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Tuning carrier transport properties of thienoisoindigo-based copolymers by loading fluorine atoms onto the diarylethylene-based electron-donating units

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ABSTRACT

Herein, we demonstrate an effective fine-tuning of carrier transport properties in polymer semiconductors by loading fluorine atoms on polymeric π-systems. To a thienoisoindigo-based conjugated backbones, we introduced dithiophenethene, difluorodithiophenethene, difluorodiphenylethene, and tetrafluorodiphenylethene units affording D–A copolymers, PTIDTE, PTIFDTE, PTIDFPE, and PTITFPE, respectively. PTIDTE and PTIDFPE exhibited unipolar *p*-channel transport properties with mobilities of 0.24 and 0.11 $cm^2\ V^{-1}\ s^{-1}$, respectively, whereas PTIFDTE and PTITFPE afforded ambipolar transport properties with the highest hole/electron mobilities of 0.072/0.017 $cm^2\ V^{-1}\ s^{-1}$ and 0.017/0.0034 $cm^2\ V^{-1}\ s^{-1}$, respectively. Thin film microstructure studies (AFM and 2D-GIXRD) suggest that more ordered lamellar and predominantly edge-on molecular packing mode formed in the PTIFDTE and PTITFPE thin films though they own inferior surface morphologies. The thienoisoindigo-based polymers' backbone conformations were purposed to interpret their different molecular packing mode in solid state, revealing that single conjugated backbone conformations are much easier to form for PTIFDTE and PTITFPE.

1. Introduction

π-Conjugated polymers have received significant attention because of the advantages of tunable optoelectronic properties, mechanical flexibility, and excellent film-forming ability, therefore great application potential in low-cost large-area printed electronics such as field-effect transistors (FETs), light-emitting diodes, and photovoltaic cells [1–13]. Similar to their small molecules counterparts, conjugated polymers can act as either hole-transporting and/or electron-transporting materials in FET devices. In recent decade, significant progress has been made in the high-performance *p*-type conjugated polymers due to their synthetic accessibility and relatively high air-stability. Currently, the state-of-the-art hole mobility of high-performance *p*-type conjugated polymers are comparable with those of vacuum-deposited small molecule-based thin films and amorphous inorganic Si-based FET devices [5,14–18]. Compared to *p*-type conjugated polymers, *n*-type and ambipolar conjugated polymers are lagging behind, although efficient electron-transport are crucial to for constructing high-performance polymeric complementary circuits.

Over the past decades, constructing low-bandgap copolymers based on alternating conjugated donor–acceptor (D–A) dyads have been adopted to develop high-performance *p*-type polymer semiconductors. Among them, lactam-based units such as diketopyrrolopyrrole (DPP) and isoindigo (II) are the two famous electron-withdrawing building blocks, based on which many polymers exhibited outstanding charge carrier transport properties [5,14,15,17–22]. However, the two lactam-based units possess high energy levels of the lowest unoccupied molecular orbital (LUMO) of −3.40 and −3.50 eV, respectively [23,24]. Thus, high LUMO

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energy levels would be achieved in their derived D–A copolymers because the HOMO and LUMO are mainly located at the D and A units, respectively [25,26]. That is to say that, relying solely on the two lactam-based units tend to be unsuccessful for obtaining high-performance *n*-type and ambipolar conjugated polymers owing to the common view that deep-lying lowest LUMO energy level is a prerequisite for achieving *n*-type and ambipolar organic semiconductors. Therefore, introducing heteroatoms or heteroatom-substituted groups with strong electronegativity to effectively reduce the electron density of the D–A polymeric system has also been utilized as an alternative approach for developing *n*-type and ambipolar conjugated polymer semiconductors [5].

Compared with II unit, thienoisoindigo (TI) has a planar conjugated backbone due to the elimination of steric repulsions between the phenyl rings and the carbonyl groups of the oxindoles that occurred in II-based copolymers [27,28]. In this study, we introduced the four electron-donating units, dithienylethylene (DTE), 3,3′-difluorodithienylethylene (FDTE), 2,2′-difluorodiphenylethene (DFPE), and 2,2′,6,6′-tetrafluorodiphenylethene (TFPE), to TI-based conjugated systems affording four D–A copolymers, PTIDTE, PTIFDTE, PTIDFPE, and PTITFPE, respectively. Cyclic voltammetry measurements indicated that no apparent decreases of LUMO energy levels and enhanced reduction capacities occur in PTIFDTE and PTITFPE in comparison with their respective counterparts, PTIDTE and PTIDFPE. FET devices based on the four TI-based copolymers were fabricated and revealed that PTIDTE and PTIDFPE exhibited unipolar *p*-channel transport with decent hole mobilities of 0.24 and 0.11 $cm^2 V^{-1} s^{-1}$, respectively, whereas PTIFDTE and PTITFPE afforded ambipolar transport with hole/electron mobilities of 0.072/0.017 and 0.017/0.0034 $cm^2 V^{-1} s^{-1}$, respectively. Thin film microstructures investigations suggest that more ordered lamellar and predominantly edge-on molecular packing mode formed in the PTIFDTE and PTITFPE thin films though they own inferior surface morphologies. Depended on theoretical calculation results and crystal structures of related diarylethylene units, backbone conformations of the four TI-based copolymers were put forward to interpret their different molecular packing mode in solid state, revealing that single conjugated backbone conformation are much easier to form for PTIFDTE and PTITFPE. The work indicated that the carrier transport properties of polymer semiconductors could be effectively tuned by loading fluorine atoms on polymeric conjugated backbones.

2. Experimental section

2.1. Materials

All reagents and solvents were purchased from highest grade commercial sources such as Acros, Sigma-Aldrich, and Innochem, *etc.*, and used without further purification unless otherwise stated. Anhydrous dichloromethane and chloroform were prepared by refluxing over CaH_2 followed by distillation under nitrogen. *N*-(2-decyltetradecyl)-3-thiophenamine (**2**), and 4-(2-decyltetradecyl)-4*H*-thieno[3,2-*b*]pyrrole-5,6-dione (**3**), were synthesized according to the literature procedures [27]. (*E*)-1,2-Bis(5-(trimethylstannyl)thiophen-2-yl)ethene (**6a**), (*E*)-1,2-bis(3-fluoro-5-(trimethylstannyl)thiophen-2-yl)ethene (**6b**), (*E*)-1,2-bis(2-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (**6c**), and (*E*)-1,2-bis(2,6-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (**6d**) were synthesized following the literature procedures [14,29–31].

2.2. Characterization

^{1}H NMR and ^{13}C NMR spectra of intermediates and target polymers were characterized by on a Bruker Fourier 300 NMR spectrometer or a Bruker Avance III 400, referenced to $CDCl_3$ 7.26 ppm, d_2-$C_2D_2Cl_4$ 6.00 ppm, or $CDCl_3$ 77 ppm, respectively. High resolution mass spectrometry (HRMS) was collected on a 9.4T Solarix FT-ICR mass spectrometers. High temperature gel permeation chromatography (GPC) were carried out at 150 °C on a Polymer Labs PL 220 system using 1,2,4-trichlorobenzene (TCB) as the eluent and polystyrenes as standards. Elemental analysis was conducted on a CARLO ERBA 1106 Elemental Analyzer. The TGA measurements were performed on a Perkin–Elmer series 7 thermal analysis system under nitrogen at a heating rate of 10 °C min^{-1}. The UV-vis-NIR absorption spectra were recorded on a Hitachi U-3010 spectrophotometer. The electrochemical properties of all copolymers were characterized using an electrochemistry workstation at room temperature with a conventional three-electrode configuration in dry acetonitrile containing 0.1 M $(n\text{-Bu})_4NPF_6$, where platinum stick, Ag/AgCl and platinum wire were utilized as working electrode, reference electrode, and counter electrode, respectively. Thin film microstructures were studied on a Digital Instruments Nanoscope V atomic force microscope operated in tapping mode, and two-dimensional grazing incidence X-ray diffraction (2D-GIXRD) at a constant incidence angle of 0.2°.

(*E*)-4,4′-bis(2-decyltetradecyl)-[6,6′-bithieno[3,2-*b*]pyrrolylidene]-5,5′(4*H*,4′*H*)-dione (4). To a two-neck round flask containing 4-(2-decyltetradecyl)-4*H*-thieno[3,2-*b*]pyrrole-5,6-dione, **3** (4.9 g, 10.0 mmol) and *o*-xylene (60 mL) was added Lawesson's reagent (2.0 g, 5.0 mmol) in one portion. The reaction mixture was heated to 60 °C and stirred for 3 h under nitrogen. After cooled down to room temperature, the resulting solution was poured to H_2O (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extract was washed with brine, and then dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by silica gel column chromatography using petroleum ether as eluent to give the desired product as an purple solid (1.98 g, 42%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.52 (d, $J = 5.2$ Hz, 2H), 6.78 (d, $J = 5.2$ Hz, 2H), 3.69 (m, 4H), 1.89 (m, 2H), 1.31–1.23 (m, 80H), 0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 171.3, 151.7, 134.2, 121.2, 114.3, 111.3, 46.2, 37.2, 31.9, 31.5, 29.94, 29.67, 29.32, 26.4, 22.7, 14.0. HRMS: Calcd. for $[C_{60}H_{102}N_2O_2S_2]^+$: 947.7455; Found: 947.7457.

(*E*)-2,2′-dibromo-4,4′-bis(2-decyltetradecyl)-[6,6′-bithieno[3,2-*b*]pyrrolylidene]-5,5′(4*H*,4′*H*)-dione (5). To a 250 mL two-neck round flask containing (*E*)-4,4′-bis(2-decyltetradecyl)-[6,6′-bithieno[3,2-*b*]pyrrolylidene]-5,5′(4*H*,4′*H*)-dione, **4** (1.90 g, 2.0 mmol) and $CHCl_3$ (30 mL) was added dropwise a solution of NBS (0.73 g, 4.1 mmol) in $CHCl_3$ (10 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The resulting reaction mixture was quenched by addition of water (60 mL), and extracted with dichloromethane (2 × 50 mL). The combined organic extract was washed with brine, and then dried over anhydrous Na_2SO_4. After removal of solvent, the residue was purified by silica gel column chromatography using petroleum ether/dichloromethane as eluent to give the desired product as an blue solid (1.80 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, δ) 6.79 (s, 2H), 3.62 (m, 4H), 1.81 (m, 2H), 1.24 (m, 80H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 170.2, 150.1, 123.1, 119.6, 114.9, 114.7, 46.2, 37.2, 31.93, 31.91, 29.95, 29.68, 29.65, 29.63, 29.56, 29.36, 22.7, 14.1. HRMS: Calcd. for $[C_{60}H_{100}Br_2N_2O_2S_2]^+$: 1104.5573; Found: 1104.5580.

2.3. General synthesis and purification procedure of PTIDTE and PTIFDTE

To a Schlenk flask containing TI-based monomer, **5** (0.20 mmol) and tin monomer, **6a** or **6b** (0.20 mmol), $Pd_2(dba)_3$ (6.0 mg), $P(o\text{-tol})_3$ (17.0 mg) was added degassed chlorobenzene (5.0 mL). The solution was thoroughly degassed under Argon at −78 °C, the reaction mixture was heated to 115 °C and stirred for 24 h under