Dyes and Pigments 133 (2016) 114–119

Contents lists available at ScienceDirect

Dyes and Pigments

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

Side chain assisted different types of molecular aggregation and comparison of aggregation dependent field effect mobility

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ARTICLE INFO

Article history:
Received 1 April 2016
Received in revised form
17 May 2016
Accepted 20 May 2016
Available online 24 May 2016

Keywords:
Organic field effect transistor
N-phenylindole
Conjugated material
Diketopyrrolopyrrole
Aggregation
Synthesis

ABSTRACT

Solution-processable conjugated materials having same molecular configuration of both an electron donating *N*-phenylindole and an electron accepting diketopyrrolopyrrole derivative were directly synthesized through the regio-selective modification of 1-phenyl-1*H*-indole. The aggregation behavior of obtained DPIO and DPIE was characterized by means of UV–visible spectroscopy and 2-dimensional grazing-incidence X-ray diffraction. Both materials showed strong aggregation tendency in film, but DPIO and DPIE produced different types of molecular aggregation mostly due to the different side chains. In order to compare the aggregation-type dependent electrical property, DPIO and DPIE were adopted as semiconducting layers in organic field effect transistor, and DPIE produced much higher charge carrier mobility than DPIO. The better electrical properties of DPIE than DPIO was directly correlated with both larger intermolecular π-orbital overlap and well-connected crystalline phases.

1. Introduction

Organic field effect transistors (OFETs) have drawn great attention, because of their potential applications for large-area flexible displays and flexible memory devices, and thus have been intensively investigated [1–6]. A large number of conjugated materials have been synthesized and characterized for use as semiconducting active materials in OFETs. In general, highly crystalline materials having large crystal domain have provided outperforming device in OFETs because crystalline phase facilitates charge-carrier transfer [7–9]. One of facile approaches to increase aggregation tendency in conjugated materials is introducing both electron donating (D) and accepting (A) moieties into a molecular framework. D-A type conjugated structure causes intramolecular charge transfer, resulting in quinoidal planar-chain conformations, which are beneficial for inducing molecular aggregation via intermolecular π-π interaction [10,11].

Various electron donating or accepting groups have been adopted to synthesize conjugated materials having D-A type molecular configuration. Thiophene and selenophene are representative examples of good electron donors [12,13], and isoindigo, diketopyrrolopyrrole (DPP), benzothiadiazole, and naphthalenedicarboximide are well-known electron acceptors [14–17]. Most of researches on semiconducting materials for OFET application have focused on synthesizing D-A type conjugated polymers (CPs), because of facile intra-/inter-molecular carrier transfer along the elongated conjugation pathway [18]. However, CP has potential issues to be practically applicable, in terms of device-to-device uniformity, because its electrical property is sensitively affected by synthesized batch and applied processes in large area [19]. In the case of small molecules, they can avoid potential issues which are expected in polymeric semiconductors, providing consistent electrical properties, including device-to-device uniformity. Although small molecules can offer steady properties regardless of synthesized batch, only a few materials have been explored to be utilized for active layers in OFET, because of the inherent limitation to manipulate long range charge carrier transfer [20,21].

Indole and its derivatives are good candidates to be served as an electron donating material in D-A type molecular framework because of proficient electron donating characteristics [22]. However, indole's vulnerable susceptibility to oxidation often hampered direct substitution of protons with functional groups, especially at 2- or 3-positon of carbon in five-membered ring [23]. Since five-membered aromatic/hetero-aromatic rings provide reduced intrachain steric hindrance, resulting in better planar back-bone conformation in conjugated molecules, rather than six-membered

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http://dx.doi.org/10.1016/j.dyepig.2016.05.031
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rings, devising an effective way of extending π-conjugation through the five-membered ring of indole or its derivatives would be helpful to provide promising electron donating building block for D-A type organic semiconductors.

In this contribution, we invented a way to directly modify 1-phenyl indole. Obtained novel conjugated small molecules (DPIO and DPIE), after Suzuki-type coupling with a diketopyrrolopyrrole (DPP) derivative, exhibited strong aggregation behavior. Their aggregation tendency in film state was verified by means of both UV–visible absorption spectroscopy and 2-dimensional grazing-incidence X-ray diffraction (2D-GIXRD), and principal parameters leading to molecular aggregation were correlated with the molecular configuration calculated by means of density functional theory (DFT). When DPIO and DPIE were adopted as semiconducting active layers in OFET, they marked 3.1×10^{-5} cm^2/V·s and 4.4×10^{-3} cm^2/V·s of hole mobility, respectively. In order to verify the different electrical properties between DPIO and DPIE, their film morphologies were systematically characterized with atomic force microscopy (AFM) and polarized optical microscopy (POM).

2. Experimental section

2.1. Materials

All starting materials were purchased from commercial suppliers (Aldrich and Wako Pure Chemicals). Detailed synthetic procedures are summarized as follows, and compound **3** and **4** were prepared as previously described manner [24]. Synthesized compounds were fully characterized with ^{1}H NMR and mass spectroscopy, and elemental analysis.

2.2. 3-Bromo-1-phenyl-1H-indole (1)

Under dark condition, 1-phenyl-1*H*-indole (1.0 g, 5.17 mmol) was dissolved into DMF, and 1.0 equivalent of NBS diluted into DMF was slowly added under ice bath. Then, the mixture was warmed up to room temperature and stirred for 6 h. After adding water to the mixture, the organic layer was separated via extraction with chloroform and dried with $MgSO_4$. Compound **1** (88%) was obtained from column chromatography after elution of ethylacetate/hexane (1:10) and it was stored into n-hexane at −10 °C, to prevent oxidation. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 1H), 7.78 (s, 1H), 7.54 (m, 5H), 7.2 (m, 3H), and *m/z* EIMS 272. Anal. Calcd. for $C_{14}H_{10}BrN$: C, 61.79; H, 3.70; Br, 29.36; N, 5.15. Found: C, 61.75; H, 3.68; Br, 29.43; N, 5.14%.

2.3. 1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2)

The n-BuLi solution (1.9 ml, 2.0 M) was added drop wise to a THF/n-hexane solution containing compound **1** (1 g, 3.67 mmol) at −75 °C. After stirring for 1 h at 0 °C, 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (0.68 g, 3.67 mmol) was added to the solution at −75 °C, and the solution was additionally stirred for 2 h at room temperature. Then, the reaction was quenched with 10 ml of 1 M HCl solution. After extraction with chloroform, the organic layer was collected and dried with $MgSO_4$. After removing the solvent in vacuo, compound 2 (73%) was obtained from column chromatography using an eluent of chloroform/n-hexane (1:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (m, 1H), 7.81 (s, 1H), 7.55 (m, 5H), 7.25 (m, 3H), 1.40 (s, 12H), and *m/z* EIMS 319. Anal. Calcd. for $C_{20}H_{22}BNO_2$: C, 75.25; H, 6.95; B, 3.39; N, 4.39; O, 10.02. Found: C, 75.24; H, 6.65; B, 3.37; N, 4.39; O, 10.35%.

2.4. DPIO

Under inert conditions (N_2), compound **2** (0.47 g, 1.48 mmol) and **3** (0.33 g, 0.49 mmol) were dissolved into toluene. After adding 1–2 drop of Aliquat@366 and aqueous Na_2CO_3 (2 M, 5.6 ml) to the solution, the mixture was stirred for 10 min at room temperature. Then, Pd[0] (28.43 mg, 0.025 mmol) was added to the solution, and the mixture was stirred overnight at 110 °C. After cooling to room temperature, the solution was poured into water and extracted with chloroform. The collected organic layer was dried with $MgSO_4$, and the solvent was evaporated in vacuo. **DPIO** was obtained through column chromatography after elution with chloroform/n-hexane (1:1) and subsequent recrystallization from acetone/chloroform (65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (d, 2H), 8.12 (t, 2H), 7.78 (s, 2H), 7.60 (m, 12H), 7.48 (m, 2H), 7.40 (m, 4H), 4.22 (t, 4H), 1.90 (m, 4H), 1.30 (m, 20H), 0.88 (m, 6H) and *m/z* MALDI-TOF: 907. Anal. Calcd. for $C_{58}H_{58}N_4O_2S_2$: C, 76.78; H, 6.44; N, 6.18; O, 3.53; S, 7.07. Found: C, 76.74; H, 6.46; N, 6.12; O, 3.63; S, 7.05%.

2.5. DPIE

Final product was similarly obtained from the synthetic method for DPIO. Compound **2** (0.47 g, 1.48 mmol) and **4** (0.33 g, 0.49 mmol) were used and 0.26 g of DPIE was collected. (58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (d, 2H), 8.11 (t, 2H), 7.76 (s, 2H), 7.60 (m, 12H), 7.44 (m, 2H), 7.42 (m, 4H), 4.02 (t, 4H), 1.86 (m, 2H), 1.30 (m, 16H), 0.86 (m, 12H) and *m/z* MALDI-TOF: 907. Anal. Calcd. for $C_{58}H_{58}N_4O_2S_2$: C, 76.78; H, 6.44; N, 6.18; O, 3.53; S, 7.07. Found: C, 76.76; H, 6.44; N, 6.14; O, 3.62; S, 7.04%.

2.6. TFT device fabrication

DPIO or DPIE was dissolved in chloroform (20 mg/ml). The solution was spin-casted on octadecyltrichlorosilane (ODTS)-modified silicon wafers with a spin speed of 3000 rpm. Silicon wafers with a 300 nm thick thermally grown SiO_2 layer were cleaned with acetone, isopropyl alcohol and UVO_3 treatment prior to use and ODTS layer was fabricated by immersing the silicon wafers into ODTS/toluene (40 μl/20 ml) solution. After 1 h of reaction, the silicon wafers were annealed at 120 °C and unreacted ODTS was cleaned by sonication in toluene. Residual solvent was removed by storing the DPIO and DPIE films in vacuum oven for 1 day. Au source/drain electrodes with 50 nm thickness were thermally deposited on the DPIO and DPIE films through a shadow mask to complete the fabrication of OFETs. The channel length and width of the fabricated OFETs were 100 μm and 1500 μm, respectively.

2.7. Characterization

Atomic force microscopy (Park Scientific Instrument, Autoprobe-PC) and polarized optical microscopy (Nikon ECLIPSE LV100 POL) were utilized to characterize the morphologies of the films while crystallization characteristics of DPIO and DPIE were examined by UV–vis spectroscopy (Cary-60) and 2D-GIXRD (3C beamline in Pohang Accelerator Laboratory of Korea). All the electrical measurements of OFETs were conducted using a Keithley 4200-SCS semiconductor parameter analyzer under vacuum.

3. Results and discussions

As shown in Scheme 1, 3-bromo-1-phenyl-1H-indole (**1**) was regio-selectively synthesized via a direct bromination from 1-phenyl-1*H*-indole. The obtained compound **1** easily decomposed under ambient condition, resulting in color change from white to brown. This would be connected with the intrinsic nature of