Dyes and Pigments 114 (2015) 78–84

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis and characterization of carbazole- and α-carboline-based thiophene derivatives as organic semiconductors for organic thin-film transistors

Jaeuk Han [a, 1], Bodakuntla Thirupathaiah [b, 1], Guhyun Kwon [a], Choongik Kim [a, *], SungYong Seo [b, *]

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

ARTICLE INFO

Article history:
Received 3 October 2014
Received in revised form
28 October 2014
Accepted 30 October 2014
Available online 8 November 2014

Keywords:
Organic thin-film transistors
Carbazole
α-Carboline
Self-assembled Monolayer
Semiconductor
Thiophene

ABSTRACT

New thiophene derivatives, end-functionalized with carbazoles (9-(5-(9*H*-carbazol-9-yl)thiophen-2-yl)-9*H*-carbazole), carbazole and α-carboline (9-(5-(9*H*-carbazol-9-yl)thiophen-2-yl)-9*H*-pyrido[2,3-*b*]indole), and α-carbolines (9-(5-(9*H*-pyrido[2,3-*b*]indol-9-yl)thiophen-2-yl)-9*H*-pyrido[2,3-*b*]indole) were synthesized and characterized as organic semiconductors for organic thin-film transistors (OTFTs). The best device performance was achieved via a hexamethyldisilazane dielectric surface treatment of thermally grown Si–SiO_2 substrates prior to vapor-phase semiconductor deposition. Within this family, the semiconductor having an electron-donating (carbazole) and an electron-withdrawing (α-carboline) substituent exhibited the highest p-channel characteristic with a carrier mobility as high as 0.014 cm^2 V^{-1} s^{-1} and a current on/off ratio of 7×10^5 for top-contact/bottom-gate OTFT devices. The device characteristics have been correlated with the film morphologies and microstructures of the corresponding compounds.

1. Introduction

Over the last few decades, organic thin-film transistors have attracted considerable attention for potential applications as flexible, low-cost, solution-processable, and large-area organic electronic devices. Due to unique properties of organic semiconductors, organic thin-film transistors (OTFTs) are expected to be employed in a variety of applications such as flexible displays, printable RF-ID components, and e-papers [1–4]. To this end, considerable efforts have been concentrated on the development of novel organic semiconductors with high electrical performance and ambient stability [5–11]. Because the electrical property of organic semiconductors is highly dependent upon their chemical structure, the synthesis and characterization of novel organic semiconductors are of great importance [12–17]. Representative examples of high performance organic semiconductors include pentacene [18–20], oligothiophene [21,22], and anthradithiophene derivatives [23].

Carbazole and α-carboline are aromatic heterocyclic organic compounds based on indole structure fused with either a benzene or pyridine ring structure, respectively. Organic semiconductors based on carbazole and α-carboline moieties have extensively been studied as carrier-transport materials or host materials for optoelectronic devices such as photoreceptors and phosphorescent organic light-emitting diodes (PHOLEDs) [24–27]. Some of the requirements for a good host material to achieve high performance PHOLEDs include appropriate energy level alignment with the neighboring layers for efficient charge carrier injection and good charge carrier transporting ability, which are also suitable for the active layer in high performance OTFT devices. However, carbazole and α-carboline derivatives have scarcely been explored as organic semiconductors for OTFTs [28].

To this end, we have synthesized new organic semiconductors based on carbazole and α-carboline moieties (Fig. 1). The 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 on each compound to investigate molecular structures as well as HOMO/LUMO energy levels. Furthermore, the developed

---

* Corresponding authors.
E-mail addresses: choongik@sogang.ac.kr (C. Kim), syseo@pknu.ac.kr (S. Seo).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.dyepig.2014.10.024

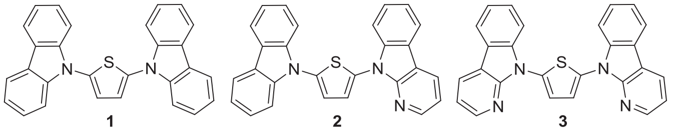

Fig. 1. Chemical structures of the carbazole and α-carboline derivatives employed in this study.

semiconductor films were employed as an active layer 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 performance. Our results revealed that OTFTs exhibited good electrical performance, with a carrier mobility as high as 0.014 $cm^2 V^{-1} s^{-1}$, a current on/off ratio of 7×10^5 for thin films of compound **2**.

2. Experimental

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 F_{254} 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 (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy was performed on a JEOL ECP-400 spectrometer at 400 MHz (^1H) and 100 MHz (^{13}C) at 294 K. Chemical shifts are reported in ppm relative to the residual non-deuterated 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). Infrared (IR) spectra were obtained on a JASCO FT/IR-4100 spectrometer. 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-(5-(9H-carbazol-9-yl)thiophen-2-yl)-9H-carbazole (1) [29–31]

2,5-Dibromothiophene (250 mg, 1.03 mmol), 9*H*-carbazole (380 mg, 2.27 mmol), CuI (59 mg, 0.31 mmol), K_2CO_3 (562 mg, 4.132 mmol), and 18-crown-6 ether (27 mg, 0.103 mmol) were dissolved in N,N-dimethylacetamide (10 mL) and the reaction mixture was heated under reflux under a nitrogen atmosphere for 20 h. The crude mixture was filtered, and the residue was washed with CH_2Cl_2. The combined filtrates were evaporated to dryness under reduced pressure. Then, the crude product was purified by flash column chromatography on silica gel to give compound **1** (132 mg, 30.9%). Spectral data matched well with values reported in the literature [30]. ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, 7.6 Hz, 4H), 7.65 (d, 8.0 Hz, 4H), 7.52 (t, 8.0 Hz, 4H), 7.35 (t, 7.6 Hz, 4H), 7.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 136.4, 126.4, 123.7, 123.6, 120.9, 120.3, 110.1.

2.2.2. Synthesis of 9-(5-bromothiophen-2-yl)-9H-carbazole [32–34]

2,5-Dibromothiophene (4.28 g, 17.69 mmol), 9*H*-carbazole (3.26 g, 19.46 mmol), CuI (1.01 g, 5.30 mmol), K_2CO_3 (9.62 g, 70.76 mmol), and 18-crown-6 ether (467 mg, 1.76 mmol) were dissolved in N,N-dimethylacetamide (100 mL) and the reaction mixture was stirred at 120 °C for 20 h under a nitrogen atmosphere. Then, N,N-dimethylacetamide was distilled under vacuum. 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 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 of 9-(5-bromothiophen-2-yl)-9*H*-carbazole (1.8 g, 31.0%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, 7.6 Hz, 2H), 7.45 (d, 4.0 Hz, 4H), 7.29–7.35 (m, 2H), 7.17 (d, 4.0 Hz, 1H), 6.99 (d, 4.0 Hz, 1H).

2.2.3. Synthesis of 9-(5-(9H-carbazol-9-yl)thiophen-2-yl)-9H-pyrido[2,3-b]indole (2) [26]

9-(5-Bromothiophen-2-yl)-9*H*-carbazole (100 mg, 0.304 mmol), α-carboline (76.7 mg, 0.457 mmol), CuI (17.4 mg, 0.091 mmol), K_3PO_4 (129.3 mg, 0.608 mmol), and *trans*-1,2-diaminocyclohexane (10.4 mg, 0.091 mmol) were dissolved in 1,4-dioxane (8 mL) under a nitrogen atmosphere. The reaction mixture was refluxed for 48 h. The 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** (39 mg, 30.8%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (dd, 1.1, 4.7 Hz, 1H), 8.39 (dd, 1.1, 7.6 Hz, 1H), 8.13 (d, 7.6 Hz, 3H), 7.78 (d, 8.0 Hz, 1H), 7.69 (d, 8.4 Hz, 2H), 7.58 (t, 7.6 Hz, 1H), 7.49 (t, 8.0 Hz, 2H), 7.29–7.43 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 146.6, 141.7, 140.4, 136.3, 134.5, 128.4, 127.4, 126.3, 123.6, 123.4, 123.1, 121.6, 121.1, 120.9, 120.8, 120.2, 116.9, 116.7, 110.7, 110.3. IR (neat, cm^{-1}): 3052, 1625, 1564, 1448, 1405, 1224, 1163. HRMS-EI (*m*/*z*): $[M^+]$ calcd for $C_{27}H_{17}N_3S$, 415.1143; found, 415.1142.

2.2.4. Synthesis of 9-(5-(9H-pyrido[2,3-b]indol-9-yl)thiophen-2-yl)-9H-pyrido[2,3-b]indole (3)

2,5-Dibromothiophene (500 mg, 2.07 mmol), α-carboline (766 mg, 4.55 mmol), CuI (236.5 mg, 1.24 mmol), K_3PO_4 (1.76 g, 8.28 mmol), and *trans*-1,2-diaminocyclohexane (141.8 mg, 1.24 mmol) were dissolved in 1,4-dioxane (20 mL) under nitrogen atmosphere. The reaction mixture was refluxed for 48 h. The 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 **3** (120 mg, 13.9%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (dd, 1.4, 5.1 Hz, 2H), 8.38 (dd, 1.4, 7.6 Hz, 2H), 8.1 (d, 7.6 Hz, 2H), 7.82 (d, 8.0 Hz, 2H), 7.55 (t, 8.0 Hz, 2H), 7.42 (s, 2H), 7.38 (t, 7.3 Hz, 2H), 7.28 (dd, 5.1, 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 146.5, 140.4, 134.4, 128.3, 127.3, 122.6, 121.5, 121.0, 120.8, 116.8, 116.7, 111.0. IR (neat, cm^{-1}): 3049, 1626, 1580, 1451, 1407, 1224, 1165. HRMS-EI (*m*/*z*): $[M^+]$ calcd for $C_{26}H_{16}N_4S$, 416.1095; found, 416.1098.

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(d) basis set as implemented in Gaussian 09 program.