Small-molecule acceptors based on 4H-cyclopenta[1,2-b:5,4-b′]dithiophene units with near-infrared absorption for nonfullerene polymer solar cells

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**ABSTRACT**

Two small-molecule acceptors 1CIC and 2CIC based on 4H-cyclopenta[1,2-b:5,4-b′]dithiophene units and 1,1-dicyanomethylene-3-indanone were developed. Compared with 1CIC, 2CIC possesses red-shift absorption, higher HOMO and LUMO energy levels, and higher electron mobility. Nonfullerene polymer solar cells based on PTB7-Th:2CIC gave a power conversion efficiency (PCE) of 3.53%, with an open-circuit voltage (V\(_{oc}\)) of 0.75 V, a short-circuit current (J\(_{sc}\)) of 10.97 mA/cm\(^2\). As contrast, PTB7-Th:1CIC cell gave a PCE of 0.26%. Our results indicated that the absorption spectra of small-molecule acceptors containing indaceno[1,2-b:5,6-b′]dithiophene (IDT) core can be efficiently extended to near-infrared region by replacing the aromatic benzene ring of with 2,2′-bithiophene.

1. Introduction

Polymer solar cells (PSCs) with bulk heterojunction (BHJ) architecture have attracted extensive attention due to their unique advantages such as low processing cost, flexibility, and light weight [1,2]. Generally speaking, PSCs employed conjugated polymers as electron donors, fullerenes or their derivatives, such as phenyl-C\(_{61}\)-butyric acid methyl ester (PC\(_{61}\)BM), phenyl-C\(_{71}\)-butyric acid methyl ester (PC\(_{71}\)BM) and indene-C\(_{5}\)_9 bisadduct (IC\(_{5}\)BA), as electron acceptors [2–5]. However, fullerene derivatives suffer from several drawbacks, like poor light absorption, limited tunability of chemical structures and energy levels, high-cost purification and morphology instability [6–9]. Therefore, non-fullerene electron acceptors, particularly small-molecule electron acceptors, have been developed rapidly in past few years [7–15]. Small-molecule acceptors with efficient absorption, tunable energy levels, good device stability, and easy synthesis and purification have become one of the hottest research topics in organic optoelectronic. Very recently, single PSCs based on small-molecule electron acceptors have successfully achieved power conversion efficiencies (PCEs) over 14%, and these have been considered as promising alternatives to fullerenes derivatives [16].

The optical and electronic properties of small-molecule acceptors with acceptor-donor-acceptor (A-D-A) structure can be easily tuned by varying the electron-donating cores or end-capping electron-withdrawing groups. Small-molecule acceptors based on indaceno[1,2-b:5,6-b′]dithiophene (IDT) [17], indacenodithieno[3,2-b]thiophene (IDTT) [7], indacenodithieno[3,2-b:2′,3′-d]thiophene (IBDT) [18], benzo[1,2-b:4,5-b′]di(cyclopenta[2,1-b:3,4-b′]dithiophene) [19], and other electron-rich units [20,21] have demonstrated excellent photo-voltaic performance. 4H-Cyclopenta[1,2-b:5,4-b′]dithiophene (CPDT), where two thiophene units are rigidified by a covalent carbon, is an excellent unit for D-A copolymers or small molecules donor material in organic solar cells (OSC) or dye-sensitized solar cells (DSSC) [22–25]. Very recently, Chen et al. reported a new nonfullerene acceptor DF-PCIC with an unfused-ring core containing one 2,5-difluorobenzene and two CPDT moieties, which yielded a decent PCE of 10.14% [26]. In this work, two small-molecule electron acceptors 1CIC and 2CIC using CPDT as the core units and 1,1-dicyanomethylene-3-indanone (IC) as the ending group were synthesized (Fig. 1). In addition, 2CIC can be regarded as a derivative of IDIC by replacing benzene ring with 2,2′-bithiophene [17]. Compared with 1CIC, 2CIC with two CPDT units possesses broader absorption spectra even to near-infrared region with optical bandgap of 1.35 eV, which is much narrower than that of IDIC (1.62 eV) [17]. PSCs based on PTB7-Th:2CIC gave a PCE of 3.53%,
which is much better than that of PTB7-Th:1CIC cell.

2. Experimental

2.1. Materials

4,4-Dihexyl-4H-cyclopenta[1,2-b:5,4-b′]dithiophene (1) and 6-bromo-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b′]dithiophene-2-carbaldehyde (2) were synthesized following the literatures [24,25]. The other materials were common commercial available products and were used as received.

2.2. Syntheses

2.2.1. Synthesis of 4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b′]dithiophene-2,6-dicarbaldehyde (2)

To a solution of compound 1 (1.52 g, 4.39 mmol) and DMF (1.5 mL, 19 mmol) in 1,2-dichloroethane (40 mL) were added POCl3 (1.5 mL, 16 mmol) at 0 °C under Ar. The mixture was syringed into the mixture and the resulting mixture was heated at 50 °C for 30 min. The compound 4 (2.0 g, 4.41 mmol) in DMF (5 mL) was syringed into the mixture and the resulting mixture was heated at 80 °C for 16 h. After cooling to room temperature, the mixture was poured into ice water, and then extracted with dichloromethane three times. The combined organic layer was washed with Na2CO3 (aq) and brine, dried over anhydrous MgSO4. After removal of solvent, the crude product was purified by silica gel using petroleum ether/dichloromethane (1:1) as eluent, yielding a yellow solid (1.19 g, 67.2%). 1H NMR (CDCl3, 500 MHz, δ/ppm): 9.91 (s, 2 H), 7.62 (s, 2 H), 1.92-1.89 (m, 8 H), 1.22-1.16 (m, 12 H), 0.97-0.91 (m, 4 H), 0.82 (t, J = 7.0 Hz, 6 H). 13C NMR (CDCl3, 125 MHz, δ/ppm): 182.85, 161.31, 146.62, 145.07, 134.87, 129.84, 118.05, 54.25, 37.67, 31.55, 29.59, 24.56, 22.59, 13.99. MALDI-TOF MS (m/z): 755.199 (M+). Elemental analysis (%) calcd for C44H58O2S4: C, 74.77; H, 5.07; N, 7.42. Found: C, 74.49; H, 5.00; N, 7.29.

2.2.2. Synthesis of 2,2′-((2Z,2′Z)-((4,4-diethyl-4H-cyclopenta[1,2-b:5,4-b′]dithiophene-2,6-diyli)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (1CIC)

To a solution of compound 2 (100 mg, 0.25 mmol) and 1,1-dicyanomethylene-3-indanone (305 mg, 1.57 mmol) in dry CHCl3 (40 mL) was added pyridine (0.6 mL) under argon. The mixture was refluxed for 20 h and then allowed to cool to room temperature. The mixture was poured into CH2OH (200 mL). The precipitate was collected and purified through a silica gel column with petroleum ether/CH2Cl2 (1:2) as eluent to give 1CIC as a black solid (147 mg, 78.6%). 1H NMR (CDCl3, 500 MHz, δ/ppm): 8.94 (s, 2 H), 8.72-8.78 (m, 2 H), 7.99-7.98 (m, 2 H), 7.83-7.78 (m, 4 H), 7.68 (s, 2 H), 1.98-1.95 (m, 4 H), 1.21-1.13 (m, 12 H), 0.96-0.90 (m, 4 H), 0.81 (t, J = 7.0 Hz, 6 H). MALDI-TOF MS (m/z): 747.149 (M+). Elemental analysis (%) calcd for C44H58O2S4: C, 70.73; H, 7.82. Found: C, 70.82; H, 7.79.

2.2.3. Synthesis of 4,4,4′,4′-tetrahexyl-4H[2,2′-bi(cyclopenta[1,2-b:5,4-b′]dithiophene)]-6,6′-dicarbaldehyde (5)

The mixture of Ni(PPh3)2Cl2 (0.43 g, 0.65 mmol), PPh3 (0.36 g, 1.36 mmol), Zn powder (0.70 g, 10.8 mmol) and KI (0.04 g, 0.27 mmol) were dissolved in fresh DMF (50 mL) and then the mixture was stirred at 50 °C for 30 min. The compound 4 (2.0 g, 4.41 mmol) in DMF (5 mL) was syringed into the mixture and then extracted with dichloromethane three times. The combined organic layer was washed with water for several times, dried over anhydrous MgSO4. After removal of solvent, the crude product was purified by silica gel using petroleum ether/dichloromethane (1:2) as eluent to give compound 5 as a red solid (0.62 g, 37.6%). 1H NMR (CDCl3, 500 MHz, δ/ppm): 9.85 (s, 2 H), 7.57 (s, 2 H), 7.11 (s, 2 H), 1.95-1.84 (m, 8 H), 1.22-1.16 (m, 24 H), 1.02-0.95 (m, 8 H), 0.82 (t, J = 7.0 Hz, 12 H). 13C NMR (CDCl3, 125 MHz, δ/ppm): 182.48, 163.19, 158.00, 147.10, 143.63, 142.06, 134.87, 129.84, 118.05, 54.25, 37.67, 31.55, 29.59, 24.56, 22.59, 13.99. MALDI-TOF MS (m/z): 747.149 (M+). Elemental analysis (%) calcd for C44H58O2S4: C, 70.73; H, 7.82. Found: C, 70.82; H, 7.79.

2.2.4. Synthesis of 2,2′-((2Z,2′Z)-((4,4,4′,4′-tetrahexyl-4H[2,2′-bi(cyclopenta[1,2-b:5,4-b′]dithiophene)]-6,6′-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (2CIC)

2CIC was synthesized by following the same procedures for 1CIC. Compound 5 (100 mg, 0.21 mmol) and 1,1-dicyanomethylene-3-indanone (250 mg, 1.29 mmol) were used as starting materials. 2CIC was obtained as a blue-black solid (77 mg, 52.4%). 1H NMR (CDCl3, 500 MHz, δ/ppm): 8.90 (s, 2 H), 8.63-8.68 (m, 2 H), 7.91-7.89 (m, 2 H), 7.77-7.73 (m, 4 H), 7.60 (s, 2 H), 7.18 (s, 2 H), 2.01-1.91 (m, 8 H), 1.24-1.19 (m, 24 H), 1.02-0.99 (m, 8 H), 0.83 (t, J = 6.9 Hz, 12 H). 13C NMR (CDCl3, 125 MHz, δ/ppm): 188.42, 166.10, 160.37.

Fig. 1. Chemical structures of PTB7-Th, IDIC, 1CIC and 2CIC.
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