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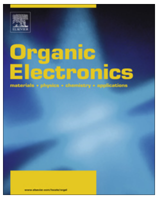

D–A copolymer with high ambipolar mobilities based on dithienothiophene and diketopyrrolopyrrole for polymer solar cells and organic field-effect transistors

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ABSTRACT

Donor–acceptor (D–A) type conjugated polymers have been developed to absorb longer wavelength light in polymer solar cells (PSCs) and to achieve a high charge carrier mobility in organic field-effect transistors (OFETs). PDTDP, containing dithienothiophene (DTT) as the electron donor and diketopyrrolopyrrole (DPP) as the electron acceptor, was synthesized by stille polycondensation in order to achieve the advantages of D–A type conjugated polymers. The polymer showed optical band gaps of 1.44 and 1.42 eV in solution and in film, respectively, and a HOMO level of 5.09 eV. PDTDP and $PC_{71}BM$ blends with 1,8-diiodooctane (DIO) exhibited improved performance in PSCs with a power conversion efficiency (PCE) of 4.45% under AM 1.5G irradiation. By investigating transmission electron microscopy (TEM), atomic force microscopy (AFM), and the light intensity dependence of J_{SC} and V_{OC}, we conclude that DIO acts as a processing additive that helps to form a nanoscale phase separation between donor and acceptor, resulting in an enhancement of μ_h and μ_e, which affects the J_{SC}, EQE, and PCE of PSCs. The charge carrier mobilities of PDTDP in OFETs were also investigated at various annealing temperatures and the polymer exhibited the highest hole and electron mobilities of 2.53 $cm^2\,V^{-1}\,s^{-1}$ at 250 °C and 0.36 $cm^2\,V^{-1}\,s^{-1}$ at 310 °C, respectively. XRD and AFM results demonstrated that the thermal annealing temperature had a critical effect on the changes in the crystallinity and morphology of the polymer. The low-voltage device was fabricated using high-*k* dielectric, P(VDF-TrFE) and P(VDF-TrFE-CTFE), and the carrier mobility of PDTDP was reached 0.1 $cm^2\,V^{-1}\,s^{-1}$ at $V_d = -5$ V. PDTDP complementary inverters were fabricated, and the high ambipolar characteristics of the polymer resulted in an output voltage gain of more than 25.

1. Introduction

Organic electronics have increasingly attracted the attention of researchers due to unique features such as solution processibility, light weight and mechanical flexibility [1–5]. In particular, the development of low band gap conjugated polymers that are synthesized through alternating copolymerization with an electron-rich unit (donor, D) and an electron-poor unit (acceptor, A) leads to high efficiency in polymer solar cells (PSCs) [6–14] and to a high charge carrier mobility in organic field effect transistors (OFETs) [15–18]. In PSCs, new D–A type polymers have been developed in order to increase the power conversion efficiency (PCE) by incorporating rigid structure in back-bone for absorbing longer wavelengths in the solar spectrum. Other approaches to enhance PCE is by replacing electron donating or withdrawing atom for adjusting the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) levels of the polymers, and by adding high boiling point process additives to control the morphology of PCBM blended films in photoactive layer [2,4]. In OFETs, the charge carrier mobility of a new D–A type polymer has been exceeding 1 $cm^2\,V^{-1}\,s^{-1}$ [15–24] by introducing planar structure of electron donor and electron acceptor unit in order to increase the crystallinity of the polymer backbone due to a strong intermolecular interaction that originates from the polar nature of D–A moieties, by reducing energy barriers

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between polymers and electrodes through adjustment of the energy levels of the polymer to approximate the work function of metal electrodes, and by treatment with heat or solvent for controlling the orientation of the polymer backbone against substrates (edge-on state or face-on state) [1,5,15–18].

Some D–A copolymers have also shown ambipolar characteristics, which can transport both hole and electron carriers, since the deep LUMO level and the high HOMO level are formed by the hybridization of D–A orbitals. The ambipolar polymers confer advantages for the preparation of CMOS-like logic circuits because of simple fabrication using a single-component solution process. With these advantages, many recent ambipolar conjugated polymers have been studied and have achieved high mobilities ($\sim$1 $cm^2 V^{-1} s^{-1}$) with balanced hole and electron transport [25–34]. In particular, 1,4-diketoppyrolo [3,4-c]pyrrole (DPP) is one of the most preferred molecular building blocks, as an electron acceptor, because a planar structure of DPP via the oxygen–sulfur interaction between carbonyl and thiophene groups leads to a strong π–π interaction and thus creates a high degree of crystallinity for a polymer backbone. DPP has two possible sites that can introduce a bulky alkyl chain for proper solubility. Therefore, DPP-based polymers synthesized with an electron donor unit show a high charge-carrier mobility in both unipolar [19–24] and ambipolar [26–34] OFETs and high efficiency in PSCs [35–38]. To enhance the intermolecular interaction of the polymer backbone, we introduced the electron donor, dithieno[3,2-b:2′,3′-d]thiophene (DTT), which is a sulfur-rich electron donor unit and has structural rigidity in π-conjugated systems due to its fused chemical structure [36–41]. In this respect, DTT-based materials have shown high charge-carrier mobilities in small molecules [39] as well as in conjugated polymers [40,41]. In previous papers, some groups reported alternating copolymers [42] and random copolymers [43] of alkylated DTT and alkylated DPP. Other groups have published papers reporting alternating copolymers with non-alkylated DTT and alkylated DPP that showed high mobility and power conversion efficiency [37,38]. With these benefits of copolymers that use DTT and DPP, we synthesized our copolymer (PDTDP) using non-alkylated DTT and alkylated DPP and investigated the ambipolar charge-transport and photovoltaic properties. By optimizing the device fabrication and materials processing, we demonstrated ambipolar OFETs with maximum hole and electron mobilities of 2.53 and 0.36 $cm^2 V^{-1} s^{-1}$, respectively, and an efficiency of 4.5% in PSCs blended with $PC_{71}BM$.

2. Experimental section

2.1. Materials

All chemicals were purchased from either Aldrich, TCI, Alfa Aesar, Acros, or Strem chemicals, and were used without further purification. We synthesized 2,6-bis(tri-*n*-butylstannyl) dithieno [3,2-b:2′,3′-d]thiophene (1) [44–46] and 3,6-bis(5-bromothien-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2) [47] according to the previously published literature. All air- and water-sensitive reactions were performed under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium and benzophenone.

2.2. Synthesis of PDTDP

Compound 1 (255 mg, 0.33 mmol), compound 2 (305 mg, 0.3 mmol), $Pd_2(dba)_3$ (13.7 mg, 5 mol%), and $P(o\text{-}tolyl)_3$ (18.3 mg, 20 mol%) were added to a 50 ml two-neck round flask purged with nitrogen. Then 15 mL of anhydrous chlorobenzene (CB) was added via syringe. The polymerization was carried out at 90 °C under a nitrogen atmosphere. After 72 h, 2-tributyl stannyl thiophene and 2-bromothiophene were sequentially added to the mixture to react with the remaining bromo and stannyl end groups, respectively. The mixture was cooled to ambient temperature and dropped into a HCl/methanol (1:1 v/v) solution. The precipitate was filtered off and purified by Soxhlet extraction with methanol (12 h), acetone (12 h), hexane (12 h), and chloroform (CF) (12 h). The solvent in the CF soluble fraction of the polymer was removed under reduced pressure and the polymer was precipitated in methanol and dried in vacuum after being filtered off to afford the desired polymer (160 mg, 50%) – GPC (CF): M_n = 13,000 g mol^{-1}, M_w = 48,000 g mol^{-1}, PDI = 3.7. ^1H NMR (400 MHz, CDCl3): δ 8.94 (m, 4H), 8.62 (s, 2H) 3.97 (d, 6H), 1.93 (m, 4H), 1.5–1.0 (m, 55H), 1.0–0.75 (s, 15H).

2.3. Measurement and characterization

^1H NMR spectra were obtained using a JEOL ECX-400P 400 MHz spectrometer in $CDCl_3$. Chemical shifts were reported as ppm relative to the TMS standard (0 ppm). The molecule mass data were obtained using a GCMS (Shimadzu, GCMS-QP2010). The molecular weight of the polymer was confirmed by GPC (Futecs, NS2001) and calibrated using polystyrene reference materials and CF as a flow solvent. Thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA 4000 from 30 to 800 °C at 10 °C per minute under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out using a Perkin Elmer DSC 4000 from 30 to 340 °C at 10 °C per minute under a nitrogen atmosphere. The optical properties of the polymer were investigated by UV–Vis spectroscopy using a Perkin-Elmer Lambda 12 UV/Visible Spectrophotometer (HP 8453) in CB solution and film on a Corning eagle 2000 glass substrate. The electrochemical properties of the polymer were performed in an acetonitrile solution with 0.1 M tetrabutylammoniumperchlorate (Bu_4NClO_4) as the supporting electrolyte, indium tin oxide (ITO) as the working electrode, a Pt wire as the counter electrode, and a Ag wire as the reference electrode using a potentiostat (Eco Chemie, AUTOLAB) at a scan rate of 50 $mV s^{-1}$. X-ray diffraction (XRD) analyses were measured using an X'Pert PRO Multi-Purpose X-ray Diffractometer from PANalytical using Cu Kα radiation at room temperature. Atomic force microscopy (AFM) data were obtained using a XE-100 from Park Systems in Non-contact mode. Transmission electron microscopy (TEM) was performed on a Tecnai TEM (FEI) operated at 200 kV.

2.4. Solar cell device fabrication

The patterned indium tin oxide (ITO)-coated glass substrate was cleaned sequentially with De-ionized water, acetone, and isopropyl alcohol for 10 min using an ultrasonic-bath. After drying, the substrate was subjected to UV–O_3 treatment for 20 min before depositing 30 nm of poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P VPAI 4083) as the hole injection layer by spin coating. The sample was baked at 150 °C for 10 min in air and moved to a nitrogen-charged glove box. The blend solution was prepared with PDTDP and $PC_{71}BM$ (Nano C) with a weight ratio ranging from 1:1 to 1:4 in ortho-dichlorobenzene (o-DCB) solvent (with or without 4 vol% diiodooctane, DIO). After heating at 100 °C for 6 h, the solution was cooled to room temperature and spin-coated onto the PEDOT:PSS layer. Finally, a cathode electrode made of Ca (20 nm) and Al (100 nm) were deposited with a shadow mask using thermal evaporation in a high-vacuum chamber ($\sim 2.0 \times 10^{-6}$ torr), and this metal-deposited region (4.64 mm^2) was defined as the photoactive area of the corresponding devices. The photocurrent density–voltage (*J*–*V*) curves were measured using a Keithley 236