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Effects of the incorporation of an additional pyrrolo[3,4-c]pyrrole-1,3-dione unit on the repeating unit of highly efficient large band gap polymers containing benzodithiophene and pyrrolo[3,4-c]pyrrole-1,3-dione derivatives

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Property modulation of 2,5-dioctylpyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (DPPD)-based high energy converting wide band gap polymers, P(BDT-TDPPDT) and P(BDTT-TDPPDT), was studied via the incorporation of an additional DPPD unit on their repeating units. A new electron acceptor (BDPPD) unit containing two DPPD units was prepared and copolymerized with the distannyl derivatives of benzodithiophene (BDT) or 2D-conjugated benzodithiophene (BDTT) to provide two new polymers, P(BDT-BDPPD) and P(BDTT-BDPPD). The optical band gaps and highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy levels of P(BDT-BDPPD) and P(BDTT-BDPPD) were 2.16 eV, 2.08 eV and −5.37 eV/–3.21 eV, −5.44 eV/–3.36 eV, respectively. The hole mobilities of P(BDT-BDPPD) and P(BDTT-BDPPD) were in the order of 10^{-4} cm^2V^{-1} s^{-1}. The polymer solar cells (PSCs) prepared with the configuration of ITO/PEDOT:PSS/P(BDT-BDPPD) or P(BDTT-BDPPD):$PC_{70}BM$/Al gave maximum power conversion efficiencies (*PCEs*) of 2.74% and 3.63%, respectively. The insertion of a BDPPD unit instead of a TDPPDT unit on the DPPD-based polymer backbone did not affect the optical and electrochemical properties considerably. On the other hand, the new polymers, P(BDT-BDPPD) and P(BDTT-BDPPD), resulted in improved photovoltaic performances compared to the reported polymers, P(BDT-TDPPDT) and P(BDTT-TDPPDT), for the devices prepared without additives.

1. Introduction

Numerous π–conjugated polymers [1–6] and fullerene derivatives [7–9] have been developed for polymer solar cells (PSCs) because of their potential applications to the easy device fabrications via solution processability at a low cost to large area [10]. The continuing efforts in the utilization of novel structured electron donating π–conjugated polymers and electron accepting fullerene derivatives in PSCs have rapidly improved the overall power conversion efficiency (*PCE*) to 10.8% [11,12] and 11.5% [13,14], respectively, in single layer and multijunction or tandem PSCs. These PSCs are now very close to commercialization, but the *PCE* still needs to be improved to more than 15% before the PSCs can be used as a promising energy production technique. The theoretical investigations strongly suggest that a *PCE* of 17% and 24% is achievable for single and multijunction solar cells, respectively, using suitable electron donor and acceptor materials [15]. In this instance, chemists are involved in the development of novel structured π–conjugated polymers or fullerene derivatives because previous reports have shown that the *PCEs* of PSCs are associated mainly with the properties of the electron donor and acceptor materials used in the photoactive layer.

Recently, a series of pyrrolo[3,4-c]pyrrole-1,3-dione (DPPD)-

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based polymers was developed for PSCs [16–23]. DPPD was prepared by attaching electron accepting imide group on the 3,4-positions of the electron rich pyrrole. The intrinsic electron rich character of pyrrole makes DPPD as a weak electron acceptor unit. Consequently, the copolymerization of DPPD with electron rich dithienopyrrole (DTP), dithienosilole (DTS) and benzodithiophene (BDT) derivatives offered large band gap polymers [16–23]. However, polymers, P(BDT-TDPPDT) and P(BDTT-TDPPDT), containing BDT or BDTT and thiophene–DPPD–thiophene (TDPPDT) displayed impressive photovoltaic performances with a maximum *PCE* of 6.74%, an open-circuit voltage (V_{oc}) of 0.86 V, a fill factor (*FF*) 71%, a short-circuit current (J_{sc}) of 10.94 mA/cm^2 and an incident photon to current efficiency ($IPCE_{max}$) of 76% and a *PCE* of 6.57% with a V_{oc} of 0.90 V, a *FF* 72%, J_{sc} of 10.12 mA/cm^2 and $IPCE_{max}$ of 73%, respectively [20]. The chemical structure of the polymers P(BDT-TDPPDT) and P(BDTT-TDPPDT) are presented in Fig. 1. Note that the PSCs prepared from P(BDT-TDPPDT) and P(BDTT-TDPPDT) exhibit improved photovoltaic parameters compared to those prepared from the most promising large band gap poly(3-hexylthiophene), P3HT [24–26]. These results suggest that the utilization of P(BDT-TDPPDT) or P(BDTT-TDPPDT) instead of P3HT in multijunction or tandem PSCs as a large band gap polymer along with a low band gap polymer might offer a very high *PCE* [13,14]. Currently, the use of P(BDT-TDPPDT) or P(BDTT-TDPPDT) as a front cell electron donor in tandem PSCs is under investigation in our laboratory.

The large band gap and high efficiency of P(BDT-TDPPDT) and P(BDTT-TDPPDT) prompted us to tune the properties and enhance their photovoltaic performances further. In this instance, relatively strong electron accepting thieno[3,4-c]pyrrole-4,6-dione (TPD) or thieno[3,4-b]thiophene (TT) or pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) derivatives were incorporated on the P(BDT-TDPPDT) backbone and the resulting low band gap random copolymers exhibited higher or comparable photovoltaic performances compared to that of P(BDT-TDPPDT) [17,18,21]. In this study, a new electron accepting monomer unit (BDPPD) containing two DPPD units was prepared and copolymerized with benzodithiophene (BDT and BDTT) derivatives to tune the photo-physical properties of P(BDT-TDPPDT) and P(BDTT-TDPPDT). The optical, electrochemical, charge transport, and photovoltaic properties of the new polymers, P(BDT-BDPPD) and P(BDTT-BDPPD), were studied and compared with those of P(BDT-TDPPDT) and P(BDTT-TDPPDT).

2. Experimental section

2.1. Materials and measurements

Reagents were obtained from Sigma–Aldrich. The compounds prepared in this study were purified by column chromatography (silica gel, Merck Kieselgel 60, 70–230 mesh ASTM). The nuclear magnetic resonance (NMR) spectra of the compounds and polymers were recorded on a Varian Mercury Plus spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C). The high resolution fast atom bombardment (FAB) mass spectra of the compounds were analyzed using a JEOL JMS-700 mass spectrometer. An Agilent 1200 Infinity Series separation module was used to determine the molecular weights of the polymers using gel permeation chromatography (GPC) with chloroform as an eluent at ambient temperature. The GPC instrument was calibrated with the polystyrene standard prior to analysis. Thermogravimetric analysis (TGA) of the polymers was performed on a TA instrument Q600-0825 at a heating and cooling rate of 10 °C/min under nitrogen. The solution and film state UV–visible absorption spectra of the polymers were recorded on a JASCO V-570 spectrophotometer and a CH Instruments Electrochemical Analyzer was used to determine the cyclic voltammogram (CV) of the polymers. The polymer cast film on the platinum working electrode was immersed in an acetonitrile solution containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), Ag/AgCl as a reference electrode and platinum wire as a counter electrode, and the measurements were then performed. Before starting the CV analysis, the instrument was calibrated with the most common ferrocene/ferrocenium ion (Fc/Fc+) standard. Atomic force microscopy (AFM) was performed using a Seiko instruments SPI 3800N-SPA 400.

2.2. Device fabrication and characterization of OTFTs

The organic field effect transistors (OFETs) were fabricated on highly n-type-doped silicon (Si) substrates with a 200 nm layer of thermally grown silicon oxide (SiO_2). The Si substrates were subjected to an UV-ozone treatment for 30 min for activation and then treated with an octadecyltrichlorosilane (OTS) self-assembled monolayer. The n-type doped Si substrate functions as a gate electrode and the SiO_2 layer acts as a gate dielectric. The chlorobenzene (CB) solution of the polymer (5 mg/ml) was spin-cast on top of the Si substrate (2000 rpm) and dried at room temperature (RT) for 30 min. The source and drain electrodes (Au, 70 nm) were deposited on top of the polymer layer by thermal evaporation in a vacuum of approximately 2×10^{-6} Torr. The channel length (L) and channel width (W) of the device was 50 μm and 3.0 mm, respectively. The output and transfer characteristics of the OFETs were measured using a Keithley semiconductor parametric analyzer (Keithley 4200). All preparation processes and the characterization of the OFETs were performed inside a N_2-atmosphere glove box. The mobility (μ) was determined using the following equation in

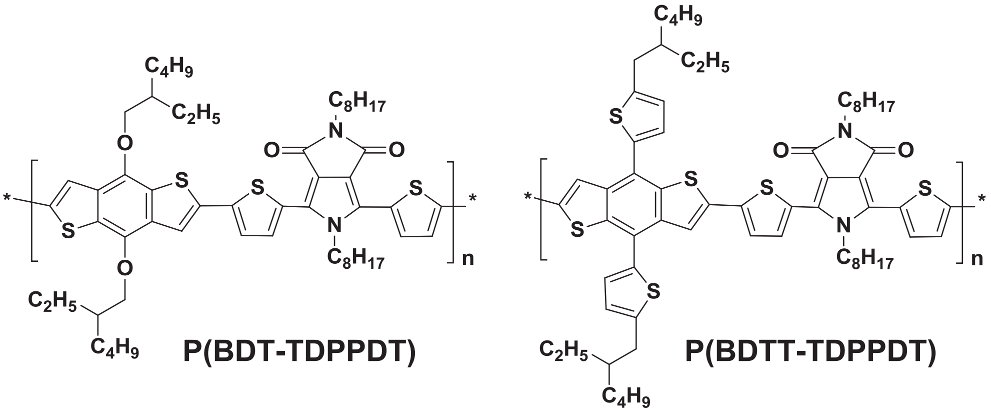

Fig. 1. Structures of pyrrolo[3,4-c]pyrrole-1,3-dione-based highly efficient large band gap polymers P(BDT-TDPPDT) and P(BDTT-TDPPDT).