



A diketopyrrolopyrrole containing molecular semiconductor: Synthesis, characterization and solution-processed 1D-microwire based electronic devices

Akshaya K. Palai, Junghyun Lee, Sujoy Das, Jihee Lee, Hyejin Cho, Seung-Un Park, Seungmoon Pyo*

Department of Chemistry, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 143-701, Republic of Korea

ARTICLE INFO

Article history:

Received 9 April 2012

Received in revised form 1 June 2012

Accepted 9 June 2012

Available online 1 July 2012

Keywords:

Carbazole

Diketopyrrolopyrrole

Organic semiconductor

Solution processing

Field-effect-transistor

Phototransistor

ABSTRACT

Highly oriented 1D-microwires of a diketopyrrolopyrrole (DPP) based semiconductor i.e. **DPP(CBZ)₂** (Carbazole capped DPP) were synthesized, characterized and applied to the fabrication of organic optoelectronic devices. 1D-microwires of **DPP(CBZ)₂** were prepared by solution processing on capillary tubes serving to pin solution. A bottom-gate, top-contact field-effect transistor employing 1D-microwire and polymeric gate dielectric showed a hole mobility of $1.24 \times 10^{-2} \text{ cm}^2/\text{V s}$, an on-to-off drain current ratio ($I_{\text{on}}/I_{\text{off}}$) of 4.7×10^3 and subthreshold slopes of 4 V/dec under ambient conditions. Under white light, a photo-sensitivity of 800 at $V_G = -40 \text{ V}$ and photoresponsivity of 830 mW/A were achieved. This work demonstrates the potential of this new molecule and the solution method for use in various opto-electronic devices such transistors, photosensors and photovoltaics.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The easily processed, conjugated organic semiconductors with high carrier mobility and good ambient stability would be crucial to the development of inexpensive and mechanically flexible printed electronics [1]. They could also act as renewable energy sources due to their amenability to high roll-to-roll processing and their being architecturally tunable over multiple length scales. Among conjugated organic semiconductors [2], diketopyrrolopyrrole (DPP) derivatives [3] are the most widely studied and used as active components in optoelectronics due to their strong electron affinity, stability and easily tunable properties. They have been used as active components in high-performance organic field-effect transistors (OFETs) [4] and efficient organic photovoltaic devices [5]. Their optical properties make them suitable for use in organic

light emitting diodes (OLEDs) [6]. Their visible absorption characteristics give them applicability as light-sensitive materials in organic phototransistors (OPTs), three terminal optoelectronic devices that use light as an additional stimulus to generate photocarriers at the gate dielectric/semiconductor interface in addition to the carriers induced by an electric field. Most DPP based semiconductors are polymeric and have been relatively well investigated. However, there are few reports of the synthesis and application of well-defined DPP based small molecules [7,5a] which are more easily purified than their polymer counterparts. OPTs with DPP based molecular semiconductors have not been reported previously [8].

The introduction of carbazole moieties to semiconducting polymers and small molecules can provide excellent electro- and photo-active properties and photochemical stability [9]. High-mobility, low-band gap polymers with carbazole moieties for photovoltaic applications have been reported by Leclerc and co-workers [9c]. Hu and co-workers reviewed organic photo-responsive materials

* Corresponding author. Tel.: +82 2 450 3397; fax: +82 2 3436 5382.
E-mail address: pyosm@konkuk.ac.kr (S. Pyo).

and devices, including carbazole derivatives [10]. They also reported high-performance OPTs with carbazole based conjugated polymers [11].

This work reports the synthesis and characterization of a new well-defined DPP molecular semiconductor end-capped with carbazole moieties, **DPP(CBZ)₂**. Its extended π -conjugation is expected to afford strong intermolecular orbital overlap and could enhance charge transport. The introduction of hexadecyl substituents on the backbone has been reported to enhance organic solubility. In the previous reports, optoelectronic devices incorporating DPP based small molecules have had active layers formed by drop casting [5a] and spin-casting [7c]. Typical solution methods may lead to non-uniform and polycrystalline thin-film domains. 1D-microwires were directly formed here from **DPP(CBZ)₂** solution on the polymer gate dielectric so as to fabricate OFETs and OPTs. This method represents a simple and efficient fabrication of high-performance and low-cost OFETs on polymer dielectrics without the need for additional processing. OFETs achieved a maximum charge carrier mobility of $1.24 \times 10^{-2} \text{ cm}^2/\text{V s}$. To test the applicability of this OFET in light sensing electronic devices, its photo-response characteristics were also investigated. A maximum photocurrent gain of 800 was obtained at $V_G = -40 \text{ V}$ and a photoresponsivity of 830 mW/A was shown by OPTs employing the 1D-microwires. This initial study shows that **DPP(CBZ)₂** can be used as an active component in organic optoelectronic devices.

2. Experimental

2.1. Materials and general information

The compounds 3,6-di(thiophen-2-yl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (**1**) [6a], 2,5-dihexadecyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) [12] and 3,6-bis(5-bromothiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**3**) [12] were prepared according to literature procedure. 4-(9H-carbazol-9-yl)phenylboronic acid was purchased from Luminescence Technology Corp. (Lumtec, Taiwan). *N*-Bromosuccinimide (NBS) was recrystallized from water prior to use. Pd(PPh₃)₄, anhydrous *N,N*-dimethylformamide (DMF) and anhydrous toluene were purchased from Aldrich. All other reagents and solvents for synthesis were obtained from commercial suppliers and purified according to standard procedures [13]. For OFET fabrication, poly(4-vinylphenol) (PVP) ($M_w = 20,000 \text{ g/mol}$) polymer, poly(melamine-co-formaldehyde) (PMF) ($M_n = 511 \text{ g/mol}$) cross-linker and propylene glycol monomethyl ether acetate (PGMEA) solvent were used in the preparation of the polymer gate dielectric. They were purchased from Aldrich and used without further purification. Analytical thin layer chromatography (TLC) was performed on glass plates, precoated with silica gel 60 F₂₅₄ (Merck). Column chromatography was performed on silica gel 60 (0.063–0.200 mm, 70–230 mesh, Merck). Melting point (Mp) was determined using Melting point apparatus (MEL-TEMP II, USA) equipped with a thermometer. ¹H and ¹³C spectra were recorded in CDCl₃ on a Bruker Avance 400 spectrom-

eter. High resolution ESI-FTMS was performed with a Thermo LTQ-Orbitrap XL mass spectrometer. UV-vis measurements were performed in solution (CH₂Cl₂) in quartz cell as well as solid film of **DPP(CBZ)₂** on a Varian Cary 500 spectrometer. Solid film was made by drop casting chloroform solution of **DPP(CBZ)₂** on quartz substrate. Cyclic voltammetry (CV) experiment was carried out using COMPACTSTAT.e: Portable Electrochemical Interface & Impedance Analyser (IVIUM Technologies). CV measurement was recorded in 1,2-dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte (scan rate: 50 mV s⁻¹). DCM was dried over calcium hydride and degassed under argon before using. The supporting electrolyte (Bu₄NPF₆) was purchased from Aldrich and used as received. The experiment was performed inside glovebox at room temperature with a three electrode system consisting of a platinum electrode as working electrode, a platinum mesh counter electrode, and an Ag/AgCl reference electrode with ferrocene as an internal standard.

2.2. Synthesis

2.2.1. 3,6-Bis(5-bromothiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**3**)

To a solution of 2,5-dihexadecyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) (200 mg, 0.266 mmol) in 25 mL of chloroform and 5 mL of acetic acid, NBS (100 mg, 0.586 mmol) was added slowly. The reaction container was protected from light and stirred at room temperature overnight. The reaction mixture was quenched with MeOH (100 mL) and the resultant solid was filtered and dried to give a purple solid. The material was further purified by column chromatography using CHCl₃ as eluent to obtain purple solid with 63% yield. ¹H NMR (400 MHz, CDCl₃, δ): 8.68 (d, 2H), 7.24 (d, 2H), 3.98 (t, 4H), 1.69 (m, 4H), 1.25 (m, 52H), 0.87 (t, 6H).

2.2.2. 3,6-Bis(5-(4-(9H-carbazol-9-yl)phenyl)thiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **DPP(CBZ)₂**

Compound **3** (50 mg, 0.055 mmol), 4-(9H-carbazol-9-yl)phenylboronic acid (50 mg, 0.174 mmol, 3.15 equiv.) and Pd(PPh₃)₄ (6 mg) were added to a 50 mL schlenk flask containing argon-degassed toluene (4 mL). The above mixture was subjected to three vacuum/argon refill cycles, and to it an aqueous 2 M K₂CO₃ (1.2 mL, N₂ degassed overnight) was added via syringe. The reaction was stirred for 30 min under argon at an ambient temperature, and vacuum/argon cycles were repeated 3 more times to ensure the oxygen removal. The reaction mixture was then heated at 85 °C for 6 h and monitored via TLC. After completion of the reaction removal of toluene, extraction with chloroform, repetitive washing with water, drying over MgSO₄, and removal of the solvent in vacuo afforded the crude product which was then purified using column chromatography (silica gel, CHCl₃ and petroleum ether mixture as eluent) and gave the product as a dark blue solid (50 mg, 72%). Mp: 202 °C. ¹H NMR (400 MHz, CDCl₃, δ): 9.05 (d, 2H), 8.15 (dd, 4H), 7.92 (d, 4H), 7.71 (d, 4H), 7.65 (d, 2H), 7.58 (dd, 4H), 7.51 (m, 4H), 7.30 (m, 4H), 4.18 (t, 4H),

Download English Version:

<https://daneshyari.com/en/article/1264040>

Download Persian Version:

<https://daneshyari.com/article/1264040>

[Daneshyari.com](https://daneshyari.com)