calcd C, 58.00; H, 8.21. Found: C, 58.14; H, 7.95.

3.2.8. 2,3-Dibromo-5-dodecylthiophene[28] ***2b***. Synthesized in a similar fashion as 2,3-dibromo-5-hexylthiophene. Yield (two steps): 29%. Bp 169–172 °C/0.02 Torr. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (3H, t, J=6.9 Hz), 1.26 (18H, m), 1.61 (2H, m), 2.71 (2H, m), 6.60 (1H, t, J=0.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 29.0, 29.3, 29.5, 29.6, 30.4, 31.0, 31.9, 107.4, 112.8, 126.9, 147.3. Anal. Calcd C, 46.84; H, 6.93; Br, 38.95; S, 7.82. Found: C, 46.88; H, 6.21; Br, 38.97; S, 7.86.

3.2.9. 2,5-Bis(3-bromo-5-hexyl-2-thien-2-ylmethyl)thiophene ***3a***. 2,3-Dibromo-5-hexylthiophene (4.65 g, 14.3 mmol) was dissolved in 5:2 ether/THF and purged with argon. At −78 °C, ^{n}BuLi (17.12 mmol) was dropwise added and stirred for 10 min. Then, a solution of 2,5-thiophenedicarboxaldehyde (1.00 g, 7.13 mmol) in THF, chilled to −78 °C, was added and the reaction mixture allowed to warm to room temperature. After addition of water, the aqueous layer was extracted with ether and the combined organic layers were washed with satd NH_4Cl, and water and dried over $MgSO_4$ (anhyd). Evaporation of the solvents yielded a yellow liquid, which was dissolved in 1,2-dichloroethane. ZnI_2 (3.43 g, 10.7 mmol) and $NaCNBH_3$ (3.49 g, 55.7 mmol) were added and the reaction mixture was stirred overnight. A color change from orange to pink to yellow was observed. The reaction mixture was then filtered through Celite, washed with aq satd NH_4Cl, dried over $MgSO_4$, and the solvent evaporated. Column chromatography using hexanes yielded 3.80 g (88%) of a yellow oil that was used immediately in the next step without further purification due to instability. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (6H, t, J=6.9 Hz), 1.29 (12H, m), 1.60 (4H, m), 2.69 (4H, t, J=7.8 Hz), 4.15 (4H, s), 6.59 (2H, t, J=0.6 Hz), 6.68 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.5, 28.7, 29.8, 30.2, 31.1, 31.5, 107.9, 125.1, 126.5, 134.7, 140.7, 144.5.

3.2.10. 2,2′-[2,5-Thiophenediylbis(methylene)]bis[5-hexylthiophene-3-carboxaldehyde] ***4a***. ^{n}BuLi (4.36 mL, 10.0 mmol) was chilled to −78 °C in ether. 2,5-Bis(3-bromo-5-hexyl-2-thien-2-ylmethyl) thiophene (2.75 g, 4.56 mmol) was added dropwise as a solution in ether. Ten minutes after addition, degassed DMF (774 μL, 10.0 mmol) was added and the reaction mixture stirred for 1 h. The mixture was poured into ice-cold satd NH_4Cl and extracted into ether (200 mL). The combined organic layers were washed with water before drying over $MgSO_4$ (anhyd). Column chromatography using a gradient of 0–10% ethyl acetate in hexanes yields a pink oil (0.77 g, 34%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (6H, t, J=6.9 Hz), 1.29 (12H, m), 1.60 (4H, m), 2.72 (4H, t, J=7.6 Hz), 4.57 (4H, s), 6.70 (2H, s), 7.05 (2H, s), 9.97 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.5, 28.5, 28.7, 29.8, 31.1, 31.5, 123.8, 125.6, 136.6, 141.0, 144.4, 152.1, 184.5. Anal. Calcd C, 67.16; H, 7.25. Found: C, 67.14; H, 7.01.

3.2.11. 2,7-Dihexylthieno[3,2-f:4,5-f′]bis[1]benzothiophene ***1a***. 2,2′-[2,5-Thiophenediylbis-(methylene)]bis[5-hexylthiophene-3-carboxaldehyde] **4a** was dissolved in dry benzene and Amberlyst-15 (0.200 g) was added. The reaction mixture was stirred and heated for 2 days under Dean–Stark conditions. After cooling, dichloromethane was added and the mixture was filtered through a cotton plug. After washing with satd NH_4Cl (aq), the mixture was dried over $MgSO_4$ (anhyd) and the solvent evaporated leaving a reddish-brown solid. Purification by column chromatography (2% ethyl acetate/hexanes) yielded a white solid 0.489 g (71%). Mp 224–225 °C. IR ν_{max} 3050 (w), 2956, 2927 (s), 2873, 2849, 1466 (s), 1462, 1437, 1421, 1259, 1223, 1130, 1048, 884 (s), 858, 835, 725, 613 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (6H, t, J=7.2 Hz), 1.33 (12H, m), 1.78 (4H, m), 2.94 (4H, t, J=7.5 Hz), 7.12 (2H, s), 8.14 (2H, s), 8.43 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.6, 28.8, 30.9, 31.0, 31.6, 114.5, 115.6, 120.2, 133.2, 135.5, 137.9, 138.9, 146.7. Anal. Calcd C, 72.36; H, 6.94. Found: C, 72.34, H, 6.96.

3.2.12. 2,5-Bis(3-bromo-5-dodecyl-2-thien-2-ylmethyl)thiophene ***3b***. Synthesized in a similar procedure as the hexyl analog **3**. Yield: 5.04 g (72%) of a yellow oil used without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (6H, t, J=6.9 Hz), 1.29 (36H, m), 1.58 (4H, m), 2.69 (4H, t, J=7.6 Hz), 4.15 (4H, s), 6.59 (2H, s), 6.68 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 29.0, 29.3, 29.4, 29.5, 29.62, 29.63, 29.7, 29.8, 30.1, 31.1, 31.9, 107.9, 125.1, 126.5, 134.7, 140.7, 144.5.

3.2.13. 2,2′-[2,5-Thiophenediylbis(methylene)]bis[5-dodecylthiophene-3-carboxaldehyde] ***4b***. Synthesized in a similar approach as hexyl analog **4**. Due to the low solubility in the chilled ether, THF was used as solvent for the lithiation. Yield: 0.888 g (42%) of a pink oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (6H, t, J=6.9 Hz), 1.33 (36H, m), 1.60 (4H, m), 2.71 (4H, t, J=7.2 Hz), 4.56 (4H, s), 6.70 (2H, s), 7.05 (2H, s), 9.97 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 28.5, 29.0, 29.27, 29.3, 29.5, 29.6, 29.8, 31.1, 31.9, 123.9, 125.6, 136.6, 141.0, 144.4, 152.1, 184.4. Anal. Calcd C, 71.80; H, 9.04. Found: C, 71.59; H, 9.11.

3.2.14. 2,7-Didodecylthieno[3,2-f:4,5-f′]bis[1]benzothiophene ***(1b)***. Synthesized in a similar procedure as the hexyl analog **1a**. Mp

174–175 °C. Yield: 108 mg (38%). IR ν_{max} 3054 (w), 2955, 2914 (s), 2873, 2847, 1466, 1455, 1436, 884 (s), 859, 840, 721, 614 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (6H, t, J=6.6 Hz), 1.26 (36H, m), 1.78 (4H, m), 2.93 (4H, t, J=7.2 Hz), 7.11 (2H, s), 8.14 (2H, s), 8.43 (2H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): 14.1, 22.7, 29.1, 29.35, 29.37, 29.5, 29.6, 29.7, 31.0, 31.9, 114.6, 115.6, 120.1, 133.1, 135.4, 137.8, 138.8, 146.7. Anal. Calcd C, 75.89; H, 8.92. Found: C, 75.71; H, 8.90.

3.3. Spectroscopic measurement

3.3.1. Absorption spectroscopy. A JASCO V-570 UV–VIS–NIR Spectrophotometer was used for acquisition of absorption spectra; a Jobin-Yvon-Horiba Fluorolog III spectrofluorimeter was used for fluorescence measurements with a 100 W Xenon lamp as excitation source, and a R-928 detector (V=950 V).

3.3.2. Fluorescence lifetime measurement. A Jobin-Yvon-Horiba Fluorolog III spectrofluorimeter with a pulsed diode laser of excitation wavelength 282 nm served to determine the fluorescence lifetime, whereas the decay data was analyzed using Data Analysis Software and decay fits with values of χ^2 between 0.99 and 1.5 were considered to be within the acceptable range.

3.3.3. Determination of the fluorescence quantum yield. The fluorescence quantum yield was determined under dilute conditions ($\sim$100 nM) to avoid self-quenching of fluorophores and inner filter effects. Anthracence in ethanol was used as a standard to determine the fluorescence quantum yield of the unknown samples. The excitation wavelength used for the reference and standard sample was 280 nm for **1a** and 330 nm for **1b**. The fluorescence quantum yield of **1a** and **1b** was determined using the following equation:[30]

$$\phi_{unk} = \phi_{std} \times \frac{F_{unk}}{F_{std}} \times \frac{A_{std}}{A_{unk}} \times \frac{n^2_{unk}}{n^2_{std}}$$

where 'ϕ_{unk}' and 'ϕ_{Std}' are the quantum yield of the sample of interest and that of the reference sample, respectively. The quantum yield of anthracene in ethanol was taken to be 0.31.[22] 'F_{unk}' and 'F_{std}' are the integrated intensities of the emission spectrum of the analyte and that of the reference sample, respectively. 'A' corresponds to the optical density of the samples taken at the excitation wavelength and finally 'n' is the refractive index of the solvents used. In the above equation, standard (std) refers to anthracene in ethanol, and unknown (unk) refers to **1a** (**1b**) molecules.

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Supplementary data

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