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N-acylated isoindigo based conjugated polymers for *n*-channel and ambipolar organic thin-film transistors

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ABSTRACT

Donor/acceptor polymers with *N*-acylated isoindigo as acceptor units have been synthesized. The thermal, optical, electrochemical, and charge-transport properties of the polymers have been investigated. The new polymers show broad absorption from 450 to 900 nm. Due to the strong electron accepting characteristic of *N*-acylated isoindigo, the new polymers exhibit narrow optical band gaps and deep LUMO energy levels compared with the polymers based on *N*-alkylated isoindigo. The new polymers show *n*-type transport behavior and balanced ambipolar transport behavior in organic thin film transistors (OTFT) device.

1. Introduction

Conjugated polymers (CPs) have attracted considerable interests because of their applications in organic photovoltaic (OPV) [1], organic thin film transistors (OTFT) [2], and organic light-emitting diodes (OLED) [3] devices. The strategy of incorporating donor (D) and acceptor (A) units into the CP backbones has shown significant improvement on OTFT device performances, due intermolecular D and A interactions [4]. The electron-deficient isoindigo (iI) units have been incorporated into many polymers for high-performance OPV and OTFT applications [5,6].

Low-lying LUMO energy levels are required for *n*-type materials to achieve effective charge injection and ambient stability in OTFT devices. There were some reports on structure modification of isoindigo based polymers for achieving *n*-type or ambipolar semiconducting materials [7]. Fluorination of isoindigo building block can reduce both HOMO and LUMO levels of the polymer and can result in high performance ambipolar materials [7a]. The polymers with deep LUMO energy levels were also achieved by copolymerization of isoindigo with other electron-deficient building blocks to form all acceptor based polymers [7b]. However, those approaches usually required significant amount of synthetic effort. Side chains of CPs not only affect the intermolecular interaction of polymers but also influence the HOMO and LUMO energy levels of polymers. In our previous work, we reported a simple method to reduce the LUMO energy levels of benzodipyrrolidone-based polymers by *N*-acylation of lactam nitrogens to form electron deficient imide moieties [8]. Herein, we reported new conjugated polymers based on *N*-acylated isoindigo. The new polymers based on *N*-acylated isoindigo showed lower LUMO level and smaller bandgap than similar polymers based on *N*-alkylated isoindigo.

2. Experimental

2.1. Materials

All chemicals were reagent grades and purchased from Sigma–Aldrich, Adamas Reagent, and TCI Chemical. Toluene was distilled over calcium hydride under nitrogen before use. All

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reactions were carried out under nitrogen unless otherwise noted. Chromatographic separations were carried out on silica gel (200–300 mesh). Compound 6,6′-dibromoisoindigo [5c], 2,6-bis(trimethyltin)-4,8-di(2,3-dihexylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b*']dithiophene (BDT-T) [9] and 2,6-bis(trimethyltin)-4,8-di(2-octyldodecyloxy)-benzo[1,2-*b*:4,5-*b*']dithiophene (BDT-O) [10] were prepared according to the literatures.

2.2. Instruments

^{1}H and ^{13}C NMR spectra were measured on a Mercury plus 400 MHz machine in $CDCl_3$ at 293 K. Gel permeation chromatography (GPC) analyses were performed on a shimadzu LC-20 A coupled with refractive index detector using THF as eluent with polystyrenes as standards. Thermogravimetric analyses (TGA) was carried out on a TA instrument QS000IR at a heating rate of 20 °C/min under nitrogen gas flow. Differential scanning calorimetry (DSC) analyses were performed in a nitrogen atmosphere using a Pyris 1 instrument. X-ray diffraction patterns of thin films were obtained with a Panalytical X'Pert–Pro MRD diffractometer equipped with a nickel-filtered Cu Kα1 beam and a X′ Celerator detector, using a current of 40 mA and an accelerating voltage of 40 kV. Polymer samples were deposited on the Si/SiO_2 substrate. UV–vis spectra were recorded on a Perkin Elmer Lambda 20 UV–vis spectrophotometer. The electrochemical cyclic voltammetry study was conducted on a CHI 600 electrochemical workstation with platinum disk, platinum wire, and Ag/Ag^+ electrode as working electrode, auxiliary electrode, and reference electrode, respectively. Measurement was carried out under nitrogen atmosphere in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) at a scan rate of 50 mV s^{-1}. The potential of the Ag/Ag^+ reference electrode was internally calibrated with the ferrocene/ferrocenium redox couple (Fc/Fc^+), which had a known energy level of −4.8 eV [11].

2.3. OTFT devices fabrication and characterization

Organic field-effect transistors were constructed on OTS-modified SiO_2/Si substrates with a top-contact configuration. Solutions of the polymers in dichlorobenzene were spin-coated on the substrates in air at room temperature. The source and drain electrodes were patterned through the mask using thermal evaporation method. The device channel lengths were 80 μm, and the channel widths were 8800 μm. The devices were stored at ambient conditions prior to the measurements. The field-effect mobility was calculated in the saturation region using the following equation: $I_{ds} = (WC_i/2L)\mu(V_G - V_T)^2$, where I_{ds} is the drain-source current, W and L are the channel width and length, μ is the field-effect mobility, C_i is the capacitance per unit area of the insulation layer (SiO_2, 11 nF cm^{-2}), V_T and V_G are the gate and threshold voltages, respectively.

2.4. Synthesis of monomers and polymers

2.4.1. Synthesis of monomer M1

2-Ethylhexanoyl chloride (5.81 g, 35.70 mmol) was added slowly to a suspension of 6,6′-dibromoisoindigo (1.50 g, 3.57 mmol) in pyridine (40.0 mL). The mixture was refluxed for 8 h, and then was cooled to room temperature. Water (100 mL) was added and the mixture was extracted with dichloromethane. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by flash chromatography on silica gel with dichloromethane/hexane (1:1) as eluent to give a red solid (1.87 g, 78.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.72 (d, $J = 8.7$ Hz, 2H), 8.51 (d, $J = 1.9$ Hz, 2H), 7.38 (dd, $J = 8.7, 2.0$ Hz, 2H), 3.83–3.88 (m, 2H), 1.78–1.84 (m, 4H), 1.54–1.68 (m, 4H), 1.28–1.35 (m, 8H), 0.94–0.98 (m, 6H), 0.87–0.90 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.50, 167.37, 142.93, 132.43, 129.86, 128.43, 128.13, 121.16, 119.70, 47.45, 31.49, 29.65, 25.39, 23.13, 14.23, 11.83. Anal. calcd for $C_{32}H_{36}Br_2N_2O_4$: C 57.16, H 5.40, N 4.17; found: C 57.02, H 5.34, N 4.25.

2.4.2. Synthesis of polymer ***P1***

M1 (0.2017 g, 0.3000 mmol), 2,6-bis(trimethyltin)-4,8-di(2,3-dihexylthiophen-5-yl)-benzo[1,2-*b*;4,5-*b*']dithiophene (0.3050 g, 0.3000 mmol), $Pd_2(dba)_3$ (0.0055 g, 0.0060 mmol), P(*o*-toly)$_3$ (0.0073 g, 0.0240 mmol) and degassed toluene (10.0 mL) were added to a Schlenk tube. The solution was subjected to three cycles of evacuation and admission of nitrogen and was stirred for 24 h at 110 °C. After cooled to room temperature, the mixture was poured into methanol (100 mL) and was stirred for 2 h. A blue precipitate was collected by filtration. It was washed with methanol and hexane in a Soxhlet extractor for 24 h each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a blue solid with metallic luster was collected (0.26 g, 72.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.65–8.14 (br, 4H), 6.89–7.43 (br, 6H), 3.75–3.89 (br, 2H), 3.01–2.67 (br, 8H), 1.94–0.67 (m, 70H). Anal. calcd for $(C_{74}H_{92}N_2O_4S_4)_n$: C 73.96, H 7.72, N 2.33; found: C 73.86, H 7.63, N 2.43. GPC (THF): $M_n = 92.2$ kDa, $M_w = 206.2$ kDa, PDI = 2.24.

2.4.3. Synthesis of polymer ***P2***

The same procedure was used as for polymer **P1**. Compounds used were $Pd_2(dba)_3$ (0.0055 g, 0.0060 mmol), P(*o*-toly)$_3$ (0.0073 g, 0.0240 mmol), M1 (0.2017 g, 0.3000 mmol), and 2,6-bis(trimethyltin)-4,8-di(2-octyldodecyloxy)-benzo[1,2-*b*;4,5-*b*'] dithiophene (0.3327 g, 0.3000 mmol). After workup, a blue solid with metallic luster was obtained (0.27 g, 69.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.76–8.35 (br, 4H), 7.21–7.43 (br, 4H), 3.72–4.46 (br, 6H), 2.09–0.62 (br, 92H). Anal. calcd for $(C_{82}H_{120}N_2O_6S_2)_n$: C 76.11, H 9.35, N 2.16; found: C 76.66, H 9.51, N 2.21. GPC (THF): $M_n = 78.4$ kDa, $M_w = 164.8$ kDa, PDI = 2.10.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route for monomers and conjugated polymers is shown in Scheme 1. 6,6′-Dibromoisoindigo can be readily *N*-acylated at lactam nitrogens by acyl chloride in pyridine. Both *N*-acylated isoindigo-based conjugated polymers were synthesized via the Stille cross-coupling polymerization with toluene as the solvent and $Pd_2(dba)_3$/P(*o*-tol)$_3$ as the catalyst to give purple-blue materials. The crude polymers were purified by precipitating in methanol and washing with methanol and hexane in a Soxhlet extractor for 24 h each. Residue was extracted with hot chloroform or chlorobenzene in an extractor for 24 h. The new polymers exhibited good solubility in common organic solvents such as chloroform, toluene, xylene, and *o*-dichlorobenzene (*o*-DCB). The chemical structures of the polymer **P1** and **P2** were verified by ^{1}H NMR spectroscopy. The number-average molecular weight (M_n) and the polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (GPC) with THF as eluent against polystyrene standards.

3.2. Thermal properties

The thermal stabilities of the polymers were evaluated by thermogravimetric analysis (TGA) under nitrogen (Fig. 1). The temperature of 5% weight-loss was chosen as onset point of decomposition (T_d). The polymers showed good thermal stability with T_d over 340 °C (as shown in Table 1 and Fig. 1). Neither