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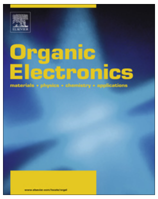

2,1,3-Benzothiadiazole-5,6-dicarboxylic imide based low-bandgap polymers for solution processed photodiode application

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ABSTRACT

Six low-bandgap donor–acceptor polymers, **PDIC20/8-BTh**, **PDIC20/8-BDT**, and **PDIC20/8-DTS**, with 2,1,3-benzothiadiazole-5,6-dicarboxylic imide (DI) as the electron-accepting unit and BTh, BDT, and DTS as donors, were synthesized and investigated as photodetecting materials. All the polymers exhibited broad absorptions covering 300–900 nm, low-lying LUMO energy levels, and good thermal stability. They were employed as active layers of photodetectors with the device configuration of ITO/PEDOT:PSS/active layer (polymer:$PC_{61}BM$)/C_{60}/Al by solution casting method. With C_{60} as an electron-extracting as well as hole-blocking layer, the dark currents were effectively reduced and the obtained photodetectors exhibited high detectivities ($\sim 10^{12}$ Jones) with panchromatic coverage from the ultraviolet to near-infrared region at low operating voltage and room temperature. The device made of **PDIC20-BTh** bahaved better comprehensive performance including high photocurrent, low dark current, and superior spectral range than others. Gaussian calculations were conducted to better understand the distinguishing performances of polymer photodetectors at the molecular level. The conformations of both donor and acceptor units played important roles in determining the overall performance.

1. Introduction

Photodetectors (PDs) covering from ultraviolet (UV)–visible to the near-infrared (NIR) region are of critical importance in wide fields such as environmental monitoring, remote sensing, night surveillance, and biological imaging [1–3]. Over the past decades, both inorganic and organic compounds have been investigated as panchromatic photodetecting materials, including inorganic quantum dots (e.g., PbS [4] and HgTe [5]), small organic molecules (e.g., porphyrins [6,7], squaraine [8], and phthalocyanine [9,10]), and low-bandgap conjugated polymers [11,12]. Polymer PDs stand out with the advantages of lightweight, reasonable cost, large-area flexibility, low operating potential, and good polymer tailorability [1]. In 2007, Yang firstly reported a high-performance NIR polymer PD based on a low-bandgap polymer polythieno[3,4-*b*]thiophene (**PTT**) [11]. A great breakthrough work reported by Gong et al. fabricated an effective panchromatic photodetector covering 300–1450 nm using a low-bandgap polymer, poly(5,7-bis(4-decanyl-2-thienyl)-thieno(3,4-b)diathiazole-thiophene-2,5) (**PDDTT**), as the active layer [12]. Nevertheless, from then on, few low-bandgap polymers were investigated as photodetecting materials, and most of their devices showed relatively low detectivities [13–18]. Therefore, there is an urgent need to develop new polymeric photodetecting materials with low operating potential, flexible solution-processability, and high detectivity, and further gain deep insight into the corresponding molecular design and device optimized strategies.

The low-bandgap polymers in the active layers are crucial for polymer PDs. Donor–acceptor (D–A) approach has been demonstrated as the most successful method to produce low-bandgap polymers. Benzothiadiazole (BT) is known as an excellent acceptor unit in low-bandgap polymers applied in polymer solar cells (PSCs) [19,20]. However, the absorption spectra of BT-based polymers primarily lie in the visible region, which are not suitable for NIR detection. Modification of BT unit with electron-negative atoms, such as nitrogen [21] or fluorine atom [22], could only slightly red-shift the absorptions. Fusing another electro-withdrawing ring is an alternative method to resolve the problem. Benzobisthiadiazole (BBT) [23] and thiadiazoloquinoxaline (TQ) [24] are two well-known acceptors which can effectively extend absorptions to the NIR region. However, the LUMO orbitals of the resultant polymers are too low for normal exciton separation and

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charge transfer in the system of bulk heterojunction with $PC_{61}BM$ as an acceptor. On the other hand, dicarboxylic imide is another electron-deficient unit, the electro-withdrawing ability of which is weaker than that of thiadiazole. Moreover, the power conversion efficiencies (PCEs) of imide-based PSCs exceed 7% [25,26]. Combining BT with imide could result in a new acceptor, 2,1,3-benzothiadiazole-5,6-dicarboxylic imide (DI), whose energy level would locate between BT and BBT [27].

Recently, Zheng and coworkers prepared PSCs based on DI acceptor with a high PCE of 5.19% [28], demonstrating its practical applications in photoelectric fields. Nevertheless, the absorptions of polymers were only located in the UV–vis regions. Additionally, the structures of donors and side chains also significantly affect properties of polymers [29,30]. In order to greatly narrow the polymer bandgap, strong donors were usually selected to couple with strong acceptors. Therefore, in this article, three strong donors, benzo[1,2-b:4,5-b′]dithiophene (BDT) [31], dithieno[3,2-b:2′,3′-d]silole (DTS) [32], and bithiophene (BTh) [33] were polymerized with DI bearing different alkyl chains to prepare low-bandgap polymers for panchromatic photodetectors. The absorption spectra of polymers were successfully shifted to the NIR region, and the corresponding solution-processed devices showed high detectivities (beyond 10^{12} Jones from 350 to 800 nm) covering the UV to NIR region at low operating voltage and room temperature.

2. Experimental

2.1. Materials

2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo-[1,2-b:4,5-b′]dith-iophene [31], 4,4′-bis(2-ethyl-hexyl)-5,5′-bis(trimethyltin)-dithieno[3,2-b:2,3-d]silole [32], and 5,5′-bis(trimethylstannyl)-4,4′-bis(dodecyl)-2,2′-bithiophene [33] were purchased from Zhongshenghuateng Technology Co. Ltd. 4,8-Di(thiophen-2-yl)isobenzofuro[5,6-c][1,2,5]thiadiazole-5,7-dione and N-(2-ethylhexyl)-4,7-di(5-bromothien-2-y-l)-2,1,3-benzothiadiazole-5,6-dicarboxylic imide (**M2**) were synthesized according to the published literature [28]. $Pd(PPh_3)_4$ was recrystallized from EtOH before polymerization. Toluene, acetonitrile, and chlorobenzene were purified by distillation over CaH_2. All other reagents were purchased from J&K, Aldrich, Acros, and TCI Chemical Co., respectively, and used as received unless otherwise specified.

2.2. Methods

^1H NMR and ^{13}C NMR spectra of monomers and intermediates were recorded on a Bruker ARX400 (400 MHz) spectrometer at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts were reported in ppm with tetramethylsilane (0 ppm) as an internal standard. ^1H NMR spectra of polymers were performed on Bruker-500 at ambient temperature ($CDCl_3$) or elevated temperature (1,2-dichlorobenzene-d4). High-resolution mass spectra were made on a Bruker BIFLEX III mass spectrometer. Thermogravimetric analyses (TGA) were performed on a TA Instrument Q600 analyzer under a N_2 flow rate of 100 mL min^{-1}. For differential scanning calorimetry (DSC) experiments, the temperature was heated to a high temperature at a heating of 20 °C min^{-1} and kept isothermal for 10 min, cooled to room temperature at a rate of 2 °C min^{-1}, and then heated to a high temperature at a heating of 20 °C min^{-1} with a TA DSC Q100 instrument. The glass transition temperatures (T_g) were gained from the second heating processes of DSC curves. Gel permeation chromatography (GPC) was performed on GPC apparatus with a Water 2410 refractive-index detector and a Water 515 pump with THF as solvent or on Polymer Laboratories PL-GPC220 at 140 °C using 1,2,4-tricholorobenzene (TCB) as an eluent. All GPC curves were calibrated against a series of polystyrene standards. UV–vis–NIR absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Cyclic voltammetries (CVs) were carried out on a CHI840B electrochemical workstation. Platinum disk and a platinum wire were used as working electrode and counter electrode with a silver wire as pseudoreference electrode. All the energy level calculations were referenced to an internal standard of ferrocene (Fc/Fc^+).

2.3. Device fabrication and characterization

For each PD, the corresponding polymer (10 mg) together with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$, 10 mg) were co-dissolved in chlorobenzene and stirred overnight at 40 °C. The PDs were made on pre-patterned indium-tin-oxide (ITO)-coated glass substrates with a sheet resistance of 10 Ω/sq. The ITO substrates were already cleaned by ultrasonic treatment in detergent, de-ionized water, acetone, and isopropyl alcohol before treated with UV/ozone cleaning for 15 min. Then, a 35 nm layer of PEDOT: PSS (Clevios™ P VP AI 4083) was spin-coated (3000 rpm) and subsequently dried in oven at 110 °C for 30 min. After that, chlorobenzene solutions containing the polymer and $PC_{61}BM$ at a weight ratio of 1:1 were spin-coated (600–800 rpm), resulting a thickness of 100 nm. Prior to depositing the aluminum electrode, a 30 nm hole blocking layer C_{60} was thermally evaporated at 5×10^{-4} pa (0.1 nm s^{-1}). The device area defined as the overlap between the ITO and Al electrodes was 0.16 cm^2.

After fabricating the devices in the vacuum chamber, they were took out and tested under ambient condition without any encapsulation. The current–voltage characteristics were measured by using a Keithley 236 source measurement unit with a halogen tungsten lamp as the light source. The absorption spectrum and the external quantum efficiency (EQE) were determined with a setup made by Beijing 7-Star Optical Instruments Co., Ltd. For the frequency response, a 405 nm laser diode (Sanyo, DL-4146-301S), a waveform generator (Agilent 8114A) and a trans-impedance amplifier (Femto DHPCA-100), as well as a 500 MHz bandwidth oscilloscope (Agilent 54825A) were used. The current–voltage and EQE measurements took about 1 h, and the signal did not decay during the measurement. The bandwidth of the devices were calculated by fast Fourier transform (FFT) and calibrated by a Si PIN photodetector (S5821-01, Hamamatsu). Atomic force microscopy (AFM) images were collected with a scanning probe microscope (SPI 3800N, Seiko Instruments Inc.) in DFM tapping mode.

2.4. Computational method

The quantum chemical calculations were performed using the Gaussian 09 program package [34]. All calculations were done in two repeat units. The geometries of all molecules were optimized with density functional theory (DFT) using B3LYP hybrid functional with a basis set limited to 6–31 g(d) [35]. Each optimization was verified by frequency analysis for real energy minimization. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated based on the optimized structures, and the orbital pictures were prepared with GaussView 5.0 [36]. To simplify the calculations, the long alkyl chain was simplified as a methyl group.

2.5. Synthesis

2.5.1. N-(2-octyldodecayl)-4,7-di(thien-2-yl)-2,1,3-benzothiadiazole-5,6-dicarboxylic imide

4,8-Di(thiophen-2-yl)isobenzofuro[5,6-c][1,2,5]thiadiazole-5,7-dione (2.08 g, 5.6 mmol), 2-octyldodecayl amine (2.02 g, 6.7 mmol), and DMF (30 mL) were successively added into a