

## Poly(diketopyrrolopyrrole–terthiophene) for Ambipolar Logic and Photovoltaics

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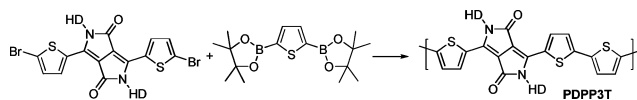
Polymers based on diketopyrrolopyrrole (DPP) have been known for a relatively long time<sup>1</sup> but are only recently emerging as promising candidates for use in optoelectronic applications, particularly in field-effect transistors (FETs)<sup>2</sup> and organic photovoltaic cells (OPCs).<sup>3,4</sup> OPC efficiencies up to 4.45% have been reached with DPP polymers and oligomers.<sup>3c,4c</sup> Here we present a new DPP based polymer, PDPP3T (Figure 1), that features high, almost balanced charge carrier mobilities for both electrons and holes in combination with an extended optical absorption toward the IR region. These favorable characteristics allow PDPP3T to be used for the construction of a FET-based inverter and to further enhance the power conversion efficiency of DPP-based materials for OPCs.

PDPP3T was designed to have an unsubstituted terthiophene unit between each pair of DPP units along the chain.<sup>3d</sup> In comparison with other DPP polymers that generally have more extended and complex conjugated segments and carry solubilizing chains,<sup>3</sup> terthiophene induces additional planarity, which enhances packing and charge carrier mobility. By using extended side chains [i.e., 2-hexyldecyl (HD)] on DPP, we compensated for the expected loss in solubility. This allowed us to obtain PDPP3T in high molecular weight, which is a crucial factor for its photovoltaic performance (see below).

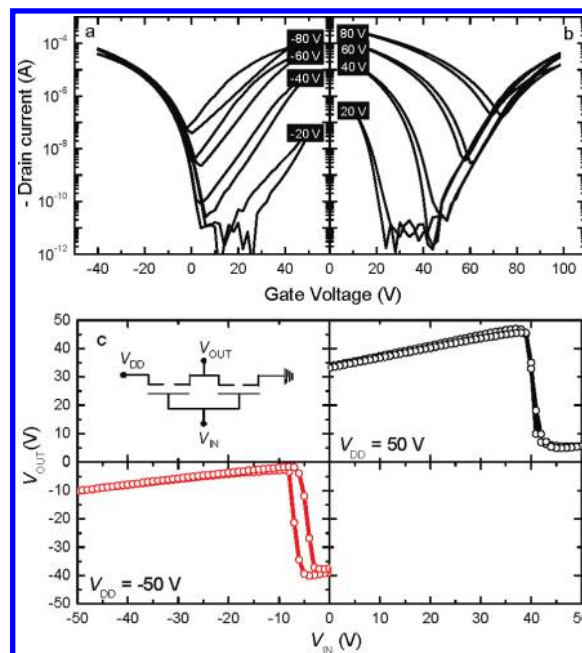
PDPP3T was synthesized by Suzuki polymerization from the dibromo-DPP monomer<sup>2a</sup> and 2,5-thiophenebis(boronic ester) (Figure 1). The use of Pd<sub>2</sub>(dba)<sub>3</sub>/PPh<sub>3</sub> as the catalyst yielded PDPP3T with  $M_n = 54\,000$  g/mol [polydispersity index (PDI) = 3.15]. Of all the organic solvents tested, PDPP3T readily dissolves (>1 mg/mL) only in chloroform. A much lower  $M_n$  of 10 000 g/mol (PDI = 2.4) was obtained when Pd(PPh<sub>3</sub>)<sub>4</sub> was used as the catalyst. Details of synthesis and characterization are given in the Supporting Information (SI).

The onset of optical absorption at 1.36 eV in *o*-dichlorobenzene (ODCB) solution and at 1.30 eV in a thin film (see the SI) classifies PDPP3T as a small-band-gap polymer. The HOMO and LUMO levels were found at +0.07 and −1.49 V vs Fc/Fc<sup>+</sup> by cyclic voltammetry in ODCB solution (i.e., −5.17 and −3.61 eV vs vacuum) (see the SI).

FETs with PDPP3T ( $M_n = 54\,000$  g/mol) as the semiconductor were fabricated on a heavily doped silicon wafer covered by a 200 nm thick layer of thermally grown silicon dioxide, which acted as common gate electrode and gate dielectric, respectively. Gold electrodes were defined by standard photolithography. The polymer was applied by spin-coating and subsequently dried in vacuum at 110 °C for 72 h to remove traces of solvent. Charge transport was studied as a function of bias at room temperature. Typical ambipolar



**Figure 1.** Synthesis and structure of PDPP3T. Reaction conditions: Pd<sub>2</sub>(dba)<sub>3</sub>, PPh<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, Aliquat 336, toluene/water, 115 °C, 72 h.



**Figure 2.** Ambipolar transfer characteristics for (a) negative and (b) positive drain biases, varying from  $\pm 20$  to  $\pm 80$  V in steps of 20 V. (c) Inverter characteristics of an inverter based on two identical FETs. The channel length and width were 10 and 2500  $\mu\text{m}$ , respectively.

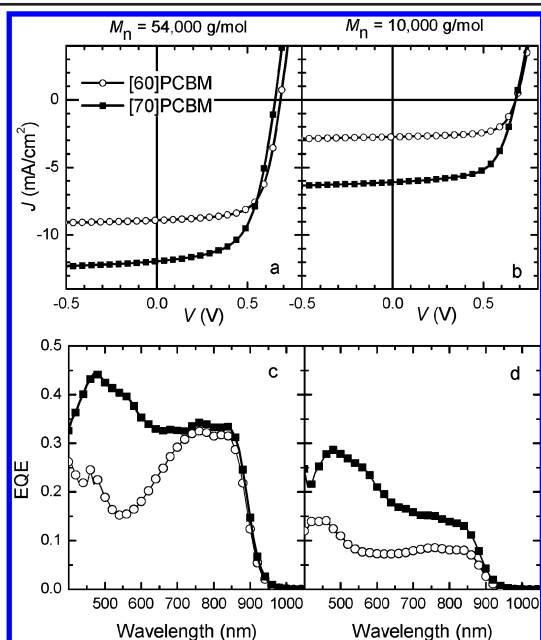
transfer characteristics are presented in Figure 2a,b for negative and positive drain biases. The PDPP3T transistors exhibited nearly balanced hole and electron mobilities of 0.04 and 0.01  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , respectively. These values are among the highest reported for single-component ambipolar transistors.<sup>2a</sup> Surprisingly, these mobilities were found to be almost independent of molecular weight: the  $M_n = 10\,000$  g/mol version of PDPP3T gave  $\mu_h = 0.05 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and  $\mu_e = 0.008 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  (see the SI).

Two identical ambipolar transistors were combined into inverters, with the common gate as the input voltage (Figure 2c inset).<sup>5</sup> Figure 2c shows the output voltage ( $V_{\text{OUT}}$ ) as a function of the input voltage ( $V_{\text{IN}}$ ) at constant supply bias ( $V_{\text{DD}}$ ). The steepness of the inverter curve indicated a gain of  $\sim 30$ , which is comparable to that of state-of-the-art CMOS-like inverters<sup>6</sup> and much higher than usually obtained for unipolar logic.<sup>7</sup>

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**Figure 3.** (a, b)  $J$ - $V$  curves and (c, d) EQEs for PDPP3T:PCBM bulk-heterojunction solar cells with (a, c) high and (b, d) low  $M_n$ .

Photovoltaic cells containing PDPP3T ( $M_n = 54\,000$  g/mol) and [6,6]phenyl-C<sub>61</sub>-butyric acid methyl ester ([60]PCBM) were fabricated by spin-coating on a PEDOT:PSS/ITO transparent front electrode. The LiF/Al back electrode was evaporated in vacuum. Cells with an active layer spin-coated from chloroform had a relatively low performance because of formation of larger [60]PCBM clusters.<sup>3a</sup> Control over the morphology is crucial for bulk-heterojunction solar cells, and several strategies to accomplish a more favorable morphology, such as thermal treatment and the use of processing additives, have been developed.<sup>8</sup> Adding a small amount ( $\sim 25$  mg/mL) of diiodooctane (DIO) to the mixture before spin-coating significantly improved the efficiency of the cells, mainly as a result of an increase in photocurrent. The best cells were obtained for PDPP3T:[60]PCBM in a 1:2 weight ratio and gave an open-circuit voltage ( $V_{oc}$ ) of 0.68 V, a fill factor (FF) of 0.67, and a short-circuit current density ( $J_{sc}$ ) of 8.3 mA/cm<sup>2</sup> under simulated AM1.5 (100 mW/cm<sup>2</sup>) conditions,<sup>9</sup> resulting in an estimated power conversion efficiency ( $\eta$ ) of 3.8% (Figure 3a). The monochromatic external quantum efficiency (EQE) showed a very sharp onset at the optical band gap and rose to  $\sim 33\%$  in the 750–850 nm region (Figure 3c).

To increase the photocurrent in the visible region, we changed the electron acceptor to [70]PCBM, which possesses an increased absorption coefficient in that part of the spectrum.<sup>10</sup> Because [70]PCBM is less soluble in chloroform than [60]PCBM, an increase of the DIO concentration to  $\sim 100$  mg/mL was required to reach optimum device performance. The optimized cells had PDPP3T:[70]PCBM in a 1:2 weight ratio and provided  $V_{oc} = 0.65$  V,  $J_{sc} = 11.8$  mA/cm<sup>2</sup>, and FF = 0.60, resulting in an  $\eta$  value of 4.7%. The need for a larger amount of DIO with [70]PCBM strengthens the view of Lee et al.<sup>11</sup> that the role of the processing additive is to keep the fullerene in solution longer, giving the polymer more time to aggregate. This reduces the formation of large PCBM crystals and realizes a superior morphology of the active layer. The EQE of the cell with [70]PCBM was similar to that of the [60]PCBM cell in the long-wavelength region but much higher in the visible region, accounting for the higher short-circuit current.

In contrast to the constant FET mobility, a dramatic reduction in OPC performance was observed when the lower- $M_n$  (10 000

g/mol) version of PDPP3T was used in combination with [60]PCBM or [70]PCBM (Figure 3b,d). Under identical processing conditions, the power conversion efficiency did not exceed 1.3 or 2.7%, respectively. The differences were caused by a reduction in photocurrent (Figure 3b,d vs 3a,c) and exemplify the importance of molecular weight as a crucial parameter in the formation of efficient bulk heterojunctions. In this respect, it is interesting to note that the use of DIO did not have an effect on  $\mu_h$  or  $\mu_e$  for pure PDPP3T (see the SI).

With  $V_{oc} = 0.65$ – $0.68$  V and an optical band gap ( $E_g$ ) of 1.30 eV, the PDPP3T:PCBM combination approaches the minimum offset of  $eV_{oc} = E_g - 0.6$  eV that we recently put forward as being a threshold for bulk-heterojunction solar cells.<sup>12</sup> The fact that we approached the minimum offset required for electron transfer to occur could be the reason that the EQE was less than that found in the more efficient (6%) cells published lately.<sup>13</sup>

In conclusion, PDPP3T exhibits ambipolar transport in FETs with nearly balanced electron and hole mobilities in the  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> range, making it an interesting candidate for CMOS-like circuits. At a high molecular weight, PDPP3T reaches  $\eta = 4.7\%$  in photovoltaic cells when combined with [70]PCBM and has a photoresponse up to 900 nm.

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**Supporting Information Available:** Synthetic procedures and spectroscopic and electrochemical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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