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Synthesis and properties of a novel narrow band gap oligomeric diketopyrrolopyrrole-based organic semiconductor

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ABSTRACT

A trimer of diketopyrrolopyrole (DPP), Tri-BTDPP, was synthesized and characterized. Tri-BTDPP has a HOMO level of −5.34 eV, a low band gap of 1.33 eV, and a hole mobility of ~10^{-3} cm^2 V^{-1} s^{-1} in organic field effect transistors (OFETs). Organic photovoltaic (OPV) devices using the donor/acceptor blends of Tri-BTDPP and $PC_{71}BM$ exhibited low power conversion efficiencies (PCE) of up to 0.72%, even though the desirable optical and electronic characteristics of this compound as a donor semiconductor for achieving high performance for OPV. Through an intensive study of the active layer using AFM, XRD, and DSC, it was found that Tri-BTDPP and $PC_{71}BM$ were unable to intermix and formed oversized Tri-BTDPP phases, resulting in poor charge separation. Some guidance on how to improve the OPV performance of Tri-DPP compounds is provided.

1. Introduction

Organic photovoltaics (OPVs) or organic solar cells represent a promising technology to provide sustainable and cost-effective energy because OPVs can be manufactured at high throughputs using printing technologies. They have attracted enormous attention from the scientific community and industry for the last decade [1–9]. Depending on the molecular weight, the organic semiconductors used in OPVs can be either polymers or small molecules, both of which have achieved high power conversion efficiencies (PCE) of about 10% in single-junction devices [10–13]. Small molecule organic semiconductors have well-defined structures and much higher purity than their polymer counterparts. Their syntheses do not suffer from large batch-to-batch variations as those of polymers. However, solution-processed small molecules often show poor film formation capability compared to polymers. Consequently, OPVs based on solution-processed small molecules often have low fill factors (FFs). To improve the solution processability while maintaining other merits of small molecules, oligomeric organic semiconductors with molecular weights between those of polymers and small molecules are being studied recently. Power conversion efficiencies (PCE) of 6–9% have been achieved with oligomer semiconductors [14–16], which are comparable to those of small molecule [1–4] and polymer solar cells [17–19].

Diketopyrrolopyrrole (DPP) derivatives such as Pigment Red 254 (C.I.56110) are well known dyes and pigments [20]. DPP is currently one of the most widely studied electron-accepting building blocks for constructing low band gap semiconductors including small molecules, oligomers, and polymers for OPVs [21–30]. A series of oligomers consisting of two DPP terminal units and different cores such as naphtodithiophene and benzodithiophene (DPP-Core-DPP) were reported to achieve a PCE of 4–5% [25,26]. In 2013, Nguyen's group reported Tri-DPP (DPP-DPP-DPP) having one bisphenyl DPP unit flanked by two bisthiophene DPP units [22,31], which showed improved charge transport, quality of the film, FF and PCE (5.5%) of

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the OPV devices. It is known that bisphenyl DPP unit is non-coplanar with a large dihedral angle of ~20–40° due to the steric repulsion between the phenyl ring and the DPP core [30]. Here, we report a new DPP oligomer consisting of three bisthiophene DPP units in order to achieve a coplanar structure. A coplanar molecular geometry is expected to contribute to greater crystallinity, improved charge transport, and a lower band gap of the semiconductor. We used this new DPP compound as an electron donor (combined with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as electron acceptor) in OPV devices.

2. Experimental section

2.1. Materials and measurements

All reagents and chemicals were purchased from commercial sources and used without further purification. 3-(5-Bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo [3,4-*c*]pyrrole-1,4-dione (**1**) and 2,5-bis(2-octyldodecyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)-2,5-dihydropyrrolo [3,4-*c*]pyrrole-1,4-dione (**2**) were prepared as described in the literature [32,33].

^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz and 300 MHz Bruker NMR using $CDCl_3$ as solvent and tetramethylsilane (TMS, 0 ppm) as a reference. High resolution electrospray technique mass spectrometry was used for Tri-BTDPP and MALDI-TOF for the by-product. Cyclic voltammetry (CV) measurements were conducted using a DY2000EN electrochemical workstation in a 0.1 M tetrabutylammonium hexafluorophosphate electrolyte solution in acetonitrile at room temperature at a scan rate of 50 mV s^{-1}. The working electrode and counter electrode were platinum electrodes and the reference electrode was Ag/AgCl (0.1 M) electrode. The reference electrode was calibrated against the redox potential of ferrocene/ferrocenium (Fc/Fc^+). A Pt disk with a semiconductor thin film formed by drop-casting a chloroform solution was used as the working electrode. AFM imaging was carried out at room temperature using an AFM Nanoman from Bruker Instrument with Nanoscope 5 controller. Images were obtained in tapping mode using silicon tips (PointProbe® Plus AFM-probe, Nanosensors, Switzerland). Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo DSC 1 Stare system at a heating/cooling rate of 10 °C min^{-1}. The molecular packing was characterized by wide-angle X-ray diffraction (XRD, PANalytical X'Pert Pro MPD) using the Cu Kα radiation. θ/2θ scans were performed to the drop cast films at room temperature.

2.2. Device and characterization

The photovoltaic properties were tested in both conventional solar cells and inverted solar cells adopting respectively the structures of ITO/PEDOT:PSS/Tri:BTDPP:$PC_{71}BM$/(Ca)/Al and ITO/ZnOx/TriBTDPP:$PC_{71}BM$/MoO_3/Ag. For conventional solar cells fabrication, ITO–coated glass substrates were successively cleaned in ultrasonic baths of acetone/ethanol/isopropanol for 10 min, followed by oxygen plasma treatment for 15 min. An aqueous solution of PEDOT:PSS, previously filtrated with a 0.2 μm filter, was deposited by spin-coating at 4000 rpm for 60 s. The layer was dried in an oven at 100 °C under vacuum for 30 min. Then, a solution of Tri-BTDPP:$PC_{71}BM$ (1:1, 15 mg mL^{-1}) in chloroform containing optional 1 vol.% DIO were spin-coated on top of PEDOT:PSS under nitrogen atmosphere. The thickness of the active layer was ~90 nm. The solvents were removed by annealing the active layer at 80 °C for 10 min. Calcium (10 nm) and then aluminum (80 nm) were thermally evaporated onto the active layer through shadow masks under 2–4 × 10^{-6} mbar. The effective area was 10 mm^2.

For inverted solar cell, after similarly pre-cleaning the ITO-coated substrates, a solution of ZnO_x prepared with 0.15 M of zinc acetate and 0.15 M of ethanol amine in ethanol was spin-coated at 2000 rpm for 60 s. The layer was annealed at 180 °C for 1 h. The active layer was prepared and deposited as for the conventional solar cells. To complete the device, molybdenum (IV) oxide (10 nm) and silver (80 nm) were thermally evaporated onto the active layer through shadow masks under 2–4 × 10^{-6} mbar. The effective area was 10 mm^2.

The devices were characterized using a K.H.S SolarCelltest-575 solar simulator with AM 1.5G filters set at 100 mW cm^{-2} with a calibrated radiometer (IL 1400BL). The current density-voltage (J-V) curves were measured with Labview controlled Keithley 2400 SMU. Devices were characterized under nitrogen in a set of glove boxes (O_2 and H_2O < 0.1 ppm).

Bottom-gate, bottom-contact field effect transistors (OFETs) were fabricated using Fraunhofer IPMS templates of heavily n-doped Si with 200 nm-thick silicon oxide and gold electrodes. Substrates were cleaned with successive acetone and IPA baths followed by 15 min of UV-ozone treatment. A solution of 5 mg mL^{-1} of Tri-BTDPP in chloroform was spin-coated at 2500 rpm for 40 s on top of transistor substrates in the nitrogen-filled glovebox to form a 40 nm-thick layer. The dimensions of the channel were L = 5 μm and W = 1 cm. Transistors were measured using a semiconductor analyzer (Keithley 4200) coupled with a probe station.

2.3. Synthesis

2.3.1. 6,6′-((2,5-Bis(2-octyldodecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2′-bisthiophene]-5′,5-diyl))bis(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (Tri-BTDPP)

A 100 mL dry three-necked round bottom flask was charged with compound **1** (1.5 g, 0.0025 mol, 2.1 eq), compound **2** (1.40 g, 0.0012 mol, 1 eq), P(*o*-tolyl)$_3$ (28.7 mg, 0.09 mmol, 0.08 eq) and anhydrous toluene (49 mL) under argon. Then, $Pd_2(dba)_3$ (21.9 mg, 0.024 mmol, 0.02 eq) dissolved in anhydrous toluene (1 mL) was added into the flask through a syringe. The mixture was heated to reflux and the color of the solution turned from purple to blue gradually. The reaction was monitored by the thin layer chromatography (TLC) analysis of the reaction mixture. After 60 h, no appreciable starting materials were detected and the reaction was terminated by cooling the reaction mixture to room temperature. The solution was poured into methanol (600 mL) and stirred for 30 min. The resulting precipitate was filtered and purified using column chromatography on silica gel with a mixture of dichloromethane (DCM) and hexane (with a volume ratio of 6:4) and then pure chloroform as eluent to afford 1.65 g (72%) of the crude product and 0.60 g (26%) of 6,6′-([2,2′-bithiophene]-5,5′-diyl) bis(2,5-bis(2-ethylhexyl)-3-(thiophen-2-yl)-2,5-dihydropyrrolo [3,4-*c*]pyrrole-1,4-dione) (**3**), a by-product formed by the mono-coupling of compound **1** and **2**. The crude product obtained by the first column separation contains the target Tri-BTDPP and the by-product 3-(5′-(2,5-bis(2-ethylhexyl)-3,6-dioxo-4-(thiophen-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2′-bithiophen]-5-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**4**), formed by the homo-coupling of **1**. 0.50 g of this crude product was further purified on silica gel column chromatography at 50 °C using a mixture of chloroform/toluene (volume ratio: 1/1) as eluent to afford 0.39 g pure Tri-BTDPP as a dark blue solid and 0.11 g of the by-product **4**. The total amounts of Tri-BTDPP and **4** in 1.65 g of the crude product are estimated to be 1.29 g (56%) and 0.36 g (16%), respectively. Data for Tri-BTDPP: ^{1}δH NMR ($CDCl_3$, 400 MHz) 8.93 (2H, d, J = 4.2 Hz), 8.91 (2H, d, J = 4.2 Hz), 8.85 (2H, dd, J = 3.9, 1.1 Hz), 7.49 (2H, dd,