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Organic field-effect transistor and its photoresponse using a benzo[1,2-b:4,5-b′]difuran-based donor–acceptor conjugated polymer

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ABSTRACT

Organic field-effect transistors (OFETs) were fabricated through a solution process with a donor–acceptor (D–A) conjugated polymer poly{4,8-bis(2′-ethylhexylthiophene)benzo [1,2-b;3,4-b′]difuran-*alt*-5,5-(4′,7′-di-2-thienyl-5′,6′-dioctyloxy-2′,1′,3′-benzothiadiazole)} (PBDFTDTBT) as the active layer, which is a highly efficient D–A conjugated polymer as a donor in polymer solar cells with a power conversion efficiency (*PCE*) over 6.0%. The OFET devices showed a hole mobility of 0.05 cm^2/Vs and an on/off ratio of 4.6×10^5. Those are one of the best performance parameters for OFETs based on D–A conjugated polymers including benzo[1,2-b:4,5-b′]dithiophene (BDT) or benzo[1,2-b:4,5-b′]difuran (BDF) unit. The photoresponse of OFETs was investigated by modulating light with various intensities. The devices produced a photosensitivity (I_{light}/I_{dark}) of 1.2×10^5 and a photoresponsivity of 360 mA W^{-1} under white light illumination. The drain current in saturation region increases gradually with increasing illumination intensity. The threshold voltage exhibited a positive shift from −15.6 V in darkness to 27.8 V under illumination, which can be attributed to the well-known photovoltaic effect resulting from the transport of photogenerated holes and trapping of photogenerated electrons near the source electrode in organic phototransistors. Meanwhile, the devices showed good stability and with no obvious degeneration for 3 months in air. The study suggests that D–A conjugated polymers including BDF unit can be potentially applied in OFETs and organic phototransistors in addition to highly efficient polymer solar cells.

1. Introduction

As compared with conventional inorganic electronics, organic electronics show many advantages, such as light weight, flexible, transparent, and low cost. Since the first organic effect-field transistor (OFET) was reported in 1986 [1], it has attracted considerable attention as a viable

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alternative to amorphous silicon field-effect transistors due to their flexibility, low cost, and amenability to the fabrication over large area, as well as the great potential applications in organic light-emitting diodes (OLEDs) flat-panel display, plastic radio frequency identification (RFID) circuits and sensors [2–5]. During the past two decades, lots of progress focused on the materials and device fabrication techniques were obtained for improving the device performance [6–9]. Especially, conjugated polymers as one of versatile active semiconductor candidates are widely used in organic electronics and optoelectronics, which in turn dramatically accelerate the development of organic electronic and optoelectronic devices [10–14].

Recently, benzo[1,2-b:4,5-b′]dithiophene (BDT) unit has emerged as an attractive donor component for polymer solar cells (PSCs) due to its large planar and conjugated structure, promoting cofacial π–π stacking, benefiting the charge transport, and affording a power conversion efficiency (*PCE*) of 7.0–8.0% [15,16]. Benzo[1,2-b:4,5-b′]difuran (BDF), having a similar structure to the BDT unit, attracts increasing attention as well [17–19]. When combining BDF unit with a suitable acceptor moiety, it may achieve a high mobility that leads to high-performance organic electronic devices. The BDF-based polymers successfully used in PSCs as the electron donor showed a *PCE* of 5.0% [17]. However, for BDF-based polymers used in OFET, the reported mobility is only in the range of $10^{-3} \sim 10^{-5}$ cm^2/Vs and the on/off ratio is less than 10^4 [20–23].

We reported the synthesis of a new BDF-based donor-acceptor (D–A) conjugated polymer poly{4,8-bis(2′-ethylhexylthiophene)benzo[1,2-b;3,4-b′]difuran-*alt*-5,5-(4′, 7′-di-2-thienyl-5′,6′-dioctyloxy-2′,1′,3′-benzothiadiazole)} (PBDFTDTBT, Fig. 1a) that showed a remarkable *PCE* of 6.0% in PSCs [24]. However, the device is not fully optimized and the full potential of this material is yet to be explored. In this article, we report our investigations on this new BDF-based conjugated polymer and demonstrate that it can be used in OFETs and phototransistors. We find that the mobility is 0.05 cm^2/Vs and the on/off ratio is larger than 10^5, which are the best performance parameters for organic field-effect transistors based on D–A conjugated polymers with benzo[1,2-b:4,5-b′]difuran (BDF) unit. The phototransistor devices show a photosensitivity (I_{light}/I_{dark}) of 1.2×10^5 and a photoresponsivity of 360 mA W^{-1} under white light illumination. Furthermore, the devices are observed highly stable in ambient environment. Our study indicates that the BDF-based D–A conjugated polymer PBDFTDTBT has high potentials for the applications not only in PSCs, but also in OEFT and organic phototransistor devices.

2. Experiment

2.1. Material synthesis

The detailed synthesis process of PBDFTDTBT is shown in Ref. [24]. 2,6-Bis(trimethyltin)-4,8-bis(2′-ethylhexylthiophene)benzo[1,2-b;3,4-b′]difuran (0.174 g, 0.2 mmol), 4,7-di(5-bromothiophen-2-yl)-5,6-dioctyloxybenzo-[c][1,2,5]-thiadiazole (0.143 g, 0.2 mmol) and 12 mL of dry toluene were mixed in a two-necked flask, which was flushed with N_2 for 10 min. Then $Pd(PPh_3)_4$ (10 mg) was added into the flask. After flushing with N_2 for 20 min, the oil bath was heated to 115 °C carefully, and the reactant was stirred for 24 h at this temperature under a N_2 atmosphere. Then the reaction mixture was cooled to room temperature, the polymer was precipitated by the addition of 100 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexanes and chloroform. The polymer was recovered as a solid from the chloroform fraction by rotary evaporation. Finally, the blue solid was obtained (0.122 g, yield: 68%). 1H NMR (400 MHz, $CDCl_3$, ppm): 7.75–7.32 (br, 6H), 7.13–6.73(br, 4H), 4.41–4.00(br, 4H), 3.31–2.76 (br, 6H), 2.20–0.63(br, 58H). Anal. Calcd for $(C_{66}H_{84}N_2O_4S_5)_n$ (%): C, 70.17; H, 7.49; N, 2.48. Found (%): C, 70.21; H, 7.43; N, 2.49.

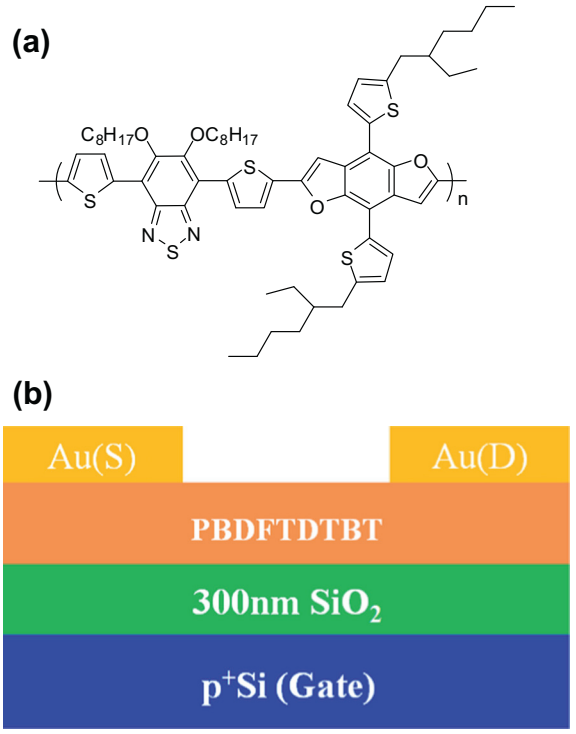

Fig. 1. (a) Chemical structure of D–A conjugated polymer PBDFTDTBT. (b) OFET device configuration.

2.2. Organic field-effect transistor fabrication

A bottom-gate/top-contact coplanar configuration is used to fabricate OFETs (Fig. 1b). Heavily p$^+$ doped silicon wafer substrates (Si-Mat, Germany) covered with a thermally grown 300 nm SiO_2 layer were used as the gate, of which the capacitance is 10 nF/cm^2. The substrates were carefully cleaned with de-ionized water, acetone and absolute ethyl alcohol in the ultrasonic bath for 15 min each. Then the hydrophilic treatment of these silicon wafers were performed by soaking in a mixture of deionized water, 25% ammonium hydroxide and 30% H_2O_2 (5:1:1