Synthesis and Properties of Hexyl End-Capped Thiophene Oligomers Containing Anthracene Moiety in the Center

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A series of new organic semiconductors hexyl end-capped thiophene-anthracene oligomers containing the anthracene moiety in the center of the oligomers are synthesized. The target oligomers have been obtained by Stille coupling reactions as key step reactions. The synthesized thiophene-anthracene oligomers were characterized by ^{1}H-NMR, ^{13}C-NMR and high-resolution mass spectroscopy, respectively. All of the oligomers are soluble in chlorinated solvents. Their optical, thermal and electrochemical properties were measured. The hexyl end-capped oligomers and their unsubstituted oligomers exhibit the same absorption behavior in dilute toluene solution. Hexyl end-capped bis-terthienylanthracene oligomer is observed to show liquid crystalline mesophase at 166 °C in heating process. The thermal analyses as well as the electrochemical measurement data indicate that the designed materials show better thermal and oxidation stability than the corresponding oligothiophenes without anthracene core. Fluorescence lifetimes and fluorescence quantum yields of the thiophene-anthracene oligomers are measured to be 10-14 ps and 3.4-9.9 × 10^{-3} which are much shorter and lower than those of oligothiophenes respectively.

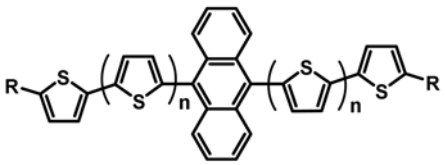
Key Words : Thiophene oligomer, Anthracene, Stille reaction, Thiophene-anthracene oligomer

Introduction

Conjugated oligomers attract much attention by their unique optical and semiconducting properties.[1] They can be used as organic light-emitting diodes (OLEDs),[2] organic thin film transistors (OTFTs)[3] and photovoltaic cells.[4] Among them, the acenes and thiophene oligomers represent two of the most studied series of compounds for use as organic semiconductors.[5] Thiophene containing oligomers have been extensively explored as the active materials for OTFT applications due to the easiness in chemical modification of their structures, allowing to fine-tuning of their optical and electronic properties.

Pentacene is known to exhibit the highest mobility (μ > 1 $cm^2V^{-1}s^{-1}$, $I_{on}/I_{off} > 10^6$) as a *p*-type semiconductor on vacuum deposition.[6] However, pentacene is highly sensitive to oxidation leading to rapid degradation of the material unless it is manipulated under rigorous exclusion of oxygen.

Anthracene may be a good candidate for *p*-type semiconductor for OTFTs[5b] because anthracene single crystals have good hole mobilities measured by time-of-flight photocurrent technique and have high chemical stabilities.[7] Recently Suzuki synthesized anthracene oligomers, oligo(2,6-anthrylene)s, which demonstrate highly extended π conjugation and planarity. OTFTs with oligo(2,6-anthrylene)s have shown mobilities greater than 0.1 $cm^2V^{-1}s^{-1}$. But anthracene dimers are only slightly soluble in aromatic solvent such as 1,2-dichlorobenzene and further the trimers are almost insoluble in organic solvent.[8] Most recently, thiophene-anthracene oligomer, 2,6-bis(5'-hexylthiophen-2-yl)anthracene has been used as active component in TFTs showing attractive device characteristics, e.g. relatively high mobility as high as 0.50 $cm^2V^{-1}s^{-1}$ and on/off ratios great than 10^7, which have been attributed to the closely packed face-to-face stacking and the wide band gap of the material.[9]



1 n = 1, R = *n*-C_6H_{13}
2 n = 2, R = *n*-C_6H_{13}
3 n = 1, R = H
4 n = 2, R = H

Scheme 1. Structure of thiophene-anthracene oligomers **1**-**4**.

In this investigation, we designed and synthesized new materials, thiophene oligomers containing anthracene in the center **1**-**4** aiming to obtain new semiconducting materials of high stability, high solubility and high mobility (Scheme 1). The introduction of hexyl-end substituents to the oligomers as **1** and **2** favor the ordered arrangement of the molecules in their solid state, which facilitates the charge transport through π–π^* orbital stacking of the molecules.[10] These end groups might also improve the material solubility so that solution-processable FETs can be fabricated.

Experimental Section

Chemicals and instruments. Chemical reagents were purchased from Aldrich Chemical Co. and were used without further purification. Tetrahydrofuran (THF) was distilled over sodium in the presence of benzophenone. 2-Hexylthiophene (**5**), 2-(tri-*n*-butylstannyl)-5-hexylthiophene (**6**) and 2-(tri-*n*-butylstannyl)thiophene (**7**) were synthesized according to literature procedures.[11] The tributylstannyl compounds **6** and **7** were used in the Stille coupling without further purification. Stille coupling reactions were carried out with conventional heating under nitrogen.

^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Mercury 300 MHz spectrometer. The thermal gravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/SDTA 851, and differential scanning calorimetric analyses (DSC) were performed on a Perkin-Elmer Pyris 1 instrument under N_2 atmosphere at a rate of 10 °C/min. The absorption and photoluminescence (PL) spectra were measured using a Jasco V-570 UV-vis spectrometer and a Hitach F-4500 or Hitachi F-3010 fluorescence spectrometer in toluene respectively at room temperature. Fluorescence quantum yields (ϕ_f) were estimated using a toluene solution of perylene as a standard with a known value of $\phi_f = 0.75$.[12] The fluorescence lifetime in the picosecond regime was measured in toluene using fluorescence up-conversion method. The second harmonic oscillation (405 nm) of the fundamental pulse (810 nm, 120 fs at 1 kHz) of a Ti:sapphire laser system was used to excite the sample in a cell with a 1.0 mm optical path length. The residual fundamental and the fluorescence were focused in a BBO type I crystal to generate a sum-frequency oscillation, which was detected by a photomultiplier.

The electrochemical experiments were performed using a CHI617b and the electrochemical cell was consisted of the platinum electrode (2 mm diameter), a Pt wire counter electrode, and a Ag/AgCl reference electrode. The electrochemical properties were evaluated by cyclic voltammetry, using tetrabutylammonium perchlorate (Bu_4NClO_4, TBAP) and dichloromethane (Aldrich, HPLC grade) as supporting electrolyte. Experiments were performed at room temperature.

9,10-Bis(2-thienyl)anthracene (8).[13] A mixture of 9,10-dibromoanthracene (9 g, 26.78 mmol), 2-tributylstannylthiophene **7** (18.7 mL, 58.92 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.2 g) in dry toluene (250 mL) was heated under nitrogen. The reaction mixture was refluxed for 3 days during which time a precipitate formed. After cooling, the solid was collected by filtration and washed several times with hexane, methanol and water to give yellow solid **8** (8.99 g, 98%). M.p. 243 °C.

^{1}H-NMR ($CDCl_3$) δ 7.23 (dd, 2H, J = 3.2, 1.2 Hz, thiophene-H), 7.33 (dd, 2H, J = 4.8 Hz, 3.2 Hz, thiophene-H), 7.39-7.44 (m, 4H, ArH), 7.65 (dd, 2H, J = 4.8 Hz, 1.2 Hz, thiophene-H), 7.86-7.91 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ125.7, 126.7, 126.8, 127.2, 129.5, 130.2, 131.5, 138.9.

9,10-Bis(5-bromo-2-thienyl)anthracene (9). In the absence of light, *N*-bromosuccinimide (3.11 g, 17.5 mmol) was added portionwise at room temperature to a solution of 9,10-bis(2-thienyl)anthracene **8** (3 g, 8.76 mmol) in DMF (10 mL), stirred for 3 h, poured onto ice, and the precipitate was filtered. Chloroform was added to the mixture and the organic phase was washed with water. The solution was dried over Na_2SO_4 and concentrated *in vacuo* to afford the product **9** (4.38 g, 72%). M.p. 250-251 °C.

^{1}H-NMR ($CDCl_3$) δ6.79 (d, 2H, J = 3.3 Hz, thiophene-H), 7.28 (d, 2H, J = 3.3 Hz, thiophene-H), 7.44-7.48 (m, 4H, ArH), 7.91-7.95 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) 113.1, 126.1, 126.4, 129.5, 130.0, 130.1, 131.3, 140.5 HRMS (M^+, 497.8742, Calcd 497.8752).

9,10-Bis(5'-bromo-2,2'-bithiophen-5-yl)anthracene (10). 9,10-Bis(5'-bromo-2,2'-bithiophen-5-yl)anthracene **10** was synthesized with *N*-bromosuccinimide (1.4 g, 7.86 mmol) and 9,10-bis(2,2'-bithiophen-5-yl)anthracene **3** (2 g, 3.93 mmol) in the same manner as in the preparation of bis-bromide **9**. After similar work up the remained organic residue was washed several times with hexane to give yellow solid **10**. (2.19 g, 84%) M.p. over 300 °C.

^{1}H-NMR ($CDCl_3$) δ6.99-7.03 (m, 4H, thiophene-H), 7.11 (d, 2H, J = 3.3 Hz, thiophene-H), 7.32 (d, 2H, J = 3.3 Hz, thiophene-H), 7.43-7.47 (m, 4H, ArH), 7.97-8.00 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ111.2, 124.0, 124.1, 126.0, 126.6, 129.7, 130.4, 130.7, 131.4, 138.0, 138.4, 138.7 HRMS (M^+, 661.8510, Calcd 661.8496).

9,10-Bis(5'-hexyl-2,2'-bithiophen-5-yl)anthracene (1). A mixture of 9,10-bis(5-bromo-2-thienyl)anthracene **9** (5 g, 9.99 mmol), 2-tributylstannyl-5-hexylthiophene **6** (9.15 g, 20.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.4 g) in dry DMF (200 mL) was heated under nitrogen. The reaction mixture was refluxed for 3 days. The DMF was removed under reduced pressure and then the reaction mixture was extracted with 1 M HCl solution and chloroform. The organic layer was washed with water, dried over Na_2SO_4 and then removed solvent at reduced pressure. The remained organic residue was washed several times with hexane, methanol and water to give yellow solid **1**. (3.37 g, 50%) The product was further purified by gradient sublimation (2×10^{-2} Torr).

^{1}H-NMR ($CDCl_3$) δ0.91 (t, 6H, J = 7.2 Hz, -$(CH_2)_5C\underline{H}_3$), 1.23-1.48 (m, 12H, -$CH_2CH_2(C\underline{H}_2)_3CH_3$), 1.62-1.78 (m, 4H, -$CH_2C\underline{H}_2(CH_2)_3CH_3$), 2.84 (t, 4H, J = 7.2 Hz, -$C\underline{H}_2(CH_2)_4CH_3$), 6.73 (d, 2H, J = 3.3 Hz, thiophene-H), 7.07 (t, 4H, J = 3.3 Hz, thiophene-H), 7.30 (d, 2H, J = 3.3 Hz, thiophene-H), 7.42-7.46 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ 14.1, 22.6, 28.8, 30.2, 31.6, 31.6, 122.9, 123.5, 124.9, 125.8, 126.7, 129.9, 130.3, 131.4, 134.6, 137.1, 139.5, 145.6 HRMS (M^+, 674.2182, Calcd 674.2182).

9,10-Bis(5''-hexyl-2,2':5',2''-terthiophen-5-yl)anthracene (2). A mixture of 9,10-bis(5'-bromo-2,2'-bithiophen-5-yl)-anthracene **10** (5 g, 7.52 mmol), 2-tributylstannyl-5-hexylthiophene **6** (7.04 g, 15.0 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.3 g) in dry DMF (200 mL) was heated under nitrogen. The reaction mixture was refluxed for 3 days. The reaction was worked up in a similar way to the preparation of **1** to give yellow solid **2** (3.08 g, 48.8%).

^{1}H-NMR ($CDCl_3$) δ 0.91 (t, 6H, J = 7.2 Hz, -$(CH_2)_5C\underline{H}_3$), 1.23-1.48 (m, 12H, -$CH_2CH_2(C\underline{H}_2)_3CH_3$), 1.62-1.78 (m, 4H, -$CH_2C\underline{H}_2(CH_2)_3CH_3$), 2.81 (t, 4H, J = 7.2 Hz, -$C\underline{H}_2(CH_2)_4CH_3$), 6.71 (d, 2H, J = 3.3 Hz, thiophene-H), 7.03 (d, 2H, J = 3.3 Hz, thiophene-H), 7.05 (d, 2H, J = 3.3 Hz, thiophene-H), 7.12 (d, 2H, J = 3.3 Hz, thiophene-H), 7.15 (d, 2H, J = 3.3 Hz, thiophene-H), 7.37 (d, 2H, J = 3.3 Hz, thiophene-H), 7.43-7.47 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ 14.1, 22.6, 28.8, 30.2, 31.6, 123.4, 123.5, 123.6, 124.4, 124.9, 125.9, 126.7, 129.8, 130.5, 131.4, 134.5, 135.3, 137.1, 137.8, 138.9, 145.8 HRMS (M^+, 838.1926, Calcd 838.1918).

9,10-Bis(2,2'-bithiophen-5-yl)anthracene (3). A mixture of 9,10-bis(5-bromo-2-thienyl) anthracene **9** (5 g, 9.99 mmol), 5-tributylstannylthiophene **7** (9 g, 23.80 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.4 g) in dry DMF (200 mL) was heated under nitrogen. The reaction mixture was refluxed for 3 days. The reaction was worked up in a similar way to the preparation of **1** to give yellow solid **3** (3.8 g, 75%). The product was further purified by gradient sublimation (2×10^{-2} Torr).

^{1}H-NMR ($CDCl_3$) δ 7.05-7.09 (m, 4H, thiophene-H), 7.12 (d, 2H, J = 3.3 Hz, thiophene-H), 7.27 (d, 2H, J = 3.3 Hz, thiophene-H), 7.39 (d, 2H, J = 3.3 Hz, thiophene-H), 7.43-7.47 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ 123.8, 123.9, 124.5, 125.9, 126.7, 127.9, 129.9, 130.4, 131.4, 137.2, 137.8, 139.0 HRMS (M^+, 506.0288, Calcd 506.0286).

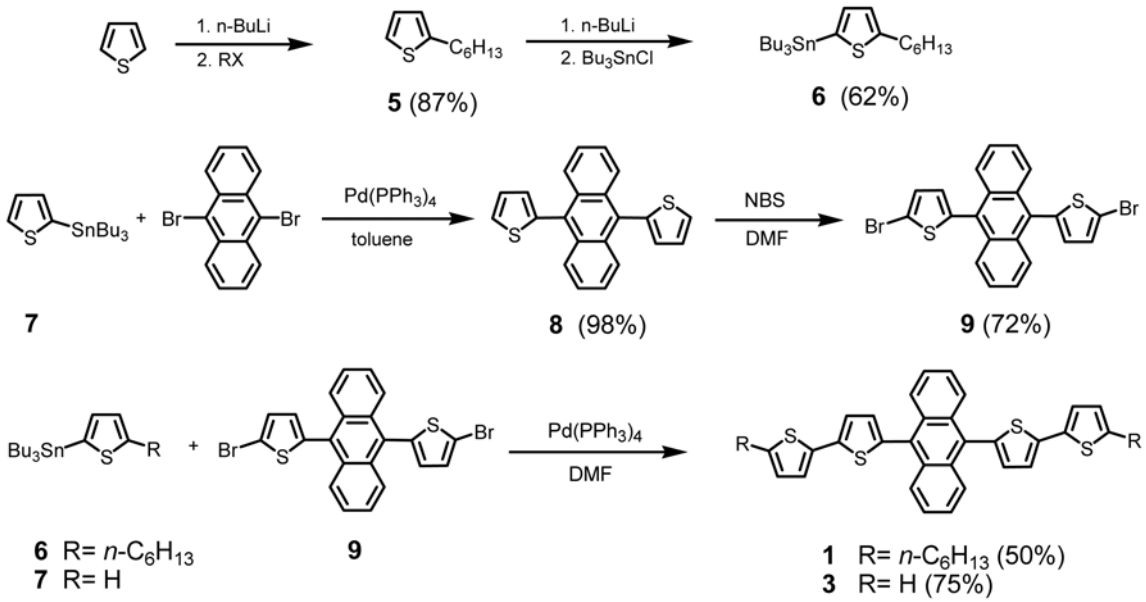
9,10-Bis(2,2':5',2''-terthiophen-5-yl)anthracene (4). A mixture of 9,10-bis(5'-bromo-2,2'-bithiophen-5-yl)anthracene **10** (5 g, 7.52 mmol), 5-tributylstannylthiophene **7** (6.3 g, 16.88 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.2 g) in dry DMF (250 mL) was heated under nitrogen. The reaction mixture was refluxed for 3 days. The reaction was worked up in a similar way to the preparation of **2** to give yellow solid **4** (3.13 g, 62%).

^{1}H-NMR ($CDCl_3$) δ 7.05 (dd, 2H, J = 3.3, 1.2 Hz, thiophene-H), 7.12-7.14 (m, 4H, thiophene-H), 7.17 (d, 2H, J = 3.3 Hz, thiophene-H), 7.22-7.26 (m, 4H, thiophene-H), 7.39 (d, 2H, J = 3.3 Hz, thiophene-H), 7.43-7.47 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ 123.7, 123.8, 124.5 (doublet), 124.6, 126.0, 126.7, 127.9, 129.8, 130.5, 131.4, 136.0, 136.5, 137.2, 138.0, 138.7 HRMS (M^+, 670.0037, Calcd 670.0040).

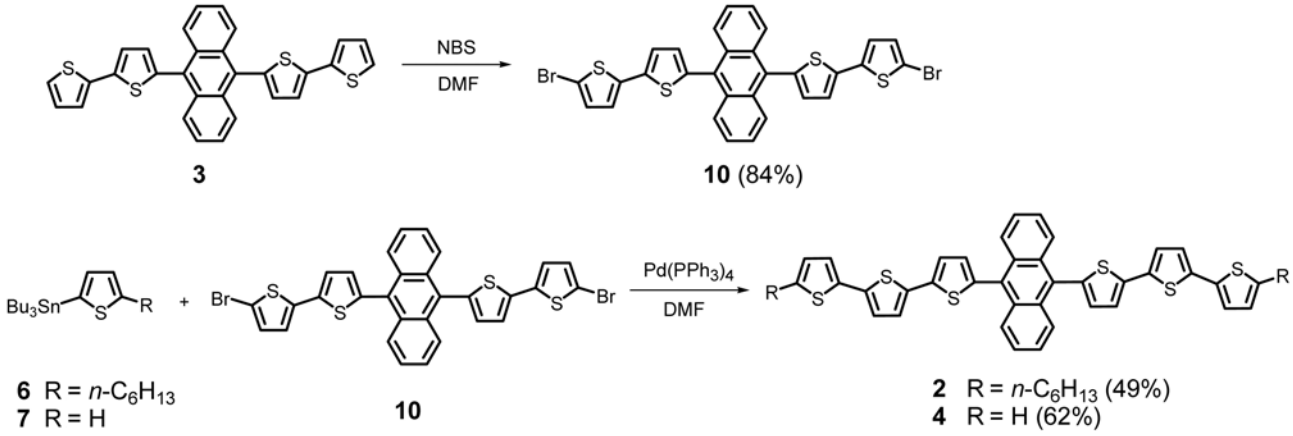
Results and Discussion

Synthesis. Scheme 2 and 3 outline the synthetic steps to prepare thiophene-anthracene oligomers **1-4**. Lithiation/stannylation reactions of thiophene and 2-hexylthiophene produce the tributylstannylthiophene **6** and **7** in excellent yields (> 90%). Stille cross-coupling reaction of the tributylstannylthiophene **7** with 9,10-dibromoanthracene using $Pd(PPh_3)_4$ as a catalyst affords bis-thienylanthracene **9** (TAT) in an excellent yield (98%) which is much greater than the reported yield[13] of Suzuki coupling reactions using 2-thiophene boronic acid (56%). Bis-bromination of **9** (TAT) with 2 equivalent of *N*-bromosuccimide (NBS) produces dibromo-TAT **10** in a very good yield (72%) without any contamination of its cumbersome monobrominated compound. Another Stille cross-coupling reaction of stannylthiophene **6** and **7** with dibromoanthracene **10** generate the target bis-thienylanthracene products **1** and **3**. Subsequent sublimations allow further purified bright yellow crystalline solid-state bis-thenylanthracene **1** and **3**. Bis-bromination reaction of **3** followed by Stille coupling reactions similar to the preparation of bis-thienylanthracene **1** and **3** yields the terthienylated anthracene **2** and **4**.

All the thiophene-anthracene oligomeric materials are soluble in chlorinated solvents and ^{1}H-NMR and ^{13}C-NMR spectra were performed in $CDCl_3$ solution at room temperature. Figure 1 shows ^{1}H-NMR spectra of two synthesized



Scheme 2. Synthesis of the thiophene-anthracene oligomers **1** and **3**.



Scheme 3. Synthesis of the thiophene-anthracene oligomers **2** and **4**.

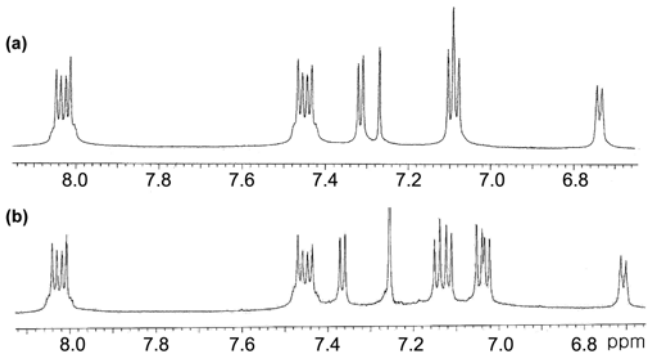


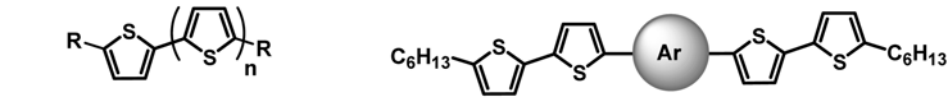
Figure 1. ^{1}H-NMR spectra of hexyl end-capped thiophene-anthracene oligomer **1** (a) and **2** (b).

hexyl end-capped thiophene-anthracenes **1** and **2**. The high resolution mass spectrometric analyses confirm that all newly synthesized compounds including target compounds **1-4** have the predicted chemical structures.

The ^{1}H-NMR spectra show multiplets in the region of 8.00-8.04 ppm for four α-H atoms of anthracene unit and another multiplets in the region of 7.42-7.46 ppm for four other H atoms which clearly support the presence of the anthracene moiety in the center of the oligomeric structures. Doublets (J = 3.3 Hz) in the region of 6.7-7.5 ppm appear for β-hydrogens of thiophenes. Along with disappearance of 113.1 and 111.2 ppm peaks for C-Br present in the ^{13}C-NMR spectra of the starting material **9** and **10**, the spectral feature of products **1-4** including appearance of new peaks in the region of 130 ppm are consistent with carbon-carbon bond formation between α-position of thiophenes.

As the number of thiophene moiety in the oligomers increases, their solubility becomes decreased. The hexyl end-capped oligomers **1** and **2** are more soluble in organic solvents than non-hexyl substituted oligomer **3** and **4** which are consistent with observations made in previous investigations.[10]

Absorption and emission properties. Optical investigation of the influence of inclusion of anthracene ring into conjugated oligothiophene molecules was made by utilizing UV-vis absorption and photoluminescence (PL) spectroscopy. The absorption and emission spectra of thiophene-anthracene oligomers **1-4**, in toluene solution and in the solid state, are depicted in Figure 2. For hexyl end-capped oligothiophenes the λ_{max} values in THF solution were previously reported to be red-shifted by about 10 nm with respect to the non-hexyl substituted counterparts (**16** (**2T**) = 304 nm, **11** (**DH-2T**) = 316 nm; **17** (**3T**) = 357 nm, **12** (**DH-3T**) = 374 nm; **18** (**4T**) = 391 nm, **13** (**DH-4T**) = 402 nm; **19** (**5T**) = 418 nm, **14** (**DH-5T**) = 426 nm; **20** (**6T**) = 436 nm, **15** (**DH-6T**) = 440 nm).[14] However, our synthesized hexyl



11 DH-2T, n = 1, R = *n*-C_6H_{13}
12 DH-3T, n = 2, R = *n*-C_6H_{13}
13 DH-4T, n = 3, R = *n*-C_6H_{13}
14 DH-5T, n = 4, R = *n*-C_6H_{13}
15 DH-6T, n = 5, R = *n*-C_6H_{13}
16 2T, n = 1, R = H
17 3T, n = 2, R = H
18 4T, n = 3, R = H
19 5T, n = 4, R = H
20 6T, n = 5, R = H

21 DH-TTPTT Ar = 1,4-benzyl
22 DH-TTPPTT Ar = 4,4'-biphenyl
23 DH-TTFTT Ar = 2,7-fluorenyl
24 DH-TTPhTT Ar = 2,7-phenanthrenyl

Scheme 4. Structure of thiophene oligomer **11**-**20** and thiophene co-oligomer **21**-**24**.

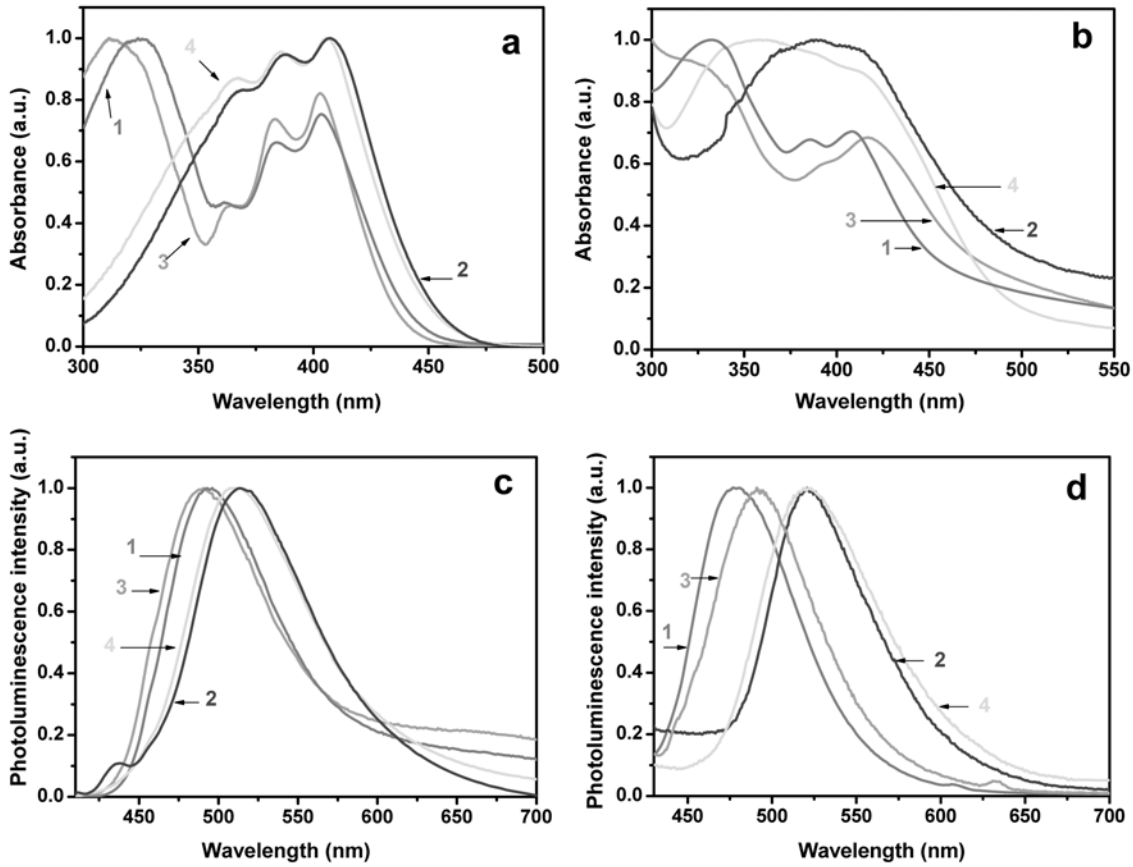


Figure 2. Optical absorption (UV-vis) of (a) toluene solution and (b) film, emission (PL) spectra of (c) toluene solution and (d) film of thienyl-anthracene oligomers (**1**: red, **2**: blue, **3**: orange, **4**: green) The PL spectra were obtained by exciting the solution at the absorption maximum. Intensities are in arbitrary units.

Table 1. Photophysical parameters of thiophene-anthracene oligomers **1**-**4**

Oligomer	Abs_{max} (nm)		PL_{max} (nm)		Φ_f [a]	τ_f(ps) [b]	k_f(s^{-1})	E_{HOMO} (eV)	E_{LUMO} (eV) [d]
	solution	film [c]	solution	film [c]					
1	403	408	493	477	4.3×10^{-3}	14	7.14×10^{10}	−5.26	−2.46
2	407	389	513	521	9.9×10^{-3}	12.5	8.00×10^{10}	−5.23	−2.50
3	403	416	491	491	3.4×10^{-3}	12.5	8.00×10^{10}	[e]	
4	406	358	510	521	7.7×10^{-3}	10.7	9.35×10^{10}	[e]	

[a]Measured using perylene as the standard (ϕ_f = 0.75).[12] [b]Monitoring wavelength is 485 nm. [c]Films were prepared by spin coating from chloroform. [d]LUMO level was derived from HOMO energy level and the optical band gap. [e]the values are not measurable due to high electrochemical reactivities leading to polymerization.[15]

end-capped thiophene-anthracene oligomers **1**-**2** and unsubstituted oligomers **3**-**4** exhibit absorption maxima in dilute toluene solution at the same wavelengths (Figure 2(a)). Compared with that of **14** (**DH-5T**), the absorption and emission maxima of 5-ring oligomer **1** in dilute solutions are blue-shifted toward higher energy by 23 nm, and they are much closer to those obtained for **13** (**DH-4T**).

When the absorption maxima of bis-bithienylanthracene **1** and **3** are compared with those of bis-terthienylanthracene **2** and **4** in solutions, their absorption maxima are red-shifted a little by 3-4 nm by increasing the number of thiophene units. However emission maxima of thiophene-anthracene oligomers are red-shifted by a larger extent 20 nm by increasing the thiophene units (Table 1) which indicate that there is a larger change in the geometry of ground and excited state in the longer oligomer **2** and **4**.

The photophysical data of the thiophene-anthracene oligomers are summarized in Table 1.

Time-resolved spectroscopic study. Since oligothiophenes are model compounds for polythiophene and show promising properties for device applications, the study of the ultrafast electronic relaxation processes attracts great interest for the understanding of their electronic behavior. Picosecond time-resolved fluorescence measurements of oligothiophenes are reported previously.[16-18] Fluorescence occurs from the lowest excited singlet state of **16** (**2T**)-**20** (**6T**) and the corresponding transitions are dipole allowed. Fluorescence lifetimes increase from about 50 ps in the case of **16**

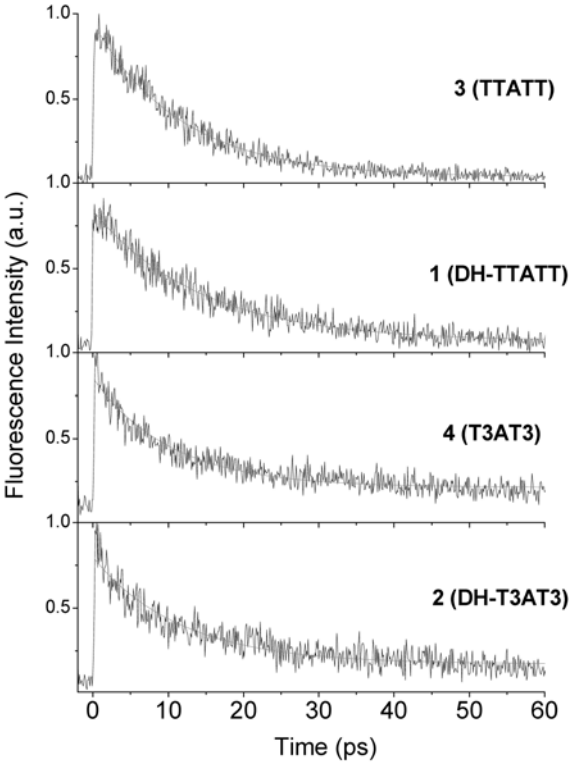


Figure 3. Temporal decay profiles of thiophene-anthracene oligomers **1**-**4**.

(**2T**), to 135 ps for **17** (**3T**), 531 ps for **18** (**4T**), 880 ps for **19** (**5T**), and 1100 ps for **20** (**6T**). The corresponding fluorescence quantum yields also increase and are reported to be 0.01 for **16** (**2T**), 0.055 for **17** (**3T**), 0.24 for **18** (**4T**), and 0.35 for **20** (**6T**). Further investigations showed that the intersystem crossing is very effective and rapid for oligothiophenes[16,17] and responsible for high nonradiative decay rates.

As a preliminary investigation, the fluorescence lifetimes of thiophene-anthracene oligomers **1-4** in the picosecond regime are measured utilizing fluorescence up-conversion method. Temporal decay profiles of thiophene-anthracene oligomer **1-4** shown in Figure 3 are obtained by monitoring their fluorescence decay at 485 nm which give the fluorescence lifetimes (τ_f) in the range of 10-14 ps (Table 1). From the fluorescence lifetime τ_f values, the deactivation rate constants k_f in toluene have been determined to be $7.14 \times 10^{10}\ s^{-1}$, $8.00 \times 10^{10}\ s^{-1}$, $8.00 \times 10^{10}\ s^{-1}$, and $9.35 \times 10^{10}\ s^{-1}$ for oligomer **1**, **2**, **3**, and **4** respectively. The fluorescence lifetime decreases and thus fluorescence deactivation rate k_f increases as the number of thiophene unit increases. The fluorescence lifetime of **2** and **4** are shorter than those of **1** and **3** and the deactivation rate constants are *vice versa*. Dihexyl end-capped thiophene-anthracene oligomers **1** and **2** have somewhat longer fluorescence lifetimes 14.0 ps and 12.5 ps comparing with those of 12.5 ps and 10.7 ps for **3** and **4** respectively. Fluorescence quantum yields (Φ_f) are observed to be very small in the range $3.4 \sim 9.9 \times 10^{-3}$. However dihexyl end-capped oligomer **1** and **2** show larger fluorescence quantum yields than unsubstituted oligomer **3** and **4**. The longer thiophene-anthracene oligomers **1** and **2** have low but twice larger quantum yields (Table 1). Interestingly the observed fluorescence lifetimes for thiophene-anthracene oligomers are much shorter than reported oligothiophenes and further the fluorescence quantum yields are also much smaller than those of oligothiophenes.[18]

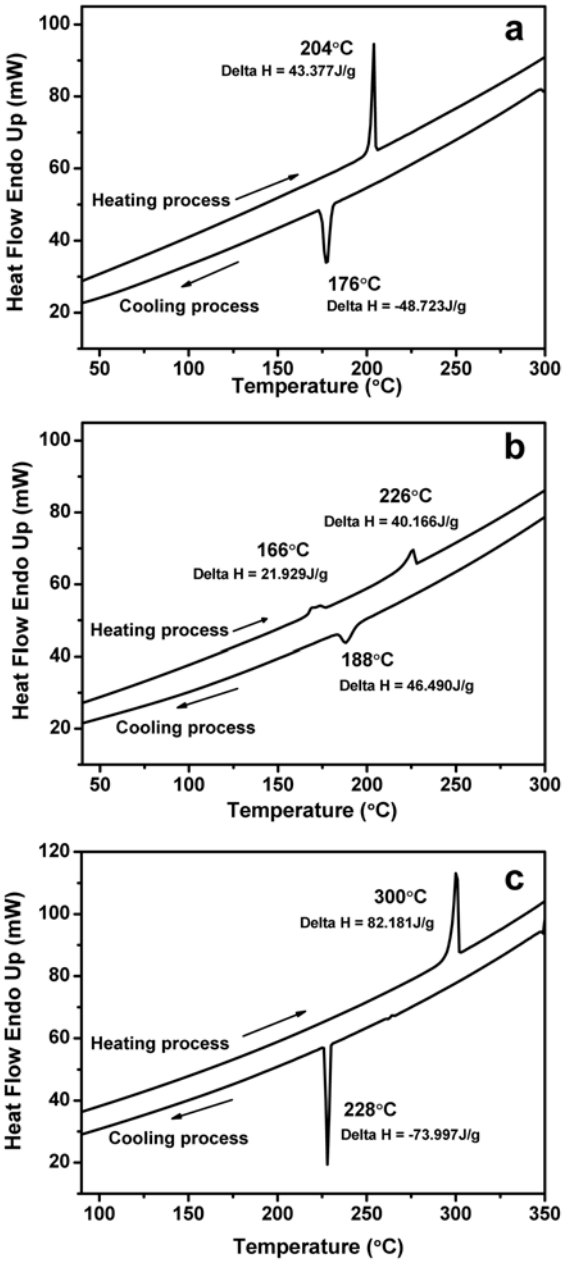


Figure 4. DSC curve of thiophene-anthracene oligomer **1** (a), **2** (b), and **3** (c).

Thermal properties. The thermal behavior of the thiophene-anthracene oligomer compounds was analyzed by DSC (Figure 4). For oligomer **1**, **2** and **3** the main endothermic peaks are detected at 204 °C, 226 °C and 300 °C, respectively which indicate that the end-capped hexyl groups lead to increase about 100 °C and the introduction of one thienyl unit at each side of the oligomeric chain results in the increase of 20 °C in the endothermic peaks. During

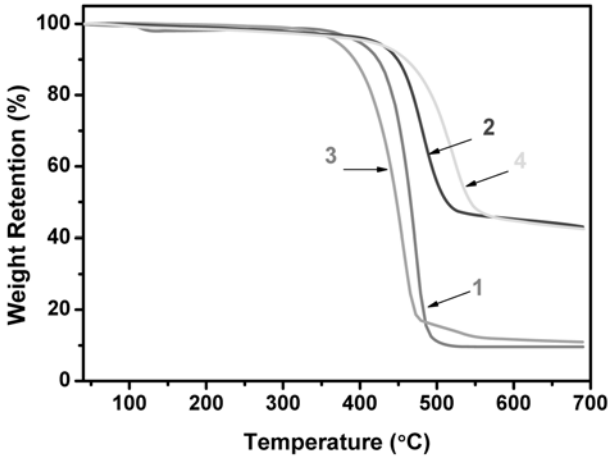


Figure 5. Thermogravimetric analysis plots for thiophene-anthracene oligomers **1**-**4**.

cooling processes the corresponding crystallization temperatures are detected to be 176 °C, 188 °C and 228 °C for oligomer **1**, **2** and **3**, respectively. Interestingly hexyl end-capped bis-terthienylanthracene oligomer **2** is observed to exhibit a liquid crystalline mesophase at 166 °C in the heating process while the shorter oligomer hexyl end-capped bis-bithienylanthracene **1** exhibits no liquid crystalline mesophase.

Thermogravimetric analyses reveal that the hexyl end-capped oligomers **1** and **2** are thermally stable up to about 400 °C which lead them to be applicable to device as a stable oligomeric material (Figure 5). The TGA thermogram of oligomer **1**, **2**, **3** and **4** revealed 5% weight loss at 398 °C, 419 °C, 369 °C and 413 °C, respectively which are much higher than the reported decomposition temperature 320 °C with α,ω-dihexylsexithiophene under similar conditions.[19] The results indicate that introduction of anthracene unit in the center of thiophene-anthracene oligomers enhances the onset decomposition temperature similarly as observed with co-oligomers containing other arene units in their center **21** (**DH-TTPTT**), **22** (**DH-TTPPTT**), **23** (**DH-TTFTT**), **24** (**DH-TTPhTT**).[20]

Electrochemical properties. The electrochemical behavior of oligomers was investigated by cyclic voltammetry to obtain their HOMO energy levels. The cyclic voltammograms were obtained from a three electrode cell in 0.1 M of TBAP in CH_2Cl_2 at the scan rate of 50 mVs^{-1}, in which the electrode cell was used with Ag/AgCl as reference electrode, platinum electrode as working electrode and Pt wire as counter electrode (Figure 6). The band gap energies of oligomer **1** and **2** between HOMO-LUMO (Table 1) are estimated to be 2.80 and 2.73 eV from the absorption end-edges of their UV-vis spectra. HOMO energy levels of oligomers **1** and **2** are derived to be −5.26 and −5.23 eV respectively by assuming that the energy of Fc/Fc^+ is 4.8 eV. Finally, their LUMO energy levels are calculated to be −2.46 and −2.50 eV from their HOMO energy levels and the optical band energy gaps (Table 1). The oligomer **1** and **2** both show one reversible oxidation wave at nearly same

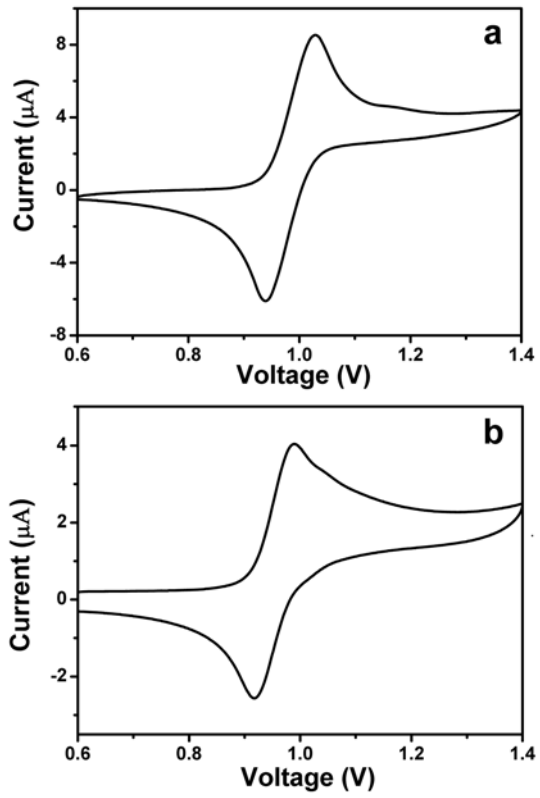


Figure 6. Cyclovoltammograms of thiophene-anthracene oligomers. (a) Bis-hexylbitheinyl-antharcene **1**, 1 mM in CH_2Cl_2, 0.1 M TBAP, $v = 50$ mVs^{-1} (b) Bis-hexylterthienylanthracene **2**, 0.5 mM in CH_2Cl_2, 0.1 M TBAP, $v = 50$ mVs^{-1}. All the potentials are quoted *vs*. the oxidation potential of ferrocene (Fc/Fc^+), −4.8 eV.

oxidation potentials at *ca.* −5.2 eV in spite that oligomer **2** contains totally two more thiophene units in the molecule comparing to the oligomer **1**. The appearance of one oxidation potentials in thiophene-anthracene oligomers **1** and **2** are different from the previously reported oxidation behavior of thiophene-arene oligomers **21** (**DH-TTPTT**), **22** (**DH-TTPPTT**), **23** (**DH-TTFTT**), **24** (**DH-TTPhTT**) which contain arene moieties other than thiophene in their center such as 1,4-phenyl, 4,4'-biphenyl, 2,7-fluorenyl, and 2,7-phenanthrenyl group. The thiophene-arene oligomers **21-24** show two reversible oxidation waves in their cyclic voltammograms yielding radical cations and dications. Although the reported thiophene-arene oligomers **21-24** behave differently giving two reversible oxidation peaks, their first oxidation potentials and their HOMO levels are in the very similar range of 0.97-1.04 eV and −5.18~−5.28 eV to those of thiophene-anthracene oligomers respectively.[20]

Summary

In summary, we have successfully synthesized a series of thiophene oligomers containing anthracene in the center of material. The target oligomers have been obtained by Stille coupling reactions as key step reactions. The synthesized thiophene-anthracene oligomers were characterized by ^{1}H-NMR, ^{13}C-NMR and high-resolution mass spectroscopy

respectively. All of the oligomers are soluble in chlorinated solvents. Their optical, thermal and electrochemical properties were measured. The hexyl end-capped oligomers and their unsubstituted oligomers exhibit the same absorption behavior in dilute toluene solution which is different from those reported for oligothiophenes. Hexyl end-capped bisterthienylanthracene oligomer is observed to show liquid crystalline mesophase at 166 °C in heating process. The thermal analyses as well as the electrochemical measurement data indicate that the designed materials show better thermal and oxidation stability than the corresponding oligothiophenes without anthracene core. Fluorescence lifetimes of the thiophene-anthracene oligomers are measured to be picosecond regime of 10-14 ps which are 5-100 times shorter than those of oligothiophenes. Further their fluorescence quantum yields are very low in the range of 3.4 ~9.9×10^{-3} and are much lower than those of oligothiophenes.

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