Article

Copyright © 2016 American Scientific Publishers
All rights reserved
Printed in the United States of America

Journal of
Nanoscience and Nanotechnology
Vol. 16, 910–919, 2016
www.aspbs.com/jnn

Novel Organic Semiconductors Based on Phenyl and Phenylthienyl Derivatives for Organic Thin-Film Transistors

Eunsoo Lee[1,†], Bodakuntla Thirupathaiah[2,†], Jaeuk Han[1], Dahae Jung[1], Guhyun Kwon[1],
Choongik Kim[1,*], and SungYong Seo[2,*]

[1] *Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Korea*
[2] *Department of Chemistry, Pukyong National University, Busan 608-737, Korea*

New phenyl and phenylthienyl derivatives end-functionalized with carbazole and α-carboline, 9-(4-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole, 9-(4-(9*H*-carbazol-9-yl)phenyl)-9*H*-pyrido[2,3-*b*]indole, 9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole, 9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-pyrido[2,3-*b*]indole, 9-(4-(5-(9*H*-carbazol-9-yl)thiophen-2-yl)phenyl)-9*H*-carbazole, and 9-(3-(5-(9*H*-carbazol-9-yl) thiophen-2-yl)phenyl)-9*H*-carbazole were synthesized and characterized as organic semiconductors for organic thin-film transistors (OTFTs). Most compounds exhibited *p*-channel characteristics with carrier mobility as high as 1.7×10^{-5} cm^2/Vs and a current on/off ratio of 10^2–10^4 for top-contact/bottom-gate OTFT devices.

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers

Keywords: Organic Thin-Film Transistors, Organic Semiconductor, Phenylthiophene, Carbazole, α-Carboline.

1. INTRODUCTION

Organic electronic devices have gained considerable interest due to their potential applications as low-cost, solution-processable, flexible electronics.[1,2] Among them, organic thin-film transistors (OTFTs) are representative examples employed for most modern electronics.[3,4] To this end, there have been extensive efforts to develop and optimize basic OTFT components—semiconductor, dielectric, and contacts. Among previously developed OTFT semiconductors, pentacene,[5–7] oligothiophene,[8,9] and anthradithiophene derivatives[10] are representative examples with high carrier mobility. There is still a need to develop and optimize novel organic semiconductors with high electrical performance and ambient stability via controlling their chemical structure, molecular interaction, and the resulting film microstructure/morphology.[11–16] Carbazole and α-carboline are aromatic heterocyclic organic compounds which contain indole structure fused with benzene and pyridine ring structure, respectively. Although organic semiconductors based on carbazole and α-carboline moieties have extensively been studied as host materials for phosphorescent organic light-emitting diodes (PHOLEDs),[17–20] they have hardly been employed for OTFTs.[21]

To this end, we have synthesized six organic semiconductors based on phenyl and phenylthienyl cores functionalized with carbazole and α-carboline moieties (Fig. 1). As shown, chemical structures of organic semiconductors were varied by linking carbazoles or carbazole/α-carboline groups with phenyl and phenylthienyl moieties. New compounds were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-vis spectroscopy, and cyclic voltammetry to obtain thermal, optical, and electrochemical data. Density functional theory (DFT) calculations were performed to determine HOMO/LUMO energy levels as well as molecular structure of each compound. Furthermore, the semiconductor films were employed as an active layer via vacuum deposition in a top-contact/bottom-gate OTFT and the resulting devices were characterized. Finally, the morphology and microstructure of the semiconducting films were investigated by atomic force microscopy (AFM) and X-ray diffraction (XRD) to correlate these properties with device

---

[*] Authors to whom correspondence should be addressed.
[†] These two authors contributed equally to this work.

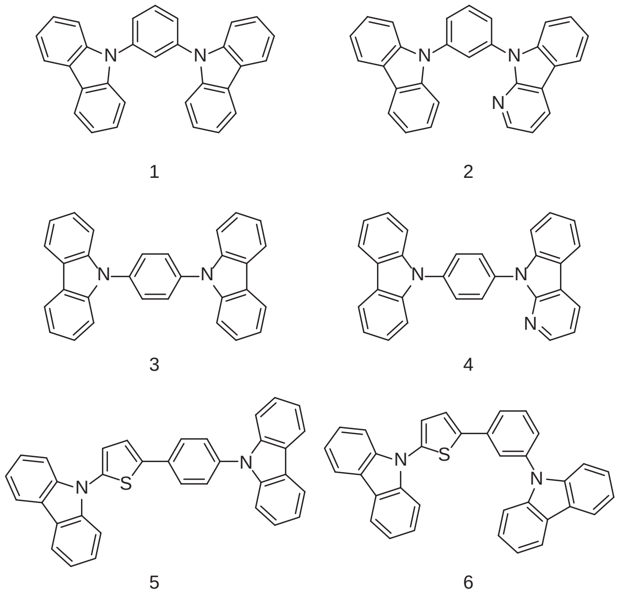


Figure 1. Chemical structures of the phenyl and phenylthienyl derivatives employed in this study.

performance. Our results revealed that most devices were active as *p*-channel OTFTs with carrier mobility as high as 1.7×10^{-5} cm^2/Vs and current on/off ratio of $\sim 10^4$.

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers

2. EXPERIMENTAL DETAILS

2.1. General Methods

Air and/or moisture sensitive reactions were carried out under an argon atmosphere in oven-dried glassware and with anhydrous solvents. All compounds were purchased from commercial sources unless otherwise noted and used without further purification. Solvents were freshly distilled (1,4-dioxane and toluene over sodium) or dried by passing through an alumina column. Thin layer chromatography was carried out on glass plates coated with silica gel SiO_2 60 F254 from Merck; visualization with a UV lamp (254 nm) or by staining with a *p*-anisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO_2 60 (0.040–0.063 μm, 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy was performed on a JEOL ECP-400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) at 294 K. Chemical shifts are reported in ppm relative to the residual protiated solvent ($CDCl_3$: $\delta H = 7.26$ ppm, $\delta C = 77.16$ ppm). All ^{13}C NMR spectra are proton decoupled. The resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *p* (pentet), *dd* (doublet of doublet), *dt* (doublet of triplet), *td* (triplet of doublet), *m* (multiplet), and *br* (broad). High-resolution mass spectrometry (HRMS) was measured on a JEOL JMS-700 spectrometer. Mass peaks are reported in m/z units.

2.2. Synthesis

2.2.1. Synthesis of 9-(3-iodophenyl)-9H-Carbazole and 9-(3-(9H-carbazol-9-yl) phenyl)-9H-Carbazole (1)

9*H*-Carbazole (3.5 g, 20.9 mmol), 1,3-diiodobenzene (10.3 g, 31.4 mmol), CuI (1.2 g, 6.3 mmol), K_2CO_3 (11.4 g, 83.7 mmol), and 18-crown-6 ether (2.8 g, 10.5 mmol) were dissolved in 150 mL of *o*-dichlorobenzene (DCB) and the reaction mixture was allowed to reflux under a nitrogen atmosphere for 35 h. Then solvent was distilled under vacuo. The crude mixture was diluted with CH_2Cl_2, filtered, and then the residue was washed with CH_2Cl_2. The combined filtrates were washed with distilled H_2O. The organic layer was dried on anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. Then the crude product was purified by flash column chromatography on silica gel to give 9-(3-iodophenyl)-9*H*-carbazole (3.62 g, 46.9%) and compound **1** (600 mg, 7.0%). Spectral data matched well with values reported in the literature.[19, 22, 23] 9-(3-Iodophenyl)-9*H*-carbazole: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (*d*, 7.7 Hz, 2 H), 7.94 (*t*, 1.4 Hz, 1 H), 7.81 (*dt*, 1.4, 8.0 Hz, 1 H), 7.57 (*ddd*, 1.1, 2.2, 8.0 Hz, 1 H), 7.38–7.43 (*m*, 4 H), 7.29–7.36 (*m*, 3 H). Compound **1**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (*d*, 7.7 Hz, 4 H), 7.86 (*t*, 8.0 Hz, 1 H), 7.84 (*d*, 1.1 Hz, 1 H), 7.72 (*dd*, 1.8, 8.0 Hz, 2 H), 7.56 (*d*, 8.0 Hz, 4 H), 7.46 (*t*, 8.0 Hz, 4 H), 7.33 (*t*, 7.7 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 139.3, 131.1, 126.1, 125.7, 125.2, 123.5, 120.4, 120.2, 109.6.

2.2.2. Synthesis of 9-(3-(9H-carbazol-9-yl)phenyl)-9H-Pyrido[2,3-b] Indole (2)

9-(3-Iodophenyl)-9*H*-carbazole (300 mg, 0.81 mmol), α-carboline (150.3 mg, 0.89 mmol), CuI (46.3 mg, 0.24 mmol), K_3PO_4 (343.9 mg, 1.62 mmol), and *trans*-1,2-diaminocyclohexane (29.2 μL, 0.24 mmol) were dissolved in 10 mL of 1,4-dioxane under a nitrogen atmosphere. The reaction mixture was refluxed for 20 h and the reaction mixture was filtered and the residue was washed with CH_2Cl_2. The combined filtrates were washed with distilled water. The organic layer was dried on anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. Then the crude product was purified by flash column chromatography on silica gel to give compound **2**[19] (147.4 mg, 44.4%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (*dd*, 1.4, 5.1 Hz, 1 H), 8.40 (*dd*, 1.4, 7.7 Hz, 1 H), 8.15 (*dd*, 5.1, 7.7 Hz, 3 H), 7.97 (*bt*, 1.4 Hz, 1 H), 7.80–7.87 (*m*, 2 H), 7.65–7.72 (*m*, 4 H), 7.51 (*dt*, 1.1, 8.0 Hz, 1 H), 7.45 (*dt*, 1.1, 8.0 Hz, 2 H), 7.26–7.38 (*m*, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 146.4, 140.5, 139.5, 138.8, 137.7, 130.7, 128.3, 127.1, 126.0, 125.6, 125.5, 124.4, 123.5, 121.0, 120.3, 120.1, 116.4, 110.3, 109.8.

2.2.3. Synthesis of 9-(4-bromophenyl)-9H-Carbazole

9*H*-Carbazole (5.02 g, 30 mmol), 1,4-dibromobenzene (14.15 g, 60 mmol), CuI (5.71 g, 30 mmol), K_2CO_3 (16.59 g, 120 mmol), and 18-crown-6 ether (3.96 g, 15 mmol) were dissolved in 100 mL of *N*,*N*-dimethylacetamide (DMA) and the reaction mixture was allowed to reflux under a nitrogen atmosphere for 45 h. Then *N*, *N*-dimethylacetamide was distilled under vacuo. The crude mixture was diluted with CH_2Cl_2, filtered, and the residue was washed with CH_2Cl_2. The combined filtrates were washed with distilled H_2O. The organic layer was dried on anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. Then the crude product was purified by flash column chromatography on silica gel to give 9-(4-bromophenyl)-9*H*-carbazole (6.53 g, 67.5%). Spectral data matched well with values reported in the literature.[24] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (*d*, 7.7 Hz, 2 H), 7.72 (*d*, 8.8 Hz, 2 H), 7.38–7.48 (*m*, 6 H), 7.30–7.34 (*m*, 2 H).

2.2.4. Synthesis of 9-(4-(9H-carbazol-9-yl)phenyl)-9H-Carbazole (3)

9-(4-Bromophenyl)-9*H*-carbazole (300 mg, 0.93 mmol), 9*H*-carbazole (186.8 mg, 1.11 mmol), CuI (53.2 mg, 0.28 mmol), K_2CO_3 (506 mg, 3.72 mmol), and 18-crown-6 ether (123 mg, 0.47 mmol) were dissolved in 10 mL of *N*, *N*-dimethylacetamide (DMA) and the reaction mixture was allowed to reflux under a nitrogen atmosphere for 24 h. The reaction mixture was allowed to cool to room temperature. Then the crude mixture was filtered, and the residue was washed with CH_2Cl_2. The combined filtrates were evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give compound **3** (35 mg, 9.2%, brsm 15.6%). Spectral data matched well with values reported in the literature.[25] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (*d*, 8.0 Hz, 4 H), 7.83 (*s*, 4 H), 7.58 (*d*, 8.0 Hz, 4 H), 7.49 (*dt*, 1.1, 8.4 Hz, 4 H), 7.35 (*dt*, 1.1, 8.4 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 136.6, 128.3, 126.1, 123.5, 120.4, 120.2, 109.7.

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 16:03:25
Copyright: American Scientific Publishers

2.2.5. Synthesis of 9-(4-(9H-carbazol-9-yl) phenyl)-9H-Pyrido [2, 3-b] Indole (4)

9-(4-Bromophenyl)-9*H*-carbazole (300 mg, 0.93 mmol), α-carboline (187.7 mg, 1.12 mmol), CuI (53.2 mg, 0.28 mmol), K_2CO_3 (506.6 mg, 3.72 mmol), and 18-crown-6 ether (24.6 mg, 0.092 mmol) were dissolved in 10 mL of *N*, *N*-dimethylacetamide (DMA) and the reaction mixture was allowed to reflux under a nitrogen atmosphere for 24 h. The reaction mixture was allowed to cool to room temperature. Then the crude mixture was filtered, and the residue was washed with CH_2Cl_2. The combined filtrates were evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give compound **4** (53 mg, 13.9% , brsm 20.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (*dd*, 1.4, 4.7 Hz, 1 H), 8.44 (*dd*, 1.4, 7.7 Hz, 1 H), 8.18 (*d*, 7.7 Hz, 3 H), 7.94 (*d*, 8.4 Hz, 2 H), 7.84 (*d*, 8.4 Hz, 2 H), 7.67 (*d*, 8.4 Hz, 1 H), 7.60 (*d*, 8.0 Hz, 2 H), 7.55 (*dt*, 1.1, 8.0 Hz, 1 H), 7.47 (*dt*, 1.1, 8.0 Hz, 2 H), 7.40 (*t*, 8.0 Hz, 1 H) 7.29–7.35 (*m*, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 146.4, 140.7, 139.8, 136.7, 135.1, 128.5, 128.4, 128.0, 127.1, 126.0, 123.5, 121.1, 121.0, 120.3, 120.1, 116.5, 116.4, 110.4, 109.8. HRMS-EI(m/z): [M^+] calcd for $C_{29}H_{19}N_3$, 409.1579; found, 409.1576.

2.2.6. Synthesis of 4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-Dioxaborolane

n-BuLi (41.18 mL, 65.9 mmol, 1.6 M in hexane) was added drop wise to the stirred solution of thiophene (5.04 g, 59.9 mmol) in 50 mL of THF at −78 °C. Then the solution was stirred for 30 min at room temperature. After cooling to −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.14 g, 59.9 mmol) in 80 mL of THF was added and the reaction mixture was allowed to stir for 30 min at room temperature. After completion of the reaction (indicated by TLC), solvent was removed under vacuum and the residue was taken up in $CHCl_3$. Aqueous 5 N HCl (50 mL) was added under vigorous stirring for 30 min. The organic layer was collected and dried over $MgSO_4$. After evaporation of the solvent the product was recrystallized from pentane (10.78 g, 86.0%). Spectral data matched well with values reported in the literature.[26] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65(*d*, 3.6 Hz, 1 H), 7.63 (*d*, 4.6 Hz, 1 H), 7.20 (*dd*, 4.7, 3.6 Hz, 1 H), 1.34 (*s*, 12 H).

2.2.7. Synthesis of 2-(4-bromophenyl) Thiophene

A mixture of 1-bromo-4-iodobenzene (2.0 g, 7.07 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (2.97 g, 14.1 mmol), $Pd(PPh_3)_4$ (408 mg, 0.35 mmol), and Na_2CO_3 (1.49 g, 14.1 mmol) were dissolved in toluene (40 mL), THF (15 mL), and H_2O (15 mL) and the reaction mixture was refluxed for 5 h. After completion of the reaction (indicated by TLC), the solvent was removed under vacuum, H_2O (30 mL) and CH_2Cl_2 (40 mL) were added. The organic layer was separated and dried on anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Then the crude product was purified by flash column chromatography on silica gel to give 2-(4-bromophenyl) thiophene (1.26 g, 74.6%). Spectral data matched well with values reported in the literature.[27] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (*d*, 3.6 Hz, 4 H), 7.29 (*d*, 4.4 Hz, 2 H), 7.07 (*dt*, 1.4, 4.4 Hz, 1 H).

2.2.8. Synthesis of 2-(3-bromophenyl) Thiophene

A mixture of 1,3-dibromobenzene (2.0 g, 8.47 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (2.67 g, 12.7 mmol), $Pd(PPh_3)_4$ (489 mg, 0.42 mmol), and Na_2CO_3 (1.79 g, 16.9 mmol) were dissolved in toluene (50 mL), THF (15 mL), and H_2O (15 mL) and the reaction mixture was refluxed for 2.5 h. After completion of the reaction (indicated by TLC), the solvent was removed under vacuum, H_2O (30 mL) and CH_2Cl_2 (50 mL) were added. The organic layer was separated and dried on $MgSO_4$. The solvent was removed under reduced pressure. Then the crude product was purified by flash column chromatography on silica gel to give 2-(3-bromophenyl) thiophene (1.58 g, 77.9%). Spectral data matched well with values reported in the literature.[28] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (*t*, 1.8 Hz, 1 H), 7.53 (*td*, 1.1, 7.7 Hz, 1 H), 7.40 (*td*, 1.1, 8.4 Hz, 1 H), 7.31 (*d*, 4.4 Hz, 2 H), 7.24 (*t*, 7.7 Hz, 1 H), 7.09 (*t*, 4.4 Hz, 1 H).

2.2.9. Synthesis of 2-Bromo-5-(4-bromophenyl) Thiophene

N-Bromosuccinimide (1.87 g, 10.5 mmol) was added in small portions to the solution of 2-(4-bromophenyl) thiophene (1.26 g, 5.27 mmol) in anhydrous THF (40 mL) at room temperature under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature under for 2.5 h. After completion of the reaction (indicated by TLC), H_2O (30 mL) and Et_2O (60 mL) were added. The organic layer was separated and dried on anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Then the crude product was purified by flash column chromatography on silica gel to give 2-bromo-5-(4-bromophenyl) thiophene (1.67 g, 99.7%). Spectral data matched well with values reported in the literature.[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (*d*, 8.4 Hz, 2 H), 7.36 (*d*, 8.4 Hz, 2 H), 7.03 (*s*, 2 H).

2.2.10. Synthesis of 2-Bromo-5-(3-bromophenyl) Thiophene

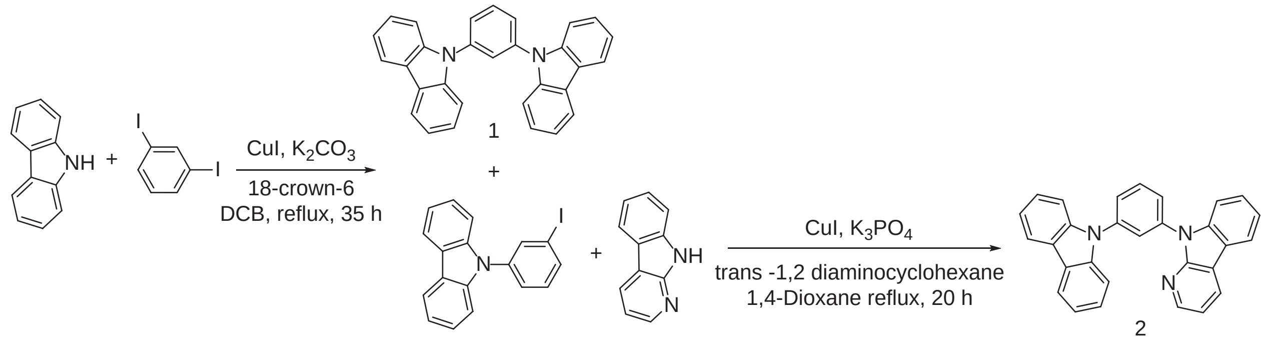
N-Bromosuccinimide (2.23 g, 12.5 mmol) was added in small portions to the solution of 2-(3-bromophenyl) thiophene (1.50 g, 6.27 mmol) in 40 mL of anhydrous THF at room temperature under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 2.5 h. After completion of the reaction (indicated by TLC), H_2O (30 mL) and Et_2O (60 mL) were added. The organic layer was separated and dried on $MgSO_4$. The solvent was removed under reduced pressure. Then the crude product was purified by flash column chromatography on silica gel to give 2-bromo-5-(3-bromophenyl) thiophene (653 mg, 65.9%). Spectral data matched well with values reported in the literature.[29] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (*t*, 1.8 Hz, 1 H), 7.42 (*dd*, 1.4, 7.7 Hz, 2 H), 7.23 (*t*, 7.7 Hz, 1 H), 7.04 (*d*, 2.5 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 135.5, 130.9, 130.7, 130.4, 128.4, 124.1, 124.0, 123.0, 112.3.

2.2.11. Synthesis of 9-(4-(5-(9H-carbazol-9-yl) thiophen-2-yl) phenyl)-9H-Carbazole (5)

2-Bromo-5-(4-bromophenyl) thiophene (100 mg, 0.31 mmol), 9*H*-carbazole (120.9 mg, 0.72 mmol), CuI (17.9 mg, 0.094 mmol), K_3PO_4 (133 mg, 0.63 mmol), and *trans*-1,2-diaminocyclohexane (11.2 μL, 0.094 mmol) were dissolved in 10 mL of 1,4-dioxane under a nitrogen atmosphere. The reaction mixture was refluxed for 24 h. Then the reaction mixture was filtered and the residue was washed with CH_2Cl_2. The combined filtrates were washed with distilled water. The organic layer was dried on anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. Then the crude product was purified by flash column chromatography on silica gel to give compound **5** (100 mg, 64.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (*dd*, 7.7, 13.5 Hz, 4 H), 7.88 (*d*, 8.4 Hz, 2 H), 7.64 (*d*, 8.4 Hz, 2 H), 7.60 (*d*, 8.4 Hz, 2 H), 7.42–7.51 (*m*, 8 H), 7.30–7.36 (*m*, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 141.5, 140.6, 138.2, 137.2, 133.0, 127.5, 127.0, 126.3, 126.0, 125.9, 123.6, 123.4, 122.3, 120.7, 120.3, 120.2, 120.1, 110.2, 109.7. HRMS-EI(m/z): [M^+] calcd for $C_{34}H_{22}N_2S$, 490.1504; found, 490.1507.

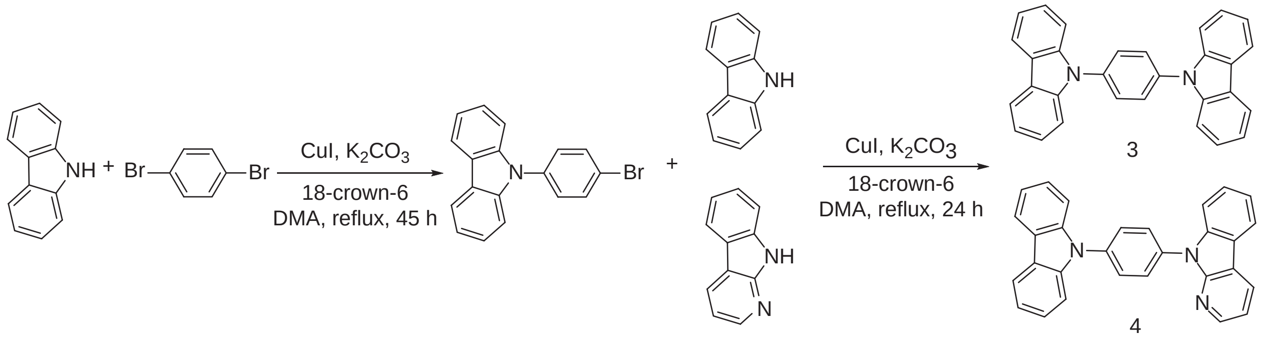
2.2.12. Synthesis of 9-(3-(5-(9H-carbazol-9-yl) thiophen-2-yl) phenyl)-9H-Carbazole (6)

2-Bromo-5-(3-bromophenyl) thiophene (200 mg, 0.63 mmol), 9*H*-carbazole (242 mg, 1.38 mmol), CuI (36.0 mg, 0.19 mmol), K_3PO_4 (266 mg, 1.25 mmol), and *trans*-1,2-diaminocyclohexane (22.6 μL, 0.19 mmol) were dissolved in 15 mL of 1,4-dioxane under a nitrogen atmosphere. The reaction mixture was refluxed for 16 h. Then the reaction mixture was filtered and the residue



Scheme 1. Synthesis of compounds **1** and **2**.

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers



Scheme 2. Synthesis of compounds **3** and **4**.

was washed with CH_2Cl_2. The combined filtrates were washed with distilled water. The organic layer was dried on anhydrous $MgSO_4$ and evaporated in vacuo to give the crude product. Then the crude product was purified by flash column chromatography on silica gel to give compound **6** (135 mg, 43.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (*dd*, 0.7, 8.0 Hz, 2 H), 8.12 (*dd*, 0.7, 8.0 Hz, 2 H), 7.88 (*t*, 2.2 Hz, 1 H), 7.72–7.75 (*m*, 1 H), 7.66 (*t*, 7.7 Hz, 1 H), 7.567 (*t*, 8.0 Hz, 3 H), 7.43–7.51 (*m*, 7 H), 7.30–7.35 (*m*, 4 H), 7.21 (*d*, 3.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 141.2, 140.7, 140.5, 138.9, 130.5, 126.3, 126.1, 126.0, 125.8, 124.6, 124.1, 123.5, 123.4, 122.5, 120.7, 120.4, 120.3, 120.29, 120.22, 120.1, 110.2, 109.7, 109.6. HRMS-EI(m/z): [M^+] calcd for $C_{34}H_{22}N_2S$, 490.1504; found, 490.1503.

2.3. Theoretical Calculation

Density functional theory (DFT) calculations on the present semiconductors were performed using the B3LYP (Becke's 3 parameters employing the Lee-Yang-Parr) functional and the 6-31G basis set as implemented in Gaussian 03W program.

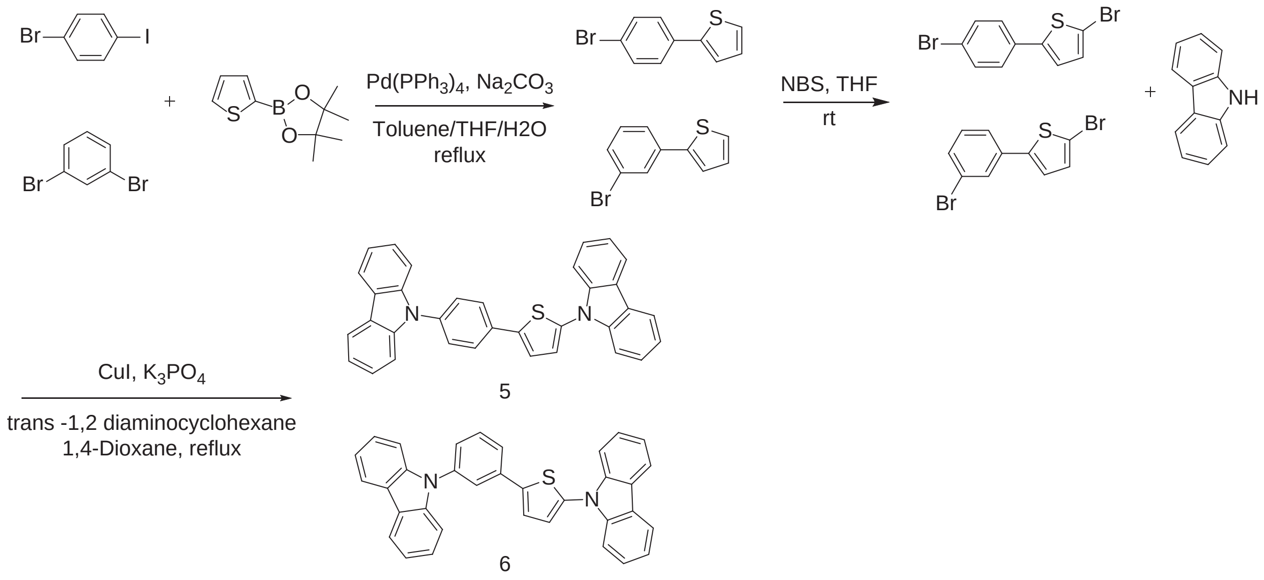
2.4. Device Fabrication

Top-contact/bottom-gate OTFTs were fabricated on a heavily *n*-doped silicon (n^{++}-Si) substrate with thermally grown silicon dioxide (300 nm SiO_2) as dielectric layer. The SiO_2/Si substrate was washed in an ultrasonic bath using acetone for 10 min, dried using a nitrogen gun, and cleaned by air plasma for 5 min (Harrick Plasma, 18 W). Various gate dielectric layers including two self-assembled monolayers (hexamethyldisilazane; HMDS and octadecyltrimethoxysilane; OTMS) and two polymer (polystyrene; PS and polymethylmethacrylate; PMMA) layers were applied onto the surface of the substrate. For HMDS treatment, a few drops of HMDS were loaded inside a self-assembly chamber under an N_2 atmosphere and the SiO_2/Si substrates were exposed to this atmosphere for 48 h to give a hydrophobic surface with aqueous contact angle of 102°. For OTMS treatment, 3 mM solution of OTMS in trichloroethylene was dropped on SiO_2/Si substrate and the substrate was spin-coated at 3000 rpm. Then, the substrate was placed in a N_2 filled closed chamber with a few mL of ammonium hydroxide solution for vapor annealing for 10 h at room temperature. The substrate was then rinsed with DI water and toluene, resulting in aqueous contact angle of 113°. Furthermore, two polymer buffer layers including PS ($M_n = 30$ kg/mol) and PMMA ($M_n = 25$ kg/mol) were spin-coated onto the SiO_2/Si substrate (10 mg/mL in toluene, 5000 rpm), resulting in thickness of ~40 nm. The organic semiconductor thin films (70 nm) were vacuum-deposited onto the substrates at 20 and 60 °C at a deposition rate of 0.4 Å s^{-1} under a pressure of 5×10^{-6} Torr. Gold source/drain electrodes (40 nm) were thermally evaporated through a shadow mask with a channel length and width of 50 and 2000 μm, respectively.

Delivered by Publishing Technology to: McMaster University
IP: 178.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers

2.5. Characterization

Thermogravimetric analyses (TGA, TA Instrument Q50-1555) were performed on each sample in a platinum crucible; the sample was heated from 40 to 700 °C at a heating rate of 10 °C min^{-1}, while the chamber was purged continuously with N_2 gas at a rate of 100 mL min^{-1}. Differential scanning calorimetry (DSC) analyses (TA instrument Q20-2487) were performed at a scan rate of 10 K min^{-1} from 40 to 300 °C. The UV-visible spectra of the compounds in chloroform were obtained using a JASCO V-660 spectrometer with quartz cuvette over the special range 200–700 nm. Cyclic voltammetry (CV) experiments were performed with a conventional three-electrode configuration (glassy carbon working electrode, platinum-wire counter electrode, and Ag/AgCl reference electrode) with supporting electrolyte of tetrabutylammonium tetrafluoroborate in the specified dry solvent on AUT302N Electrochemical Analyzer (Autolab). All electrochemical potentials were referenced to an Fc^+/Fc internal standard. The current–voltage characteristics of fabricated OTFT devices were measured at room temperature under vacuum using a Keithley 4200 SCS. Carrier mobilities (μ) were calculated in the saturation regime.[30] Film thicknesses were measured by profilometer (Dectak XT). The surface morphology and film microstructure of thin films was characterized using an atomic



Scheme 3. Synthesis of compounds **5** and **6**.

force microscope (AFM, NX10, Park Systems) and X-ray diffraction (XRD, Miniflex, Rigaku), respectively.

3. RESULTS AND DISCUSSION

3.1. Synthesis

Compounds **1** and 9-(3-iodophenyl)-9*H*-carbazole were synthesized by an Ullmann coupling of 1,3-diiodobenzene and carbazole according to the method reported in the literature.[19, 22, 23] Then 9-(3-iodophenyl)-9*H*-carbazole was treated with α-carboline to afford compound **2** (Scheme 1). 9-(4-Bromophenyl)-9*H*-carbazole was synthesized by an Ullmann coupling of 1,4-dibromobenzene and carbazole according to the method reported in the literature.[24, 25] Then 9-(4-bromophenyl)-9*H*-carbazole was further reacted with carbazole and α-carboline to give compounds **3** and **4** as shown in Scheme 2. Compound **5** was synthesized through the following route. First 1-bromo-4-iodobenzene was reacted with 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane under palladium catalyst via Suzuki coupling to give 2-(4-bromophenyl) thiophene, then bromination was tried using NBS. Finally, 2-bromo-5-(4-bromophenyl) thiophene was treated with carbazole to afford compound **5**. The synthesis of compound **6** was exactly the same as that of compound **5** except using 1,3-dibromobenzene instead of 1-bromo-4-iodobenzene as shown in Scheme 3.[26–29]

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers

3.2. Thermal and Optical Properties

Thermal properties of the new phenyl and phenylthienyl derivatives were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Sharp endotherms above 162 °C and weight loss (~5%) upon heating above 302 °C were observed (Table I), indicating thermal stability of the developed compounds in this study. The optical absorption spectra of the compounds **1–4** (phenyl derivatives) in chloroform solution showed similar patterns with $\lambda_{max} = 242$, 293 nm for compound **1**, $\lambda_{max} = 246$, 293 nm for compound **2**, $\lambda_{max} = 245$, 293 nm for compound **3**, and $\lambda_{max} = 244$, 294 nm for compound **4**, respectively (Fig. 2). Similarly, compounds **5** and **6** (phenylthienyl derivatives) exhibited λ_{max}s at similar positions as shown in Figure 2 (at 241, 293, 339 nm for compound **5** and at 246, 292, 328 nm for compound **6**, respectively). Hence, the HOMO-LUMO energy gaps calculated from the onset of the experimental

Table I. Physical and electrochemical properties of compounds **1**–**6**.

	DSC T_m (°C)	TGA (°C; 5%)	UV-Vis λ_{max} (nm)^a	E_{ox}^{peak}(V)^b	E_{gap} (eV)^a	HOMO (eV)^b	LUMO (eV)^c
1	181	302	242, 293	1.45	3.57	−5.55	−1.98
2	162	322	246, 293	1.43	3.53	−5.53	−2.00
3	321	323	245, 293	1.32	3.55	−5.42	−1.87
4	279	326	244, 294	1.33	3.52	−5.43	−1.91
5	185	369	241, 293, 339	1.23	3.31	−5.33	−2.02
6	170	353	246, 292, 328	1.12	3.32	−5.22	−1.90

Notes: [a]Measured by UV-vis spectroscopy; [b]Measured by cyclic voltammetry in *o*-$C_6H_4Cl_2$ at 25 °C (using ferrocene/ferrocenium as internal standard at +0.7 V); [c]Calculated as LUMO = HOMO + E_{gap}.

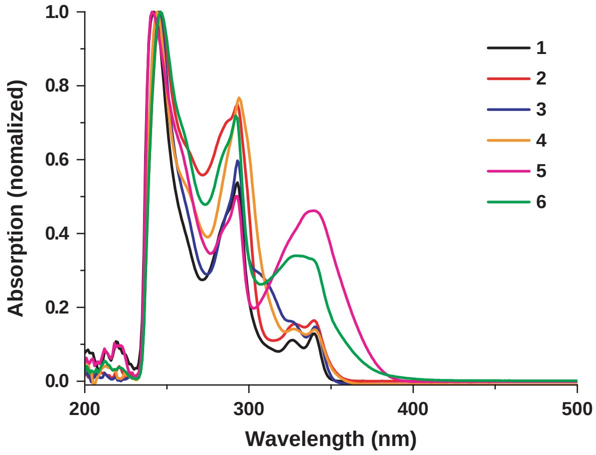


Figure 2. Optical spectra of carbazole/α-carboline derivatives.

optical absorption are ~3.55 eV for compounds **1**–**4** and ~3.30 eV for compounds **5** and **6**. These results might indicate that the compounds with longer molecular length (more chemical moieties) exhibit the greater π-conjugation.

3.3. Electrochemical Properties

Cyclic voltammetry (CV) measurements of the new compounds were performed in o-$C_6H_4Cl_2$ at 25 °C. The compounds **1** and **2** exhibited oxidation peaks at around +1.44 V (using ferrocene/ferrocenium as an internal standard at +0.7 V). The oxidation potential of compounds **3** and **4** (**3**; $E_{ox} = +1.32$ V, **4**; $E_{ox} = +1.33$ V) is slightly

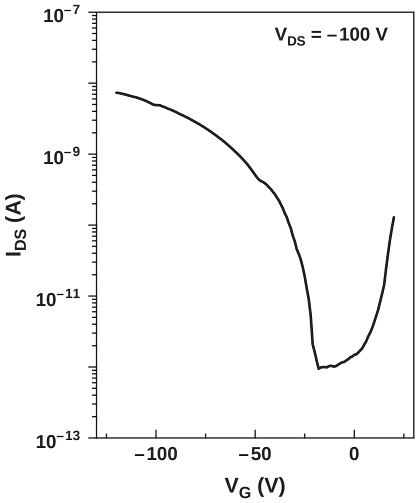


Figure 4. Representative device characteristic (transfer plot) of OTFT device fabricated with thin films of compounds 5 on HMDS-treated SiO_2 substrates ($T_D = 60$ °C).

shifted to more negative values, compared to that of compounds **1** and **2**. Phenylthienyl derivatives compounds **5** and **6** exhibited the oxidation potentials shifted to more negative values ($E_{ox} = +1.23$ V and +1.12 V, respectively) compared to compounds **1**–**4**. Hence, HOMO energy levels obtained by the conversion of oxidation potential using ferrocene as the standard were higher for compounds **5** and **6** (−5.33 and −5.22 eV, respectively), compared to compounds **1**–**4**(−5.55–−5.42 eV). The LUMO energy levels for each compound were calculated from the HOMO (from

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers

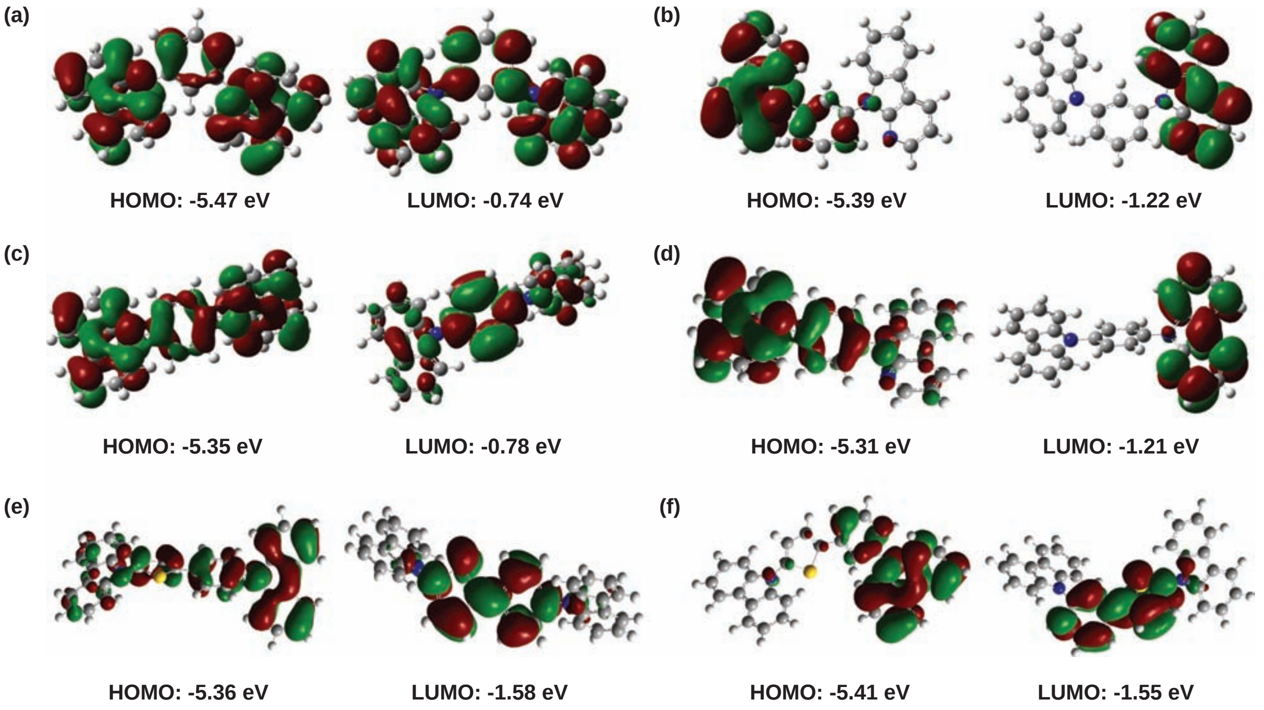


Figure 3. Molecular orbital surfaces of HOMO and LUMO by DFT calculation of compounds (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.

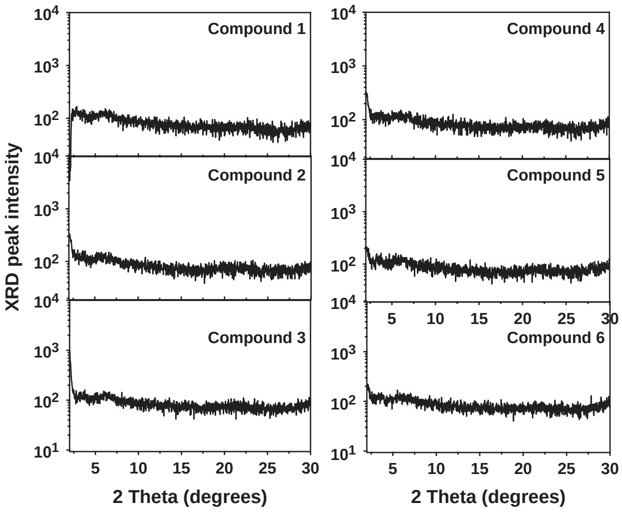


Figure 5. θ–2θ XRD scans of thin films of compounds **1**–**6**.

CV measurement) and the bandgap (from UV-vis measurement), as shown in Table I.

3.4. Theoretical Calculation

The molecular structure and HOMO/LUMO energy distribution of phenyl and phenylthienyl derivatives were determined by DFT (B3LYP) calculation with 6-31G basis sets (Fig. 3). Overall, strong electron-donating character of nitrogen of the carbazole and electron-accepting character of the α-carboline are projected on the HOMO/LUMO energy distribution. For compounds with only carbazole moieties on both ends (compounds **1**, **3**, **5**, and **6**), the HOMO was rather dispersed over the whole molecule (except compound **6**), while the LUMO was either dispersed (compounds **1** and **3**) or localized on the phenylthiophene moieties (compounds **5** and **6**). On the other hand, compounds with both carbazole and α-carboline on both ends (compounds **2** and **4**) exhibited localized HOMO and LUMO distribution; the HOMO and LUMO was localized on the carbazole and α-carboline moiety, respectively.

Delivered by Publishing Technolo
Tue
Copyright: American Sc

Table II. TFT device performance parameters based on thin films of compounds **1**–**6** employed in this study (T_D: deposition temperature, μ: carrier mobility, $I_{\text{on}}/I_{\text{off}}$: current on/off ratio, V_T; threshold voltage).

Compound	Surface treatment	T_D (°C)	μ (cm^2/Vs)	$I_{\text{on}}/I_{\text{off}}$	V_T (V)
1	HMDS	60	2.2×10^{-6}	1.8×10^{2}	−30
	PS	20	1.7×10^{-7}	2.7×10^{1}	−26
	PMMA	60	3.5×10^{-7}	3.1×10^{1}	−55
2			Not active		
3	PS	60	5.4×10^{-6}	1.1×10^{2}	−44
	PMMA	60	3.2×10^{-6}	4.2×10^{2}	−49
4	OTMS	20	1.4×10^{-6}	1.2×10^{2}	−56
	PMMA	20	$1.3.\times10^{-6}$	1.0×10^{2}	−55
5	PS	60	1.7×10^{-5}	8.2×10^{3}	−23
	OTMS	60	1.5×10^{-5}	2.6×10^{4}	−26
	HMDS	60	7.4×10^{-6}	4.5×10^{3}	−40
6	PS	60	2.1×10^{-6}	4.3×10^{1}	−65
	PMMA	60	2.1×10^{-7}	4.0×10^{1}	−32

3.5. Thin-Film Transistor Characterization

New phenyl and phenylthienyl derivatives were tested as organic semiconductors for top-contact/bottom gate OTFT devices. All of the compounds were vacuum-deposited on bare, HMDS-treated, OTMS-treated, PS-coated, and PMMA-coated SiO_2/Si substrates at 20 and 60 °C. The representative device characteristics are shown in Figure 4. Overall, devices were not active on hydrophilic bare SiO_2/Si substrates. Devices based on thin films of compounds **1**–**6** (except compound **2**) exhibited *p*-channel activity with relatively low device performance (vide infra). The OTFT devices exhibited carrier mobilities of 10^{-5}–10^{-7} cm^2/Vs and a current on/off ratio of $\sim10^2$–10^4. Unfortunately, no clear correlation between device performance, surface treatment, and deposition temperature was found in this series of compounds. Of the compounds that were employed in this study, compound **5** exhibited the

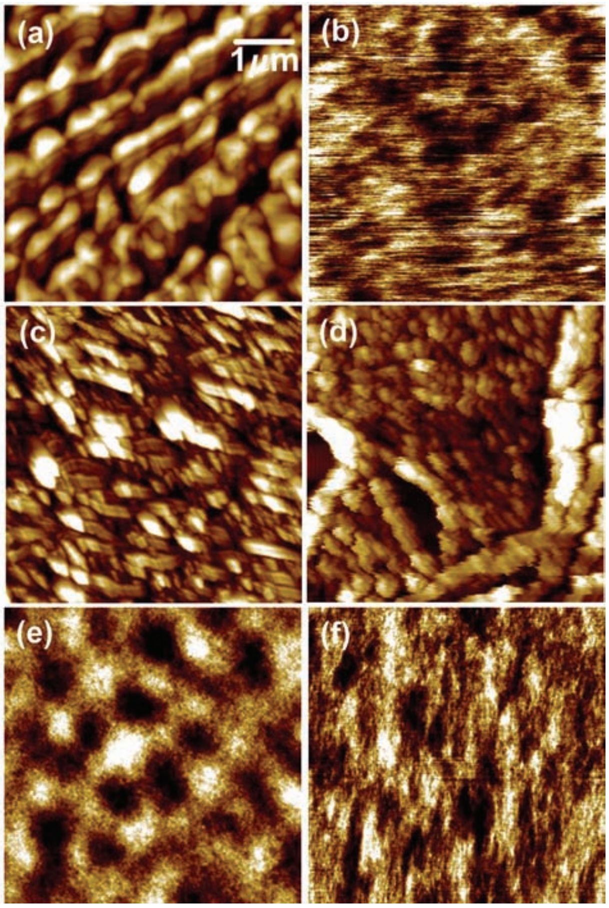


Figure 6. AFM image (5×5 μm^2) of thin films (70 nm) of (a) compound **1** (on PMMA at 60 °C), (b) compound **2** (on Bare at 60 °C), (c) compound **3** (on PMMA at 20 °C), (d) compound **4** (on PMMA at 20 °C), (e) compound **5** (on HMDS at 60 °C), and (f) compound **6** (on PS at 60 °C).

highest device performance with carrier mobility as high as 1.7×10^{-5} cm^2/Vs.

3.6. Thin-Film Microstructure and Morphology

Film microstructure and surface morphology of vacuum-deposited films were characterized using wide-angle θ–2θ XRD and AFM to evaluate device performance. Devices with high electrical performance generally exhibit films with high film crystallinity and large grain size. Figure 5 shows conventional $\theta/2\theta$ XRD scans of thin films based on compounds **1**–**6**. As shown, all of films did not exhibit any significant Bragg reflections, indicating poor film texture. Furthermore, surface morphologies of organic semiconductor thin films (70 nm) were characterized by AFM (Fig. 6). As shown, thin films of phenyl and phenylthienyl derivatives showed either ball-shaped grains with small grain sizes (compounds **1**, **3**, and **4**) or relatively smooth surface (compounds **2**, **5**, and **6**).

4. CONCLUSIONS

A family of new phenyl and phenylthienyl end-functionalized with carbazole and/or α-carboline moiety was synthesized and characterized. Thin-film transistors fabricated from these molecules exhibited *p*-channel device characteristics with relatively low electrical performance, possibly due to poor film microstructure and grain morphology. Further molecular engineering on phenyl and phenylthienyl derivatives are in progress.

Delivered by Publishing Technology to: McMaster University
IP: 173.180.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers

Acknowledgments: This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2012R1A1A1007364), and was supported by the Human Resources Development program (No. 20114010203090) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy.

References and Notes

1. (a) M. Berggren, D. Nilsson, and N. D. Robinson, *Nat. Mater.* 6, 3 (**2007**); (b) T. Sekitani and T. Someya, *Adv. Mater.* 22, 2228 (**2010**).

2. (a) J. Baek, N. S. Kang, Y. D. Lee, B. H. Kang, K. Y. Dong, J. A. Lim, Y. W. Song, J. M. Hong, and B. K. Ju, *Sci. Adv. Mater*. 5, 1775 (**2013**); (b) K. Fan, R. Li, J. Chen, W. Shi, and T. Peng, *Sci. Adv. Mater*. 5, 1596 (**2013**); (c) R. Deng, L. Zhou, M. Song, Z. Hao, and H. Zhang, *Sci. Adv. Mater*. 5, 1556 (**2013**); (d) V. Palanianthan, N. Chauhan, A. C. Poulose, S. Raveendran, T. Mizuki, T. Hasumura, T. Fukuda, H. Morimoto, Y. Yoshida, T. Maekawa, and D. S. Kumar, *Mater. Express* 4, 415 (**2014**); (e) Y. A. K. Reddy, B. Ajitha, and P. S. Reddy, *Mater. Express* 4, 32 (**2014**); (f) S. B. Choi, H. Zhao, L. S. Pu, J. H. Cho, and J. Y. Lee, *Sci. Adv. Mater*. 6, 2338 (**2014**).

3. (a) H. Usta, C. Kim, Z. Wang, S. Lu, H. Huang, A. Facchetti, and T. J. Marks, *J. Mater. Chem. C* 22, 4459 (**2012**); (b) A. C. Arias, J. D. Mackenzi, I. McCulloch, J. Rivnay, and A. Salleo, *Chem. Rev.* 110, 3 (**2010**).

4. (a) I. Kang, S. M. Park, D. H. Lee, S. H. Han, D. S. Chung, Y. H. Kim, and S. K. Kwon, *Sci. Adv. Mater*. 5, 199 (**2013**); (b) D. D. Tullio, M. Magliulo, G. Colafemmina, K. Manoli, L. Torsi, and G. Palazzo, *Sci. Adv. Mater*. 5, 1922 (**2013**).

5. J. E. Anthony, J. S. Brooks, D. L. Eaton, and S. R. Parkin, *J. Am. Chem. Soc.* 123, 9482 (**2001**).

6. T. Okamoto and Z. Bao, *J. Am. Chem. Soc.* 129, 10308 (**2007**).

7. K. Xiao, Y. Q. Liu, T. Qi, W. Zhang, F. Wang, J. H. Gao, W. F. Qiu, Y. Q. Ma, G. L. Cui, S. Y. Chen, X. W. Zhan, G. Yu, J. G. Qin, W. P. Hu, and D. Zhu, *J. Am. Chem. Soc.* 127, 13281 (**2005**).

8. I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, and M. F. Toney, *Nat. Mater.* 5, 328 (**2006**).

9. Y. Wu, P. Liu, S. Gardner, and B. S. Ong, *Chem. Mater.* 17, 221 (**2005**).

10. M. C. Chen, C. Kim, S. Y. Chen, Y. J. Chiang, M. C. Chung, A. Facchetti, and T. J. Marks, *J. Mater. Chem.* 18, 1029 (**2008**).

11. (a) H. Yan, Z. H. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dotz, M. Kastler, and A. Facchetti, *Nature* 457, 679 (**2009**); (b) B. Kang, M. Jang, Y. Chung, H. Kim, S. K. Kim, J. H. Oh, and K. Cho, *Nat. Commun*. 5, 4752 (**2014**).

12. (a) M. Alonzi, D. Lanari, A. Marrocchi, C. Petrucci, and L. Vaccaro, *RSC Advances* 3, 23909 (**2013**); (b) C. Kim, A. Facchetti, and T. J. Marks, *Science* 318, 76 (**2007**).

13. (a) T. K. An, S. M. Park, S. Nam, J. Hwang, S. J. Yoo, M. J. Lee, W. M. Yun, J. Jang, H. Cha, J. Hwang, S. Park, J. Kim, D. S. Chung, Y. H. Kim, S. K. Kwon, and C. E. Park, *Sci. Adv. Mater*. 5, 1323 (**2013**); (b) A. Chowdhury, B. Biswas, and B. Mallik, *Sci. Adv. Mater*. 5, 1297 (**2013**); (c) O. T. Kwon, J. D. Seo, W. K. Han, K. W. Jang, J. W. Hong, and T. W. Kim, *Sci. Adv. Mater*. 6, 2343 (**2014**).

14. (a) J. J. Park, W. J. Hyun, K. H. Park, S. H. Im, and O. O. Park, *Sci. Adv. Mater.* 6, 2370 (**2014**); (b) J. K. Kim and S. K. Park, *Sci. Adv. Mater*. 6, 2400 (**2014**); (c) H. Kim, D. S. Song, S. M. Kim, J. H. Jung, J. H. Kwon, D. K. Kim, G. Horowitz, M. Choi, I. M. Kang, and J. H. Bae, *Sci. Adv. Mater*. 6, 2483 (**2014**); (c) W. M. Yun, J. Jang, S. Nam, C. E. Park, S. H. Kim, and D. S. Chung, *Sci. Adv. Mater*. 6, 1676 (**2014**).

15. (a) M. A. Mohd Sarjidan, N. Jubri, S. H. Basri, N. K. Za'aba, M. S. Zaini, S. N. Zaini, and W. H. Abd Majid, *Nanosci. Nanotechnol. Lett*. 6, 1035 (**2014**); (b) C.-W. Li, S.-P. Chang, and S.-J. Chang, *Nanosci. Nanotechnol. Lett*. 6, 273 (**2014**); (c) H. Cui, T. D. Zeng, L. Shi, S. Fang, G. Chen, X. Xu, and C. Xu, *Nanosci. Nanotechnol. Lett*. 5, 209 (**2013**); (d) Y. He, X. Li, and L. Que, *J. Biomed. Nanotechnol*. 10, 767 (**2014**).

16. (a) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J. L. Breìdas, P. C. Ewbank, and K. R. Mann, *Chem. Mater.* 16, 4436 (**2004**); (b) A. Facchetti, L. Vaccaro, and A. Marrocchi, *Angew. Chem. Int. Ed.* 51, 3520 (**2012**).

17. P. Strohriegl, D. Wagner, P. Schrögel, S. T. Hoffmann, A. Köhler, U. Heinemeyer, and I. Munster, *Proc. SPIE* 8829, 882906 (**2013**).

18. K. Brunner, A. V. Dijken, H. Borrner, J. J. A. M. Bastiaansen, N. M. M. Kiggen, and B. M. W. Langeveld, *J. Am. Chem. Soc.* 126, 6035 (**2004**).

19. Y. Im and J. Y. Lee, *Chem. Commun.* 49, 5948 (**2013**).

20. B. S. Kim and J. Y. Lee, *Org. Eeletron.* 14, 3024 (**2013**).

21. (a) Y. Wu, Y. Li, S. Gardner, and B. S. Ong, *J. Am. Chem. Soc.* 127, 614 (**2005**); (b) J. Han, B. Thirupathaiah, G. Kwon, C. Kim, and S. Seo, *Dyes Pigments* 114, 78 (**2015**).

22. (a) W. Y. Hung, G. M. Tu, S. W. Chen, and Y. Chi, *J. Mater. Chem.* 22, 5410 (**2012**); (b) C. H. Chen, F. L. Wu, Y. Y. Tsai, and C. H. Cheng, *Adv. Funct. Mater.* 21, 3150 (**2011**).

23. T. Thoms, S. Okada, J. P. Chen, and M. Furugori, *Thin Solid Films* 436, 264 (**2003**).

24. (a) H. Shimizu, A. Kobayashi, S. Itoi, T. Yoshihara, S. Tobita, Y. Nakamura, and J. Nishimura, *Heterocycles* 78, 1265 (**2009**);

(b) Y. H. Chen, Y. Y. Lin, Y. C. Chen, J. T. Lin, R. H. Lee, W. J. Kuo, and R. J. Jeng, *Polymer* 52, 976 (**2011**); (c) J. K. Kwon, J. H. Cho, Y. S. Ryu, S. H. Oh, and E. K. Yum, *Tetrahedron* 67, 4820 (**2011**); (d) J. You, G. Li, and Z. Wang, *Org. Biomol. Chem.* 10, 9481 (**2012**); (e) P. Rajakumar, K. Sekar, and N. Venkatesan, *Synlett* 23, 2504 (**2012**); (f) J. Y. Hu, Y. J. Pu, Y. Yamashita, F. Satoh, S. Kawata, H. Katagiri, H. Sasabe, and J. Kido, *J. Mater. Chem. C* 1, 3871 (**2013**); (g) W. Lee, J. Y. Seng, and J. I. Hong, *Tetrahedron* 69, 9175 (**2013**).

25. (a) B. R. Kaafarani, A. O. El-Ballouli, R. Trattnig, A. Fonari, S. Sax, B. Wex, C. Risko, R. S. Khnayzer, S. Barlow, D. Patra, T. V. Timofeeva, E. J. W. List, J. L. Brédas, and S. R. Marder, *J. Mater. Chem. C* 1, 1638 (**2013**); (b) Y. Chen, D. Han, T. Wang, and X. Li, *Ind. Eng. Chem. Res.* 52, 3646 (**2013**); (c) Q. Zhang, J. Chen, Y. Cheng, L. Wang, D. Ma, X. Jinga, and F. Wanga, *J. Mater. Chem.* 14, 895 (**2004**).

26. (a) Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulaszi, and T. Baumgartner, *Chem. Eur. J.* 13, 7487 (**2007**); (b) T. Ishiyama, J. Takagi, Y. Yonekawa, J. F. Hartwig, and N. Miyaura, *Adv. Synth. Catal.* 345, 1103 (**2003**).

27. (a) A. S. Demir, Ö. Reis, and M. Emrullahoğlu, *Tetrahedron* 58, 8055 (**2002**); (b) H. Jullien, B. Quiclet-Sire, T. Teìtart, and S. Z. Zard, *Org. Lett.* 16, 302 (**2014**); (c) A. A. Kiryanov, P. Sampson, and A. J. Seed, *J. Org. Chem.* 66, 7925 (**2001**); (d) S. Hotta, H. Kimura, S. A. Lee, and T. Tamaki, *J. Heterocyclic Chem.* 37, 281 (**2000**); (e) N. Uchiyama, E. Shirakawa, R. Nishikawa, and T. Hayashi, *Chem. Commun.* 47, 11671 (**2011**); (f) R. Hirase, M. Ishihara, T. Katagiri, Y. Tanaka, H. Yanagi, and S. Hotta, *Org. Electron.* 15, 1481 (**2014**).

28. (a) L. Torun, B. K. Madras, and P. C. Meltzer, *Bioorg. Med. Chem.* 20, 2762 (**2012**); (b) A. S. Demir, Ö. Reis, and M. Emrullahoglu, *J. Org. Chem.* 68, 578 (**2003**).

29. (a) H. S. Jung, H. H. Cho, and S. H. Kim, *Tetrahedron Lett.* 54, 960 (**2013**); (b) L. T. Ball, G. C. Lloyd-Jones, and C. A. Russell, *J. Am. Chem. Soc.* 136, 254 (**2014**).

30. S. M. Sze, Semiconductor Devices: Physics and Technology, Wiley, New York (**1981**).

Received: 27 November 2014. Accepted: 21 December 2014.

Delivered by Publishing Technology to: McMaster University
IP: 179.106.152.75 On: Tue, 12 Jan 2016 10:03:25
Copyright: American Scientific Publishers