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A bis(2-oxoindolin-3-ylidene)-benzodifuran-dione containing copolymer for high-mobility ambipolar transistors[†]

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A bis(2-oxoindolin-3-ylidene)-benzodifuran-dione (BIBDF)-based low band gap polymer (PBIBDF-BT), containing a solubilizing alkyl chain bithiophene unit as a donor, has been synthesized. The polymer with a low-lying LUMO/HOMO energy level (-4.03/-5.55 eV) exhibits efficient ambipolar charge transport. The electron and hole mobilities are as high as 1.08 and 0.30 cm² V⁻¹ s⁻¹, respectively.

Organic thin-film transistors (OTFTs) based on conjugated polymers have undergone significant progress in recent years.¹ Most of the OTFTs to date show only unipolar behavior (either holes or electrons). Ambipolar OTFTs showing both n- and p-type channel performance in one device are very important for applications in large-area high-performance complementary circuits at a lower cost.² The energy levels of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are the key factors for the ambipolar semiconductors.³ The semiconductors are required to have relatively low HOMO energy levels, down to -5.0 eV for hole transport. And for stable electron transport, the LUMO energy levels as low as -4.0 eV are required.⁴ So the energy gap of semiconductors should be narrow enough to allow charge injection of both carriers. In fact, most of the common organic small molecules and polymers show band gaps of above 2 eV, which result in high injection barriers for either electrons or holes when the charges are injected from a metal electrode with a given work function.⁵ The development of high performance ambipolar materials has lagged far behind that of p-channel materials.⁶ To resolve this problem, one of the effective ways is to synthesize a low band

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^b Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Hefei University of Technology, Hefei, 230009, China gap (less than 1.8 eV) material with a deep LUMO energy level ($\sim -4.0 \text{ eV}$) to reduce the injection barrier for both charge carriers and to achieve efficient ambipolar transport.⁷ Recently, donor-acceptor (D-A) low band gap copolymers have exhibited very promising performances in OTFTs applications.⁸

D-A polymer-based devices are reported to have hole mobilities as high as about 10 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and possess electron mobilities over 1 cm² V⁻¹ s^{-1.9} A D-A polymer constructed with alternate electron-rich and deficient units could facilitate the formation of a low band gap as well as a low HOMO energy level and result in high air stability. Moreover, the addition of strong electron-withdrawing groups in the acceptor unit can reduce the LUMO energy level which has been confirmed to be beneficial to the stability of charge transport.¹⁰ (3E,7E)-3,7-bis(2-oxoindolin-3-vlidene)benzo-[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione (BIBDF) has a large fused aromatic ring with a symmetric and planar structure, which would increase the π - π overlap and intermolecular interaction. The lactone groups in the central core coupled with the lactam groups make the BIBDF unit strongly electron-deficient.¹¹ If the BIBDF is introduced into the D-A polymer backbone as an acceptor unit, the polymer would have lower LUMO and HOMO energy levels, thereby be suitable for both hole and electron injection and transport.

The insoluble D–A polymer based on bithiophene and BIBDF units was reported by Li's group.^{11*a*} To resolve the insolubility of this polymer, increasing the length of branched chains and/or introducing solubilizing alkyl chains in the dithiophene unit are proved to be effective approaches. During the preparation of this paper, Pei *et al.* reported a side-chain substituted BIBDF-based polymer with a large branch group showing high mobility.¹² Here, we independently synthesized a conjugated polymer (PBIBDF-BT, Scheme 1) by



Scheme 1 The synthetic route to a polymer.

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Fig. 1 UV-vis NIR absorption spectra of PBIBDF-BT in chloroform and in a thin film.

introducing the solubilizing alkyl chain grafted bithiophene unit as the donor and the BIBDF unit as the acceptor. The OTFT devices based on PBIBDF-BT as a semiconductor yield mobility as high as 1.08 cm² V⁻¹ s⁻¹ for electrons and 0.3 cm² V⁻¹ s⁻¹ for holes. And after three months air exposure, the mobility of the annealed devices still maintained at 0.73 cm² V⁻¹ s⁻¹ and 0.035 cm² V⁻¹ s⁻¹ for electrons and holes, respectively.

Synthesis of monomers is shown in Scheme S1 (ESI†), copolymer PBIBDF-BT was synthesized by the Stille coupling reaction. The copolymer showed good solubility and the number-average molecular weight was 38.6 kDa with a polydispersity index of 1.52. The UV-vis-NIR absorption spectra of PBIBDF-BT in dilute chloroform solution and as thin film cast from chloroform are shown in Fig. 1. In chloroform solution, PBIBDF-BT had a maximal absorption peak (λ_{max}^{abs}) at about 811 nm and an absorption band-edge (λ_{onset}^{abs}) at about 1039 nm, respectively. As a thin film, PBIBDF-BT had an absorption $\lambda_{\text{max}}^{\text{abs}}$ at 823 nm and a $\lambda_{\text{onset}}^{\text{abs}}$ at about 1047 nm. Compared to the solution, the λ_{\max}^{abs} of polymer film was red-shifted about 12 nm, which indicated the improvement of the molecule ordering due to the strong $\pi - \pi^*$ interchain interactions in the solid thin films.¹³ The optical band-gap (E_g^{opt}) of PBIBDF-BT is 1.18 eV as estimated from the absorption edge (\sim 1047 nm) of the polymer thin film. The onset oxidation potential (E_{onset}^{ox}) and onset reduction potential (E_{onset}^{red}) of the polymer were located at 0.84 V and -0.68 V (Fig. 2), respectively. The HOMO and LUMO energy levels of PBIBDF-BT were calculated from the E_{onset}^{ox} to be -5.55 eV and -4.03 eV, respectively. The very low HOMO-LUMO energy level can be attributed to the electron-deficient lactone and lactam groups on the BIBDF unit which remarkably lowered the HOMO-LUMO energy level. The low LUMO energy



Fig. 2 Cyclic voltammograms of PBIBDF-BT thin film.

level of PBIBDF-BT can rival the reported PDI ($\sim -3.9 \text{ eV}$) and NDI ($\sim -4.0 \text{ eV}$) based n-type polymers.^{1c,14} For OTFT applications, a deep LUMO energy level is beneficial to facilitate charge injection and stable electron transport and a low-lying HOMO energy level is beneficial to achieve stable hole transport and essential to resist air oxidation and thus increase device stability.

The charge transport properties of PBIBDF-BT were investigated with organic thin film transistors (OTFTs). PBIBDF-BT showed typical ambipolar field-effect charge transport. The preliminary device performances of PBIBDF-BT are listed in Table S1 (ESI^{\dagger}). An electron mobility of 0.28 cm² V⁻¹ s⁻¹ was measured for the OTFT devices without thermal annealing. In this work, the thermal annealing was performed as an effective method to optimize the device performance because thermal annealing had the ability of increasing the molecular packing order of polymer film,^{9a} which could improve the charge mobility of the semiconducting polymer. The polymer films were subsequently annealed at different temperatures (100 °C, 150 °C, 175 °C and 200 °C) in glovebox under nitrogen ambient. Fig. S1 (ESI⁺) shows the electron and hole mobilities of PBIBDF-BTbased OTFT devices thermally annealed at temperatures ranging from 100 to 200 °C. The corresponding device performances annealed at these temperatures are summarized in Table S1 (ESI⁺). The average field-effect electron mobility was increased from 0.27 to 0.68 cm² V⁻¹ s⁻¹ and correspondingly, the hole mobility was increased from 0.06 to 0.24 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The threshold voltage of the n-channel operation ranges from 24.7 V to 31.0 V, while that of the p-channel mode is in the range from -21.8 V to -46.1 V. Device performance is optimized by thermal annealing at 175 °C. The typical ambipolar output and transfer curves of the OTFTs based on PBIBDF-BT after thermal annealing at 175 °C, are shown in Fig. 3. The highest electron mobility is 1.08 cm² V⁻¹ s⁻¹ and the average mobility is 0.68 cm² V⁻¹ s⁻¹.



Fig. 3 Output (a, b) and typical transfer characteristics (c, d) of OTFTs devices based on PBIBDF-BT at an optimized annealing temperature of 175 $^\circ\text{C}.$

Meanwhile, the maximum hole mobility of $0.30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an average mobility of $0.24 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were obtained. Therefore, the thermal annealing is confirmed to have a substantial influence on charge transport. The PBIBDF-BT-based OTFT devices exhibited excellent ambipolar performance. Moreover, all the output curves of electron and hole transport showed negligible hysteresis. After three months air exposure, the mobility of the annealed devices was still maintained at $0.73 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.035 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons and holes (Table S1 and Fig. S2, ESI†), respectively. The PBIBDF-BT-based devices exhibited good environmental stability which is in agreement with the low LUMO and HOMO energy levels.

Film morphology and crystallinity played an important role in OTFT device performance. The thin film morphologies and microstructures of PBIBDF-BT were investigated using atomic force microscopy (AFM) in the tapping-mode and grazing incident X-ray scattering (GIXD). Fig. 4 and Fig. S3 (ESI⁺) show that the AFM phase images of the polymer films annealed at different temperatures. Dense nanofibrillar structures were observed over the entire area in PBIBDF-BT samples. The high mobility can be ascribed to the nanofibers that form an interconnected polymer chain network and function as a highly efficient pathway for charge carrier transport throughout the polymer film. The as-cast PBIBDF-BT films exhibited much smaller fibrillar domains as compared to the films annealed at 175 °C, implying enhanced charge transport in the annealed films. Further increase of the annealing temperature to 200 °C resulted in obvious dewetting in the film, which was responsible for the decline of field effect performance.

The molecular ordering is one of the key factors determining the device performance, and GIXD patterns of the PBIBDF-BT film without and with annealing at 175 °C, were also investigated. As shown in Fig. 4 and Fig. S4 (ESI†), the diffraction peaks of the annealed film were obviously enhanced, which is consistent with the AFM results. The film of PBIBDF-BT showed a strong out-of-plane diffraction peak (100) and also exhibited well defined (200), (300), and (400) diffraction peaks along the out-of-plane q_z axis. This revealed that the polymer film possessed a highly ordered lamellar structure and the corresponding lamellar spacing was 28.5 Å. Besides the out-of-plane peaks, the film also had an in-plane (010) diffraction peak at 1.77 Å⁻¹, which was



Fig. 4 AFM phase images and GIXD patterns of PBIBDF-BT films with and without annealing.

attributed to the π - π interchain stacking. The calculated π - π stacking distance of PBIBDF-BT was 3.55 Å. The π - π stacking distance of PBIBDF-BT was even lower than those of reported high performance DPP-based polymers, PDVT-10 (3.66 Å) and PDVT-8 (3.78 Å).^{9a} Such a small π - π distance between polymer backbones suggested the strong intermolecular interaction, which accounted for the π - π interchain stacking and the strong D-A interaction. Charge transport of the conjugated polymer is highly dependent on the intermolecular overlap integral. PBIBDF-BT, having a small π - π stacking distance that is beneficial to improve the intermolecular overlap integral, is expected to show a high charge carrier mobility.

In conclusion, the soluble low band gap D–A polymer based on bithiophene as donor and bis(2-oxoindolin-3-ylidene)-benzodifurandione as acceptor was synthesized and characterized. A certain amount of large side chains are required to ensure the solubility of the BIBDF-based polymer. Preliminary investigations on thin film transistor devices with polymer PBIBDF-BT were also carried out. The polymer PBIBDF-BT with a deep LUMO–HOMO energy level, a highly ordered lamellar structure and a small π - π stacking distance showed excellent field-effect electron and hole transport. The BIBDF unit with its strong electron-deficient nature and a perfect planar π -conjugated structure may be a useful new monomer for the construction of low band gap conjugated polymers and be applied in the high performance organic thin film transistor.

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