Articles

Synthesis and Properties of Soluble and Stable Silyl End-capped Bis-thienylanthracene Oligomers†

Jung Hei Choi, Dae Won Cho, Nam Kyoung Sung, Sung-Ho Jin,‡ and Ung Chan Yoon*

Department of Chemistry and the Center for Plastic Information System, Pusan National University, Busan 609-735, Korea
**E-mail: ucyoon@pusan.ac.kr*
‡*Department of Chemistry Education and the Center for Plastic Information System, Pusan National University, Busan 609-735, Korea*
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A series of new organic semiconductors dimethyl-*n*-octylsilyl end-capped thiophene-anthracene oligomers containing 9,10-anthracene moiety in the center have been synthesized using palladium-catalyzed Stille coupling reactions. The synthesized bis-silylated thiophene-anthracene oligomers were characterized by ^{1}H-NMR, ^{13}C-NMR and high-resolution mass spectroscopy, and are observed to have remarkably high solubility in common organic solvents. Their optical, thermal and electrochemical properties were measured. UV-vis absorption and emission spectral data on bis-silylated-, di-hexylated- and unsubstituted-thiophene-anthracene oligomers indicate that their absorption maxima are independent upon the presence of the kind of substitution in dilute solution while end-capped long-alkyl chain containing silyl groups enhance conjugation of arene backbone of the oligomers in solid film states. Absorption maxima of bis-quarterthienylanthracene in solution is closer to those obtained α,ω-dihexylsexithiophene (DH-6T). For oligomer bis-bithienylanthracene, bis-terthienylanthracene and bis-quarterthienylanthracene the main endothermic peaks are detected at 84 °C, 120 °C and 194 °C, respectively which indicate that the end-capped silyl groups lead to decrease about 100 °C comparing to the corresponding end-capped hexyl groups. Electrochemical measurements indicate that bis-silylated thiophene-anthracene oligomers have better oxidation stability than the corresponding oligothiophenes without anthracene core. Bis-quarterthienylanthracene **3** still has low HOMO level in spite that it contains totally nine arene rings in the oligomeric molecules.

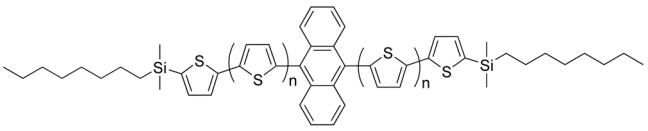
Key Words : Thiophene oligomer, Bis-oligothienylanthracene, Silyl end-capping group, Stille reaction

Introduction

Thiophene oligomers and polymers are an important class of semiconductor,[1] attracting interest in applications such as organic light-emitting diodes (OLEDs),[2] organic thin film transistors (OTFTs)[3] and photovoltaic cells.[4]

Thiophene oligomers have recently been reported to exhibit thin film mobilities,[5] particularly α,ω-dihexylsexithiophene, as high as 1.0 $cm^2V^{-1}s^{-1}$. However due to limited solubility α,ω-dihexylsexithiophene needs to perform vacuum deposition to form thin film[6] and is known to be easily oxidized because it has a narrow band gap and the less negative HOMO level.[7] The HOMO energies were modulated by introduction of phenyl, thiazole, biphenyl, fluorene, phenanthrene and anthracene ring into the thiophene oligomeric chains. Absorption measurements and electrochemical analyses indicated that all co-oligomers have wider band gap and lower HOMO levels than the corresponding thiophene oligomer, α,ω-dihexylsexithiophene.[8-10] However, most of hexyl end-capped thiophene-aryl co-oligomers have insufficient solubility for solution process. Recently we reported our investigation on the synthesis and properties of hexyl end-capped oligothienylanthracenes[10] where the hexyl end-capped oligomers exhibit the same absorption behavior in dilute solution as the unsubstituted oligomers. Further their thermal analyses and electrochemical measurements showed that the oligothienylanthracenes have better thermal and oxidation stability than oligothiophenes without anthracene core.

In present work, we designed and synthesized a series of novel bis-silylated thiophene oligomers containing anthra-



1 n = 1
2 n = 2
3 n = 3

Scheme 1. Structure of α,ω-bis-silylated thiophene-anthracene oligomers **1-3**.

†This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

cene in the center (Scheme 1). We expect that a long alkyl chain containing silyl groups might improve the material solubility and further favor the ordered arrangement of the molecules in their solid state. The effect of the structure containing a long-alkyl chain substituted silyl end-capped group on the optical properties, thermal properties, electrochemical properties of oligoarenes, bis-oligothienylanthracenes was investigated.

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 benzophenone ketyl. 9,10-Bis(5'-hexyl-2,2'-bithiophen-5-yl)anthracene (**4**), 9,10-bis(5"-hexyl-2,2':5',2"-terthiophen-5-yl)anthracene (**5**), 9,10-bis(2,2'-bithiophen-5-yl)anthracene (**6**), 9,10-bis(2,2':5',2"-terthiophen-5-yl) anthracene (**7**), 9,10-bis(2-thienyl)anthracene (**12**), 9,10-bis (5-bromo-2-thienyl)anthracene (**13**), and 9,10-bis(5'-bromo-2,2'-bithiophen-5-yl)anthracene (**14**) were synthesized according to literature procedures.[10]

^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Mercury 300 MHz spectrometer. The thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851 and DSC 822 analyzer 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 fluorescence spectrometer in toluene respectively at room temperature. The electrochemical experiments were performed using a CHI600C 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.

Synthesis of α-(dimethyl-*n*-octylsilyl)-substituted oligothiophenes 8 and 9. *n*-BuLi (2.5 M in hexane, 22 mL, 55.4 mmol) was added dropwise to a solution of thiophene or bithiophene (4.44 mL or 9.32 g, 55.4 mmol) in dry THF (100 mL) at −78 °C. The mixture was stirred at −78 °C for 30 min, followed by addition of chlorodimethyl-*n*-octylsilane (10 mL, 55.4 mmol). After stirring for 3 h at room temperature, hexanes was added to the mixture and the organic phase was washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. The remained organic residue was subjected to vaccum distillation to give product **8** (11.84 g, 84%) and was subjected to column chromatography (hexanes) to yield **9** (12.49 g, 67%) respectively as liquid.

2-(Dimethyl-*n*-octylsilyl)thiophene (8). ^{1}H-NMR ($CDCl_3$) δ 0.33 (s, 6H, -Si<u>Me</u>$_2$(CH$_2$)$_7$CH$_3$), 0.80 (t, 2H, -SiMe$_2$C<u>H</u>$_2$-(CH$_2$)$_6$CH$_3$), 0.91 (t, 3H, -SiMe$_2$(CH$_2$)$_7$C<u>H</u>$_3$), 1.20-1.42 (m, 12H, -SiMe$_2$ CH$_2$(C<u>H</u>$_2$)$_6$CH$_3$), 7.22 (dd, 1H, J = 4.8, 3.4 Hz, thiophene-H), 7.29 (dd, 1H, J = 3.4, 1.1 Hz, thiophene-H), 7.62 (dd, 1H, J = 4.8, 1.1 Hz, thiophene-H) ^{13}C-NMR ($CDCl_3$) δ −1.8, 14.2, 16.7, 22.8, 23.8, 29.3 (two carbons), 32.0, 33.6, 128.0, 130.3, 134.1, 139.0.

5-(Dimethyl-*n*-octylsilyl)-2,2'-bithiophene (9). ^{1}H-NMR ($CDCl_3$) δ 0.33 (s, 6H, -Si<u>Me</u>$_2$(CH$_2$)$_7$ CH$_3$), 0.80 (t, 2H, J = 6.5 Hz, -SiMe$_2$C<u>H</u>$_2$(CH$_2$)$_6$ CH$_3$), 0.91 (t, 3H, J = 6.5 Hz, -SiMe$_2$(CH$_2$)$_7$ C<u>H</u>$_3$), 1.20-1.42 (m, 12H, -SiMe$_2$CH$_2$(C<u>H</u>$_2$)$_6$-CH$_3$), 7.01 (dd, 1H, J = 5.0, 3.6 Hz), 7.12 (d, 1H, J = 3.6 Hz), 7.17-7.22 (m, 2H), 7.23 (d, 1H, J = 3.6 Hz) HRMS (M^+, 337.1474, Calcd 337.1474).

Synthesis of α-(tributylstannyl)-ω-(dimethyl-*n*-octylsilyl)-oligothiophenes 10 and 11. *n*-BuLi (2.5 M in hexane, 15.7 mL, 39.3 mmol) was added dropwise to a solution of α-(dimethyl-*n*-octylsilyl)-monothiophene or α-(dimethyl-*n*-octylsilyl)-bithiophene (39.3 mmol) in dry THF (100 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min, followed by addition of tributyltin chloride (10.6 mL, 39.3 mmol). After stirring for 3 h at room temperature, hexane 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 give product **10** and **11** respectively as liquid. The tributylstannyl compounds **10** and **11** were used in the Stille coupling reaction without further purification.

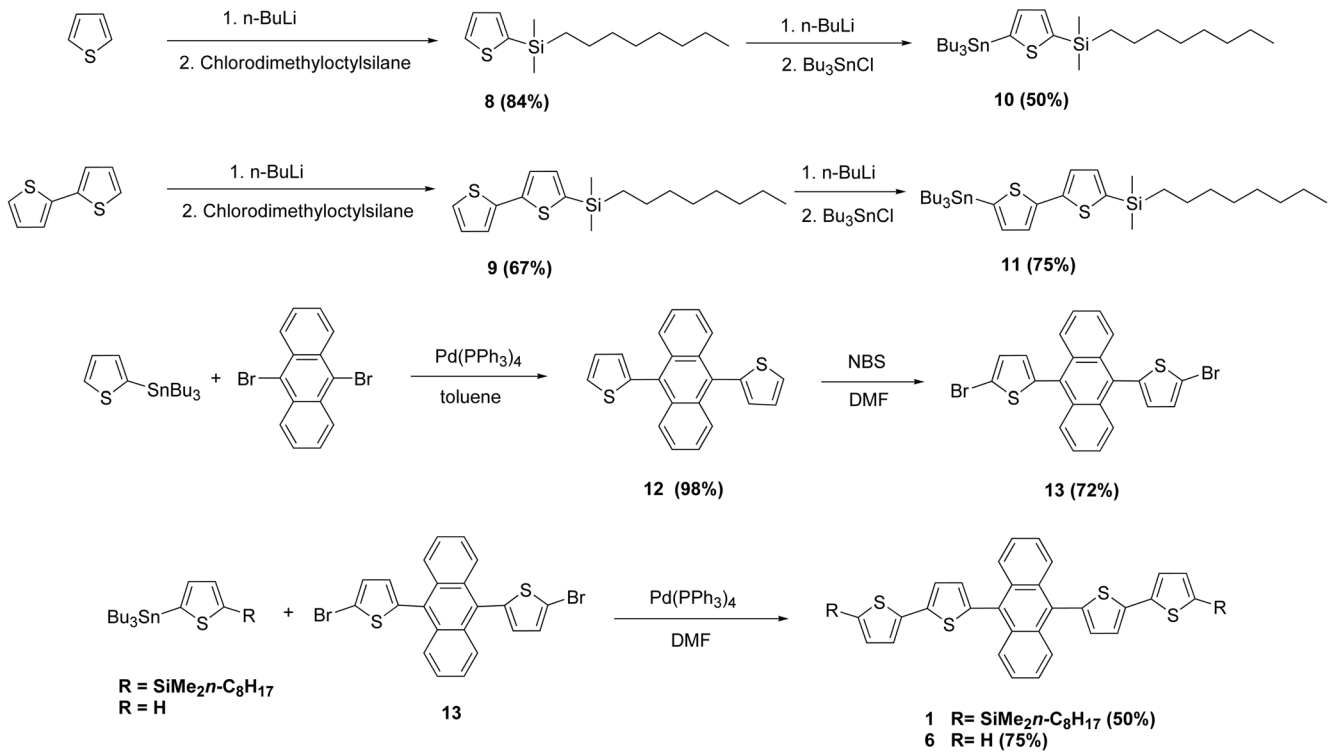
Palladium-catalyzed Stille cross-coupling reactions leading to bis-silylated thiophene-anthracene oligomers 1-3. A mixture of dibromo-TAT **13** (9.99 mmol) and α-tributylstannyl-ω-(dimethyl-*n*-octylsilyl)thiophene **10** (20.0 mmol), or dibromo-TTATT **14** (9.99 mmol) and α-tributylstannyl-ω-(dimethyl-*n*-octylsilyl)thiophene **10** (20.0 mmol), or dibromo-TTATT **14** (9.99 mmol) and α-tributylstannyl-ω-(dimethyl-*n*-octylsilyl)bithiophene **11** (20.0 mmol) containing catalyst tetrakis(triphenylphosphine)palladium(0) (0.2 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 chloroform and water. The organic layer was dried over Na_2SO_4, and concentrated *in vacuo*. The residue was then purified by column chromatography (hexane) to give solid thiophene-anthracene oligomers **1** (2.96 g, 35%), **2** (3.03 g, 30%), or **3** (3.76 g, 32%).

9,10-Bis(5'-(dimethyl-*n*-octylsilyl)-2,2'-bithiophen-5-yl)-anthracene (1). ^{1}H-NMR ($CDCl_3$) δ 0.33 (s, 12H, -Si<u>Me</u>$_2$-(CH$_2$)$_7$CH$_3$), 0.80 (t, 4H, J = 6.5 Hz, -SiMe$_2$C<u>H</u>$_2$ (CH$_2$)$_6$CH$_3$), 0.91 (t, 6H, J = 6.5 Hz, -SiMe$_2$(CH$_2$)$_7$C<u>H</u>$_3$), 1.20-1.42 (m, 24H, -SiMe$_2$CH$_2$(C<u>H</u>$_2$)$_6$ CH$_3$), 7.12 (d, 1H, J = 3.3 Hz, thiophene-H), 7.18 (d, 2H, J = 3.3 Hz, thiophene-H), 7.32 (d, 2H, J = 3.3 Hz, thiophene-H), 7.40 (d, 2H, J = 3.3 Hz, thiophene-H), 7.43-7.46 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ −1.9, 14.1, 16.6, 22.7, 23.8, 29.2 (two carbons), 31.9, 33.5, 123.8, 125.1, 125.9, 126.7, 129.9, 130.4, 131.4, 135.0, 137.8, 139.0, 139.3, 142.1 HRMS (M^+, 846.3253, Calcd 846.3267).

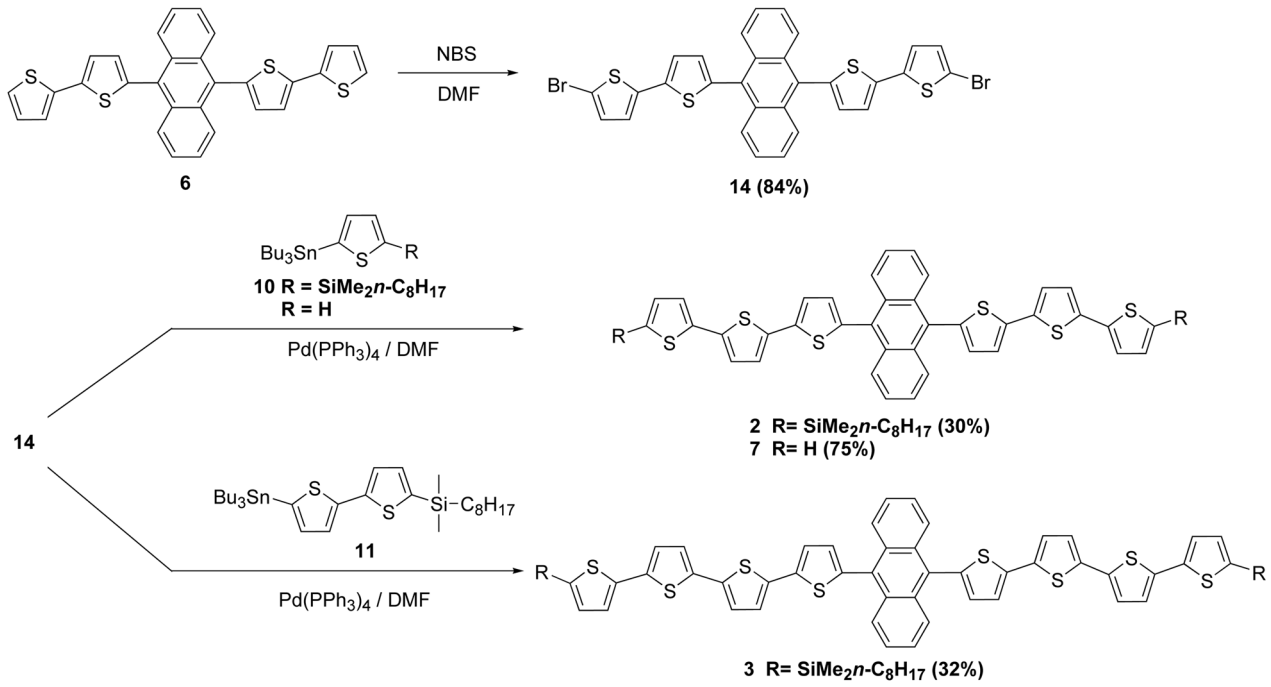
9,10-Bis(5''-(dimethyl-*n*-octylsilyl)-2,2':5',2''-terthiophen-5-yl)anthracene (2). ^{1}H-NMR ($CDCl_3$) δ 0.33 (s, 12H, -Si<u>Me</u>$_2$(CH$_2$)$_7$CH$_3$), 0.80 (t, 4H, J = 6.5 Hz, -SiMe$_2$C<u>H</u>$_2$ (CH$_2$)$_6$CH$_3$), 0.90 (t, 6H, J = 6.5 Hz, -SiMe$_2$(CH$_2$)$_7$C<u>H</u>$_3$), 1.20-1.42 (m, 24H, -SiMe$_2$CH$_2$(C<u>H</u>$_2$)$_6$ CH$_3$), 7.02-7.18 (m,

8H, thiophene-H), 7.28 (d, 2H, J = 3.3 Hz, thiophene-H), 7.38 (d, 2H, J = 3.3 Hz, thiophene-H), 7.43-7.46 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ −1.9, 14.1, 16.5, 22.7, 23.8, 29.2 (two carbons), 31.9, 33.5, 123.6, 124.4 (d), 125.0, 125.9, 126.6, 129.8, 130.5, 131.4, 135.0, 135.9, 136.5, 137.9, 138.8, 139.3, 142.1 HRMS (M^+, 1010.3063, Calcd 1010.3027).

9,10-Bis(5'''-(dimethyl-*n*-octylsilyl)-2,2':5',2'':5'',2'''-quarterthiophen-5-yl)anthracene (3). ^{1}H-NMR ($CDCl_3$) δ 0.33 (s, 12H, -Si<u>Me</u>$_2$(CH_2)$_7$$CH_3$), 0.80 (t, 4H, J = 6.5 Hz, -SiMe$_2$C<u>H</u>$_2$ (CH_2)$_6$$CH_3$), 0.90 (t, 6H, J = 6.5 Hz, -SiMe$_2$-(CH_2)$_7$C<u>H</u>$_3$), 1.20-1.43 (m, 24H, -SiMe$_2$$CH_2$($C\underline{H}_2$)$_6$ CH_3), 7.09-7.16 (m, H, thiophene-H), 7.18 (d, 2H, J = 3.6 Hz, thiophene-H), 7.25 (d, 2H, J = 3.6 Hz, thiophene-H), 7.37-



Scheme 2. Synthesis of the bis-silylated thiophene-anthracene oligomers **1**.



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

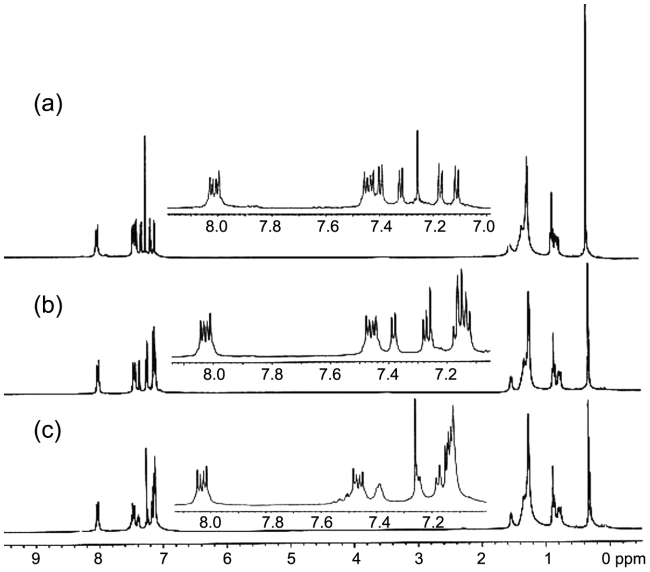


Figure 1. ^{1}H-NMR spectra of silyl end-capped thiophene-anthracene oligomer **1** (a), **2** (b) and **3** (c).

7.41 (m, 2H, thiophene-H), 7.43-7.46 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) ^{13}C-NMR ($CDCl_3$) δ −1.9, 14.1, 16.5, 22.7, 23.8, 29.2 (two carbons), 31.9, 33.4, 123.8, 124.3, 124.4 (two peaks), 124.5, 125.0, 126.0, 126.6, 129.8, 130.5, 131.4, 135.0, 135.8, 136.0, 136.2, 136.5, 138.0, 138.7, 139.5, 142.0 HRMS (M^+, 1174.2773, Calcd 1174.2782).

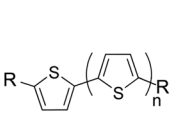
Results and Discussion

Synthesis. The route to synthesize bis-silylated thiophene-anthracene oligomers **1-3** is depicted in Scheme 2 and 3. The mono-silylated thiophene **8** and 2,2'-bithiophene **9** were prepared from the commercially available thiophene and 2,2'-bithiophene in 84% and 67% yields respectively by a sequence involving *n*-BuLi lithiation at −78 °C, followed by silylation with chlorodimethyl-*n*-octylsilane at room temperature. Lithiation/stannylation of compound **8** and **9** produce the tributylstannylthiophene **10** and **11** in moderate yields (50-75%). The syntheses of bis-silylated thiophene-anthracene oligomers **1**, **2** and **3** involved Stille coupling reaction between the dibromo-TAT **13** or dibromo-TTATT **14** and α-tributylstannyl-ω-(dimethyl-*n*-octylsilyl)oligothiophene **10** or **11** (Scheme 2 and 3). All the silylated thiophene-anthracene oligomers are highly soluble in common organic solvents such as hexanes and chloroform to allow column chromatography. The ^{1}H-NMR and ^{13}C-NMR spectra of all the thiophene-anthracene oligomers were performed in $CDCl_3$ solution at room temperature. Figure 1 shows ^{1}H-NMR spectra of three synthesized silyl end-capped thiophene-anthracenes **1**, **2** and **3**. Their ^{1}H-NMR and ^{13}C-NMR spectra along with high resolution mass spectrometric data confirm that all newly synthesized compounds including target compounds **1-3** have the predicted chemical structures and high degree of purity.

The ^{1}H-NMR spectra of the silylated oligomers **1-3** show multiplets in the region of 8.00-8.04 ppm for four α-H atoms of anthracene unit and additional multiplets in the region of 7.42-7.48 ppm for four other H atoms of the anthracene which clearly support the presence of the anthracene moiety in the center of the oligomeric structures. ^{1}H-NMR spectrum of the bis-silylated bithienyl antharcene **1** contains four doublets (J = 3.3-3.6 Hz) in the region of 7.1-7.4 ppm characteristic to four β-hydrogens of the bithiophene moiety. As the number of thiophene units increases in the oligomers **2** and **3**, additional peaks for the increased β-hydrogens of elongated thiophene moiety appear in the region of 7.1-7.4 ppm. Six methyl hydrogens attached to the silicon atom appear at 0.33 ppm. Along with disappearance of 113.1 and 111.2 ppm peaks for C-Br present in the ^{13}C-NMR spectra[10] of the starting material **13** and **14**, the spectral feature of products **1-3** including appearance of new peaks in the region of 130 ppm are consistent with carbon-carbon bond formation between α-position of thiophenes.

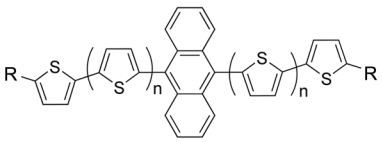
Although the solubility become decreased as the number of thiophene moiety in the oligomers increases,[10] the synthesized silyl end-capped oligomers **1-3** are highly soluble in non-polar organic solvent, hexanes and chlorinated solvent, chloroform. Further the silyl end-capped oligomers **1-2** are observed to be more soluble than their corresponding hexyl substituted oligomers **4-5**, and to be even more soluble than unsubstituted oligomers **6-7**. Especially, silyl end-capped oligomer **1** and **2** are highly soluble in hexane and are expected to be applicable to a solution process for thin film preparation.

Absorption and emission properties. The absorption and emission spectra of bis-silylated thiophene-anthracene oligomers **1-3** are measured in toluene solution and in the solid state. The spectra are shown in Figure 2 and their absorption maxima are summarized in Table 1. 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 (**15** = 304 nm, **20** = 316 nm; **16** = 357 nm , **21** = 374 nm; **17** = 391 nm, **22** = 402 nm; **18** = 418 nm, **23** = 426 nm; **19** = 436 nm, **24** = 440 nm).[11]



15 n = 1, R= H
16 n = 2, R= H
17 n = 3, R= H
18 n = 4, R= H
19 n = 5, R= H

20 n = 1, R= n-C_6H_{13}
21 n = 2, R= n-C_6H_{13}
22 n = 3, R= n-C_6H_{13}
23 n = 4, R= n-C_6H_{13}
24 n = 5, R= n-C_6H_{13}



4 n = 1, R= n-C_6H_{13}
5 n = 2, R= n-C_6H_{13}
6 n = 1, R= H
7 n = 2, R= H

However, our synthesized thiophene-anthracene oligomers exhibit absorption maxima in dilute solution at the same wavelengths regardless of kind of substitution at α- and ω-position of the oligomers as seen in examples of bis-bithienylanthracenes **1**, **4** and **6**, and in those of bis-tertienylanthracenes **2**, **5** and **7**. The absorption and emission

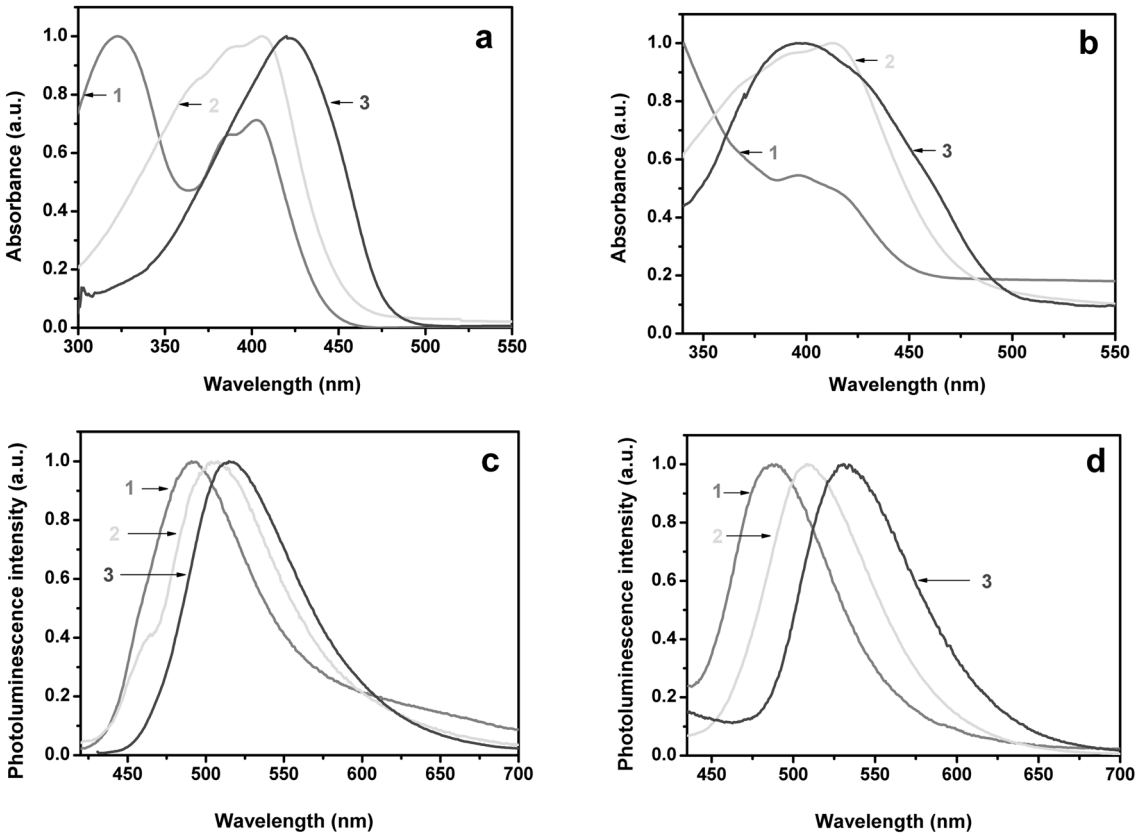


Figure 2. Optical absorption (UV-vis) of (a) toluene solution and (b) film, emission (PL) spectra of (a) toluene solution and (b) film of thienyl-anthracene oligomers (**1**: red, **2**: green, **3**: blue). The PL spectra were obtained by exciting the solution at the absorption maximum. Intensities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

Table 1. Photophysical data of oligomer **1-7**

Oligomer	Abs_{max} (nm)		PL_{max} (nm)	
	solution	film	solution	film
1	403	397	491	487
2	406	413	509	508
3	422	397	515	531
4	403	408	493	477
5	407	389	513	521
6	403	416	491	491
7	406	358	510	521

maxima of five-arene ring oligomers **1**, **4**, and **6** in dilute solutions are blue-shifted toward higher energy by 15-23 nm comparing with those of five-ring oligothiophenes **18** and **23** and they are much closer to those obtained for α,ω-dihexylquarterthiophene (**22**). When the absorption maxima of bis-bithienylanthracene **1**, **4**, and **6** are compared with those of bis-terthienylanthracene **2**, **5** and **7** in solutions, their absorption maxima are red-shifted only a little by 3-4 nm by increasing the number of thiophene units. However, absorption maxima of total nine-arene ring bis-quarter-thienylanthracene **3** in solution becomes red-shifted in a larger extend by 16 nm, and they are closer to those obtained from α,ω-dihexylsexithiophene (**24**). In contrast to the absorption behaviors of bis-thiophene-anthracene oligomers observed in solutions, their absorption maxima in solid film states undergo significant variations depending upon both the kind of substitution at α- and ω-position of the oligomers, and the number of thiophene units present in the oligomers (Table 1). Absorption maxima are red-shifted by 8-10 nm for bis-bithienylanthracenes, **1**, **4**, and **6** (**1** = 397 nm, **4** = 408 nm, **6** = 416 nm) while those show large blue-shift by 24-31 nm in bis-terthienylanthracenes, **2**, **5** and **7** (**2** = 413 nm, **5** = 389 nm, **7** = 358 nm). The variations which are observed respectively in a opposite way in the absorption maxima in the series of bithienylanthracenes and terthienyl-antharacenes provide some information about the effect of substitution group at α and ω position of the oligomers on packing of their oligomeric molecules in their solid film states. Steric hindrance caused by terminal substituents, dimethyl-*n*-octylsilyl-, and *n*-hexyl-group cause a reduction in conjugation of the short backbone of bis-bithienylanthracenes in such tight solid states. On the other hand non-polar long alkyl chains present in the terminal dimethyl-*n*-octyl-silyl-, and *n*-hexyl- groups lead to stronger aggregation of bis-terthienylanthracene oligomers **2**, **5** and **7** as a consequence of hydrophobic-lipophilic interactions that exist between alkyl chains, and thus the stronger aggregations lead to increased conjugation of the longer backbone of bis-terthienylanthracenes than those of bis-buthienylanthracenes. Interestingly our synthesized silyl end-capped thiophene-anthracene oligomers **1-3** show no or some red-shift in their absorption maxima in their solid states while the correspond-

ing hexyl substituted and unsubstituted derivative exhibit very significant hypsochromic shifts in their absorption maxima in the solid states by increasing the number of thiophene units in the oligomers.

Emission maxima of bis-silylated thiophene-anthracene oligomers **1-3** are red-shifted by a larger extent 16-18 nm in solutions and by 21 nm in solid states by increasing the thiophene units similarly to those previously observed in di-hexyl substituted- and unsubstituted-derivatives which indicate that there is a larger change in the geometry of ground and excited states of the oligomers. In a similar manner to the absorption maxima of thiophene-anthracene oligomers in solution, there are no large shift in their emission maxima in solutions upon the presence and kind of substitution at the end positions of thiophene-anthracene oligomers. However noticeable shifts in emission maxima in their more compact solid-film states are observed depending on the presences and kind of substitution groups in the oligomers which indicate that steric and hydrophobic-lipophilic interactions caused by long chain containing substituted groups are more pronounced in their solid states and affect more on the geometry of ground and excited states.

Thermal properties. The thermal stability of the thiophene-anthracene oligomer compounds was determined by using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure 3). For oligomers **1**, **2** and **3** the main endothermic peaks are detected at 84 °C, 120 °C and 194 °C, respectively. The melting point of bis-silylated oligothienylanthracenes are 100 °C lower than those of the hexyl end-capped counterparts (**4** = 174 °C: **5** = 184 °C).[10] During cooling processes the corresponding crystallization temperatures are detected to be 57 °C, 89 °C and 132 °C for oligomers **1**, **2** and **3** respectively. No phase transitions were observed for all oligomers.

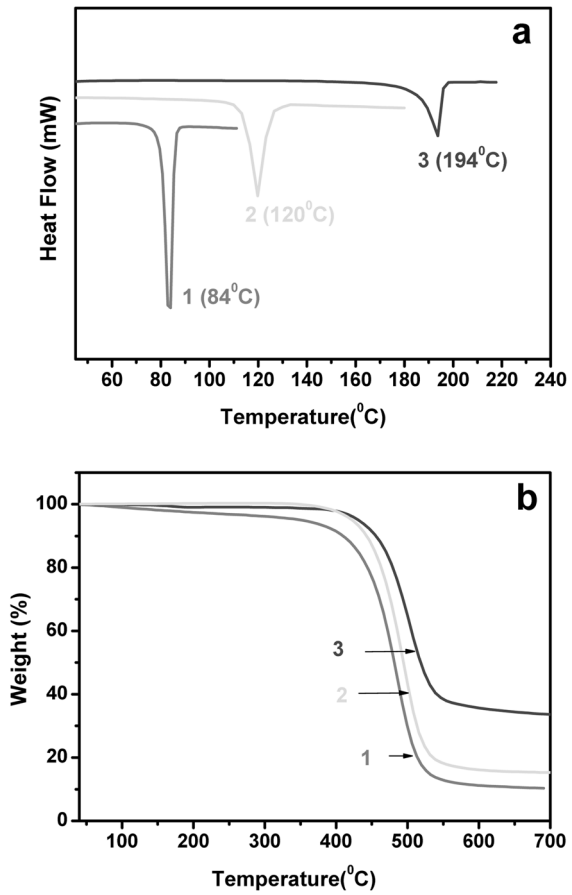


Figure 3. (a) DSC curve of thiophene-anthracene oligomers **1-3**. (b) TGA plots for thiophene-anthracene oligomers **1-3**.

The TGA thermograms of oligomers **1**, **2** and **3** revealed that 5% weight losses occurs at 353 °C, 416 °C and 431 °C, respectively which are much higher than the reported decomposition temperature 320 °C with α,ω-dihexylsexithiophene under similar conditions[12] but are comparable with those observed with the hexyl end-capped derivatives (**4** = 398 °C: **5** = 419 °C).[10] The results indicate that introduction of anthracene unit in the center of thiophene-anthracene oligomers enhances the onset decomposition temperature similarly as observed with thiophene-aryl co-oligomers.[9]

Electrochemical properties. The electrochemical behavior of the bis-silylated thiophene-anthracene oligomers was investigated by using cyclic voltammetry. A three electrode cell used to make measurement on substrates in 0.1 M of TBAP in CH_2Cl_2 at a scan rate of 50 mVs^{-1}. For this purpose, Ag/AgCl was employed as the reference electrode, a platinum electrode as working electrode, and a Pt wire as counter electrode (Figure 4). The band gap energies of oligomer **1**, **2** and **3** between HOMO-LUMO levels are estimated to be 2.81, 2.74 and 2.60 eV from the absorption end-edges of their UV-vis spectra. The HOMO energy levels of the bis-silylated thiophene-anthracene oligomers **1**, **2** and **3** were determined to be −5.32, −5.25 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 −2.51, −2.51 and −2.63 eV from their HOMO energy levels and the optical band energy gaps (Table 2). The bis-silylated oligomers **1-3** show one reversible oxidation wave. The oxidation potentials are measured to be a little but not significantly lowered by 0.3-0.5 eV as the number of thiophene unit increases as seen in the case of bis-silylated oligomers **1**, **2** and **3**, and di-hexylated oligomers **4** and **5** in spite that there are totally two more thiophene units increase in the molecules.

The cyclic voltammograms of unsubstituted thiophene-anthracene oligomers **6** and **7** measured in CH_2Cl_2 are shown in Figure 4d and 4e. Thiophene oligomers which have no substituents at α- and ω-position of the oligomers undergo reactions to form their dimers or polymers under the electrochemical measurement conditions due to high electrochemical reactivity of thiophene ring at terminal positions.[13] However cyclic voltammograms of unsubstituted thiophene-anthracene oligomers **6** and **7** which exhibit reversible oxidation waves are not significantly changed upon about twenty times of repetitive scans. The results indicate that oligothiophenes containing a anthracene unit in the center are electrochemically stable and have still low HOMO levels as expected from the previously reported investigations.[9]

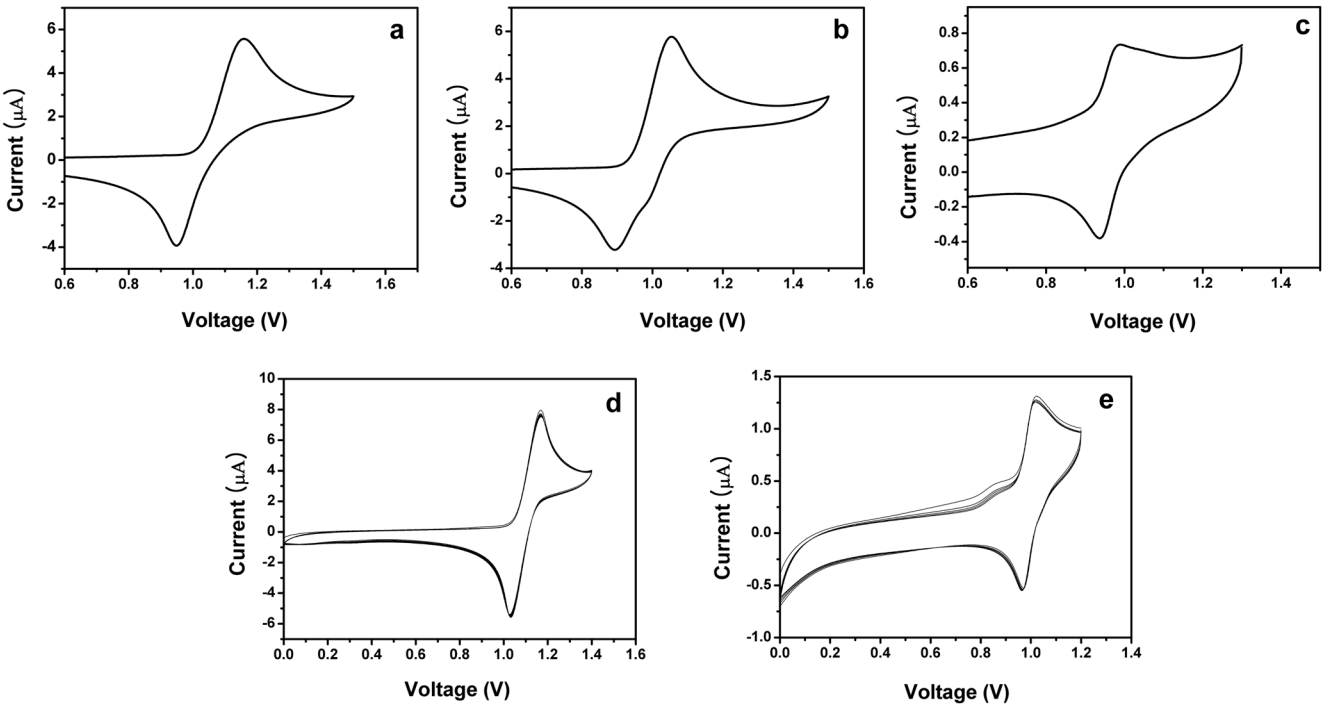


Figure 4. Cyclovoltammograms of thiophene-anthracene oligomers in CH_2Cl_2, 0.1 M TBAP, v = 50 mVs^{-1}. (a) bis-silylbithienyl-antharcene **1**, (b) bis-silylterthienylanthracene **2**, (c) bis-silylquarterthienylanthracene **3**, (d) bithienylanthracene **6**, twenty times repetitive scans (e) terthienyl-anthracene **7**, twenty times repetitive scans. All the potentials are quoted vs. the oxidation potential of ferrocene (Fc/Fc^+), –4.8 eV.

Table 2. Energy levels and band gaps determined from the optical and electrochemical measurements of the thiophene-anthracene oligomers.

Compound	Oxidation			E_g^{op}	E_{HOMO}	E_{LUMO}
	Anodic	Cathodic	Half			
1	1.10	0.98	1.04	2.81	–5.32	–2.51
2	1.06	0.89	0.98	2.74	–5.25	–2.51
3	0.98	0.93	0.95	2.60	–5.23	–2.63
4	1.09	0.92	1.00	2.80	–5.26	–2.46
5	0.99	0.92	0.95	2.73	–5.23	–2.50
6	1.18	1.03	1.10	2.84	–5.36	–2.52
7	1.02	0.96	0.99	2.77	–5.27	–2.50

Summary

In summary, we have successfully synthesized a series of new bis-silylated thiophene oligomers containing a anthracene unit in the center of oligomers by Stille coupling reactions. All the oligomers are highly soluble in common organic solvents to allow column chromatography. The synthesized bis-silylated thiophene-anthracene oligomers were characterized by ^{1}H-NMR, ^{13}C-NMR and high-resolution mass spectroscopy. Their optical, thermal and electrochemical properties were measured.

The silyl end-capped thiophene-anthracene oligomers **1**-**3** are more soluble in organic solvents than their corresponding hexyl end-capped oligomers **4** and **5**. Especially, silyl end-capped oligomer **1** and **2** are highly soluble in non-polar solvent hexane. For bis-silylated oligomers, bis-bithienylanthracene **1**, bis-terthienylanthracene **2** and bis-quarterthienylanthracene **3** the main endothermic peaks are detected at 84 °C, 120 °C and 194 °C, respectively which indicate that the melting points of silyl end-capped oligomers are lower about 100 °C than the corresponding hexyl end-capped derivatives. The TGA thermograms of thiophene-antharcene oligomers **1**, **2** and **3** revealed 5% weight loss at 353 °C, 416 °C and 431 °C, respectively which are much higher than those of the corresponding oligothiophenes. The results indicate that introduction of anthracene unit in the center of thiophene-anthracene oligomers enhances the onset decomposition temperature similarly as observed with thiophene-aryl co-oligomers.

Electrochemical measurements indicate that bis-silylated thiophene-anthracene oligomers have better oxidation stability than the corresponding oligothiophenes without anthracene core. Bis-quarterthienylanthracene **3** still has low HOMO level in spite that it contains totally nine arene rings in the oligomeric molecules.

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