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

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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 1H-NMR, 13C-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 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, attracting interest in applications such as organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs) and photovoltaic cells. Thiophene oligomers have recently been reported to exhibit thin film mobilities, particularly α,ω-dihexylsexithiophene, as high as 1.0 cm2V−1s−1. However due to limited solubility α,ω-dihexylsexithiophene needs to perform vacuum deposition to form thin film and is known to be easily oxidized because it has a narrow band gap and the less negative HOMO level. 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. 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 oligothiophenylanthracenes 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 oligothiophenylanthracenes 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-
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-oligothiophenylanthracenes 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 keyl. 9,10-Bis(5'-hexyl-2,2'-bithiophen-5-y)anthracene (4), 9,10-bis(5'-hexyl-2,2':5',2'-terthiophen-5-y)anthracene (5), 9,10-bis(2,2'-bithiophen-5-y)anthracene (6), 9,10-bis(2,2':5',2'-terthiophen-5-y)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-bithiophen-5-y)anthracene (14) were synthesized according to literature procedures. 31

1H-NMR and 13C-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 N2 atmosphere at a rate of 10 °C/min. The absorption and photo luminescence (PL) spectra were measured by using a Jasco V-570 UV-vis spectrometer and a Hitachi F-4500 fluorescence spectrometer in toluene respectively at room temperature. The electrochemical experiments were performed using a CHI660C 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 tetraetyl ammonium perchlorate (Bu4NClO4, TBAP) and dichloromethane (Aldrich, HPLC grade) as supporting electrolyte. Experiments were performed at room temperature.

**Synthesis of α-(dimethyl-n-octysilyl)-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 bi thiophene or dibithiophene (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-octysilane (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 Na2SO4 and concentrated in vacuo. The remaining organic residue was subjected to vacuum distillation to give product 8 (11.84 g, 84%) and was subjected to column chromatography (hexane) to yield 9 (12.49 g, 67%) respectively as liquid.

**2-(Dimethyl-n-octysilyl)thiophene (8).** 1H-NMR (CDCl3) δ 0.33 (s, 6H, -SiMe(CH2)3CH3), 0.80 (t, 2H, -SiMe(CH2)3CH3), 0.91 (t, 3H, -SiMe(CH2)3CH3), 1.20-1.42 (m, 12H, -SiMe2CH2(CH2)3CH3), 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) 13C-NMR (CDCl3) 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-octysilyl)-2,2'-bithiophene (9).** 1H-NMR (CDCl3) δ 0.33 (s, 6H, -SiMe(CH2)3CH3), 0.80 (t, 2H, J = 6.5 Hz, -SiMe2CH2(CH2)3CH3), 0.91 (t, 3H, J = 6.5 Hz, -SiMe2CH2(CH2)3CH3), 1.20-1.42 (m, 12H, -SiMe2CH2(CH2)3CH3), 7.01 (dd, 1H, J = 5.0, 3.6 Hz), 7.12 (d, 1H, J = 3.6 Hz) HRMS (M+ 337.1474, Calcd 337.1474).

**Synthesis of α-(tributylstannyl)-ω-(dimethyl-n-octysilyl)-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-octysilyl)-monothiophene or α-(dimethyl-n-octysilyl)-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 Na2SO4 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-TTA (9.99 mmol) and α-tributylstannyl-ω-(dimethyl-n-octysilyl)thiophene 10 (20.0 mmol), or dibromo-TTA-TAT (9.99 mmol) and α-tributylstannyl-ω-(dimethyl-n-octysilyl)thiophene 10 (20.0 mmol), or dibromo-TTA-TAT (9.99 mmol) and α-tributylstannyl-ω-(dimethyl-n-octysilyl)thiophene 11 (20.0 mmol) containing catalyst tetraakis(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 Na2SO4 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-octysilyl)-2,2'-bithiophene (1).** H-NMR (CDCl3) δ 0.33 (s, 12H, -SiMe(CH2)3CH3), 0.80 (t, 4H, J = 6.5 Hz, -SiMe2CH2(CH2)3CH3), 0.91 (t, 6H, J = 6.5 Hz, -SiMe2CH2(CH2)3CH3), 1.20-1.42 (m, 24H, -SiMe2CH2(CH2)3CH3), 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), 7.40-7.46 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) 13C-NMR (CDCl3) 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-octysilyl)-2,2'-5',2''-terthiophen-5-y)anthracene (2).** H-NMR (CDCl3) δ 0.33 (s, 12H, -SiMe2CH2(CH2)3CH3), 0.80 (t, 4H, J = 6.5 Hz, -SiMe2CH2(CH2)3CH3), 0.90 (t, 6H, J = 6.5 Hz, -SiMe2CH2(CH2)3CH3), 1.20-1.42 (m, 24H, -SiMe2CH2(CH2)3CH3), 7.02-7.18 (m, 12H, J = 3.3 Hz, thiophene-H), 7.32 (d, 2H, J = 3.3 Hz, thiophene-H), 7.40-7.46 (m, 4H, ArH), 8.00-8.04 (m, 4H, ArH) 13C-NMR (CDCl3) 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).
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) 13C-NMR (CDCl\textsubscript{3}) \(\delta\) 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\textsuperscript{+}, 1010.3063, Calcd 1010.3027).

9,10-Bis(5''-((dimethyl-\(n\)-octylsilyl)-2,2':5',2''-quartertothiophen-5-ylandanthracene (3). \(\text{^1H-NMR (CDCl}_3\text{)} \delta\) 0.33 (s, 12H, -SiMe\textsubscript{2}(CH\textsubscript{2})\textsubscript{7}CH\textsubscript{3}), 0.80 (t, 4H, J = 6.5 Hz, -SiMe\textsubscript{2}CH\textsubscript{2}(CH\textsubscript{2})\textsubscript{6}CH\textsubscript{3}), 0.90 (t, 6H, J = 6.5 Hz, -SiMe\textsubscript{2}- (CH\textsubscript{2})\textsubscript{4}CH\textsubscript{3}), 1.20-1.43 (m, 24H, -SiMe\textsubscript{2}- (CH\textsubscript{2})\textsubscript{6}CH\textsubscript{3}), 7.09-7.16 (m, 1H, 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.
tributylstannyl-chrom atography. The solvents such as hexanes and chloroform to allow column anthracene oligomers are highly soluble in common organic or
doubles \( (J = 3.3-3.6 \text{ Hz}) \) in the region of 7.1-7.4 ppm characteristic to four \( \beta \)-hydrogens of the bithiophene moiety. As the number of thiophene units increases in the oligomers 2 and 3, additional peaks for the increased \( \beta \)-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 \( ^{13} \text{C-NMR} \) 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 \( \alpha \)-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 \( \lambda_{\text{max}} \) 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; \( \lambda_{\text{max}} = 357 \text{ nm} \); \( \lambda_{\text{max}} = 391 \text{ nm} \)) for hexyl end-capped oligothiophenes. The \( \lambda_{\text{max}} \) 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; \( \lambda_{\text{max}} = 357 \text{ nm} \); \( \lambda_{\text{max}} = 391 \text{ nm} \)) for hexyl end-capped oligothiophenes.

\( ^{1} \text{H-NMR} \) spectra of all synthesized bis-silylated bithiophene anthracene 1 contains four \( \alpha \)-hydrogens of the bithiophene moiety. The synthesis of bis-silylated thiophene-anthracene oligomers 1-3 involved Stille coupling reaction between the dibromo-TAT or dibromo-TTAT and silylend-capped oligothiophenes. \( \alpha \)-silyl end-capped oligomers are highly soluble in common organic solvents such as hexanes and chloroform to allow column chromatography. The \( ^{1} \text{H-NMR} \) and \( ^{13} \text{C-NMR} \) spectra of all the thiophene-anthracene oligomers were performed in CDCl\(_3\) solution at room temperature. Figure 1 shows \( ^{1} \text{H-NMR} \) spectra of three synthesized silyl end-capped thiophene-anthracenes 1, 2 and 3. Their \( ^{1} \text{H-NMR} \) and \( ^{13} \text{C-NMR} \) 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 \( ^{1} \text{H-NMR} \) spectra of the silylated oligomers 1-3 show multiplets in the region of 8.00-8.04 ppm for four \( \alpha \)-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. The \( ^{1} \text{H-NMR} \) spectrum of the bis-silylated bithiophenyl anthracene 1 contains four doublets \( (J = 3.3-3.6 \text{ Hz}) \) in the region of 7.1-7.4 ppm characteristic to four \( \beta \)-hydrogens of the bithiophene moiety. As the number of thiophene units increases in the oligomers 2 and 3, additional peaks for the increased \( \beta \)-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 \( ^{13} \text{C-NMR} \) 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 \( \alpha \)-position of thiophenes.
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 \( \alpha, \omega \)-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-quarterthiophene 3 in solution becomes red-shifted in a larger extend by 16 nm, and they are closer to those obtained from \( \alpha, \omega \)-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 \( \alpha \) and \( \omega \)-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 an opposite way in the absorption maxima in the series of bithienylanthracenes and terthienylanthracenes provide some information about the effect of substitution group at \( \alpha \) and \( \omega \) 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-\( n \)-octylsilyl-, 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-bithienylanthracenes. Interestingly our synthesized silyl end-capped thiopheneanthracene oligomers 1-3 show no or some red-shift in their absorption maxima in their solid states while the correspond-

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

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<th>Oligomer</th>
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<th>( \text{PL}_{\text{max}} ) (nm)</th>
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<td>7</td>
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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 dihexyl 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 oligothiophenylanthracenes are 100 °C lower than those of the hexyl end-capped counterparts (4 – 174 °C; 5 – 184 °C). 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.

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 but are comparable with those observed with the hexyl end-capped derivatives (4 – 398 °C; 5 – 419 °C). 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 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 CH₂Cl₂ 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 Fe/Fe⁺ 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 CH₂Cl₂ 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. 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.
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-anthracene 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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