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High-Performance Air-Stable Organic Field-Effect Transistors: Isoindigo-Based Conjugated Polymers

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Ⓢ Supporting Information

ABSTRACT: Two conjugated polymers, **IIDDT** and **IIDT**, based on an isoindigo core were developed for organic field-effect transistors. Investigation of their field-effect performance indicated that **IIDDT** exhibited air-stable mobility up to 0.79 cm^2 V^{-1} s^{-1}, which is quite high among polymer FET materials. The facile preparation and high mobility of such polymers make isoindigo-based polymers very promising for application as solution-processable organic semiconductors for optoelectronic devices.

To replace vacuum-deposited amorphous silicon-based thin-film transistors, organic field-effect transistors (OFETs) have attracted broad interest due to their potential application.[1] Among all organic semiconductors for OFETs, polymers are extensively investigated because they offer great advantages over small molecules, such as solution processability, good mechanical properties, and thermal stability.[2] Although significant progress has been achieved in vacuum-deposited small molecules,[3] polymeric OFET materials with high mobility are still challenging.[4]

Several polythiophene-based OFETs were reported with mobility (μ) >0.5 cm^2 V^{-1} s^{-1} and an on/off ratio >10^6,[5] comparable to the values for amorphous silicon; however, their stability still must be improved for practical application.[6] An effective approach to improve the stability is to introduce electron-deficient aromatic rings into the backbone of polythiophene to lower the HOMO level.[7] Recently, Reynolds and co-workers reported the synthesis of a series of small molecules and polymers containing an isoindigo unit, which showed potential for application in photovoltaic devices.[8] Herein, we report a facile synthesis of two isoindigo-based polymers and their use as active layers to fabricate OFET devices by direct solution processing. We obtain very good field-effect performance with μ up to 0.79 cm^2 V^{-1} s^{-1}, and these devices show excellent stability in ambient conditions because of their low-lying HOMO levels.

The synthesis of polymers **IIDDT** and **IIDT** is shown in Scheme 1. Direct condensation of two commercially available compounds, 6-bromoisatin (**1**) and 6-bromooxindole (**2**), in acetic acid afforded isoindigo **3** in 86% yield. Subsequently, **3** was alkylated with 1-iodo-2-octyldodecane to give **4** in 74% yield. A Stille-coupling polymerization between **4** and bis(trimethylstannyl)

Scheme 1. Synthetic Route of Two Isoindigo-Based Polymers[a]
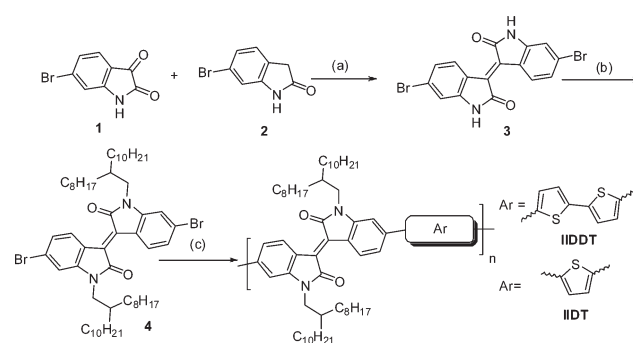
[a] Reagents and conditions: (a) AcOH/HCl, reflux, 24 h, 86%; (b) 1-iodo-2-octyldodecane, K$_2$CO$_3$, DMF, 74%; (c) bis(trimethylstannyl) thiophene or 5,5′-bis(trimethylstannyl)-2,2′-bithiophene, Pd$_2$(dba)$_3$, P(o-tol)$_3$, PhMe, 110 °C, 48 h; for **IIDDT**, 95%; for **IIDT**, 96%.

thiophene or 5,5′-bis(trimethylstannyl)-2,2′-bithiophene gave **IIDT** and **IIDDT**, respectively, in high yields. Because of the introduction of long alkyl chains, both polymers were readily soluble in common solvents, such as CHCl$_3$, toluene, and THF. Both polymers were obtained as dark metallic solids after careful purification. Molecular weights of both polymers were measured by GPC. As shown in Table 1, **IIDT** shows a M_n of about 19.8 kg/mol, while **IIDDT** shows a very high M_n up to 87.9 kg/mol. This result may be attributed to the different steric hindrance of the polymerization reaction, because the thiophene unit may cause the repulsion of the isoinidgo in the polymerization. We also measured their thermal properties. Both polymers showed decomposition temperatures >350 °C under nitrogen atmosphere, and no phase transition was observed before decomposition.

Figure 1 shows the absorption spectra of **IIDDT** and **IIDT** in CHCl$_3$ (1 × 10^{-5}), in thin film, and in annealed film. In dilute solution, two absorption bands from 300 to 520 nm for **IIDDT** obviously red-shifted relative to those of **IIDT**, due to the increase of the effective conjugation length after the introduction of bithiophene unit. However, **IIDDT** and **IIDT** exhibited a very similar absorption band from 520 to 800 nm with an onset at ∼800 nm (as shown

Table 1. Polymer Molecular Weights and OFET Performances

polymer	M_n/M_w	PDI	μ (cm^2 V^{-1} s^{-1})	$I_{on/off}$
IIDT	19 800/39 100	2.0	—[a]	—
			0.019 (0.015)[b]	$\sim 10^6$
IIDDT	87 900/185 800	2.1	0.1−0.2[a]	$\sim 10^6$
			0.79 (0.42)[b]	$\sim 10^7$

[a] Pristine film spin-coated from TCE solution. [b] Maximum values of hole mobility, after annealing at 150 °C for 20 min. Average values are in parentheses for >20 devices tested.

in Figure 1). This absorption band was a typical charge-transfer absorption from the thiophene unit to the isoindigo core, in accordance with the computational results that the HOMOs are well delocalized along the polymer chains; in contrast, the LUMOs are mostly localized on the isoindigo core (as shown in Figure 2b). The absorption peaks of **IIDDT** and **IIDT** in films do not show obvious red-shifts relative to those in the solution; however, a little increase in absorption intensities and a blue-shift of the 0−1 peak are observed. Interestingly, after annealing of the films at 150 °C, **IIDDT** showed only a little increase in the absorption intensity of the 0−0 vibrational peak;[9] in contrast, the absorption features of the annealed film of **IIDT** showed a large change, in which the 0−1 peak was largely increased and the spectral edge was slightly red-shifted, suggesting that the packing conformation of **IIDT** was largely changed and the backbone of polymers might become more planar after annealing.

CV measurements of both polymers in thin films show that **IIDDT** has a HOMO/LUMO level of −5.7/−3.7 eV, and **IIDT** has a HOMO/LUMO level of −5.8/−3.8 eV. Both polymers show much stronger oxidative peaks than their reductive peaks, and the oxidative peak of **IIDDT** seems more reversible than that of **IIDT**. This result is consistent with the device performance, in that both polymers are typical p-type semiconductors and **IIDDT** exhibited better performance. Compared with traditional thiophene or fused thiophene-based polymers, both **IIDDT** and **IIDT** showed much deeper HOMO levels, due to the electron-deficient isoindigo core.

Bottom-gate/top-contact devices were fabricated by spin-coating the polymer solutions (4 mg/mL in CHCl$_3$ or in trichloroethylene (TCE)) onto octadecyltrichlorosilane (OTS)-treated SiO$_2$ (300 nm)/n^{++}-Si substrate. The OTS self-assembled monolayer was modified according to the method reported by Bao and co-workers,[3c] which showed a high crystalline ultrasmooth surface and improved performances for vacuum-deposited OFETs. CHCl$_3$ and TCE did not show any significant difference in device performances, but TCE provides films with higher quality because of its high boiling point. For **IIDT**, direct spin-coated films did not exhibit observable field effect. However, after annealing at 150 °C, it was measured to show $\mu \approx 0.01-0.02$ cm^2 V^{-1} s^{-1} (Figure S4). As discussed above, the annealing process increased the intermolecular packings, which resulted in higher mobility. After spin-coating the solution of **IIDDT**, the pristine films exhibited $\mu \approx 0.1-0.2$ cm^2 V^{-1} s^{-1}. After annealing at 150 °C for 20 min, **IIDDT** exhibited μ up to 0.79 cm^2 V^{-1} s^{-1} and an average $\mu = 0.42$ cm^2 V^{-1} s^{-1} (>20 devices), which is an order of magnitude higher than **IIDT** (as illustrated in Figure 3). This large improvement can be attributed to better molecular packing,[10] C_2 symmetry,[11] and high molecular weight[12] of **IIDDT**. The polymer also exhibited good transfer curves with a small hysteresis. The
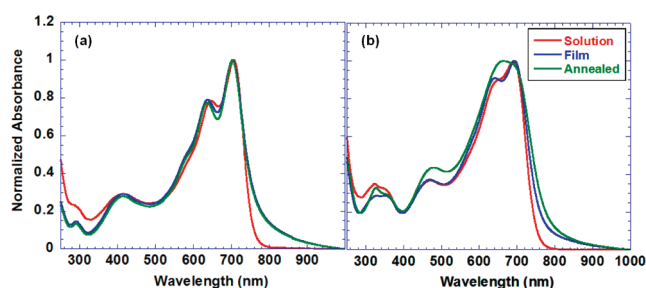

Figure 1. Normalized UV−vis absorption spectra of (a) **IIDDT** and (b) **IIDT** in CHCl$_3$ (1×10^{-5} M), in thin film, and in annealed film (at 150 °C for 20 min).
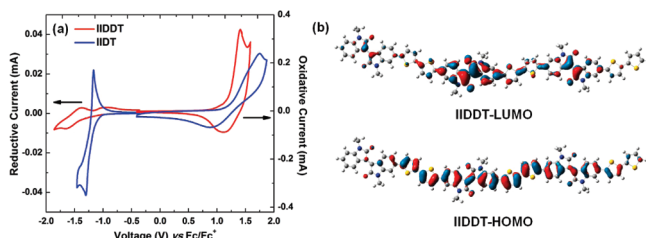

Figure 2. (a) Cyclic voltammograms of **IIDDT** and **IIDT** in thin films drop-cast on a glassy carbon and tested in Bu$_4$NPF$_6$/CH$_3$CN solution (scan rate, 50 mV s^{-1}). The oxidative currents are almost an order of magnitude higher. (b) Calculated molecular orbitals of the trimer of **IIDDT** (B3LYP/6-31G (d)).

output curves showed almost no contact resistance. Therefore, the low-lying HOMO level does not interfere with the charge injection from the Au electrode. Both polymers were stable at least for 4 months under ambient conditions, and the **IIDDT** devices were also stable at high humidity ($R_H = 60\%$) for at least 1 month (Figure S5), which may be attributed to the low-lying HOMO levels.

With the above results in hand, we employed grazing incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM) to investigate packings and morphologies of the polymer films. In the 2D-GIXD, **IIDDT** shows a strong diffraction peak at $2\theta = 3.58°$, corresponding to a d-spacing of 19.88 Å ($\lambda = 1.240$ Å) (Figures 4a and S6). Other three diffraction peaks are attributed to 002, 003, and 004 diffractions, indicating that **IIDDT** had an edge-on lamellar packing in film. In contrast, **IIDT** shows only one weak diffraction at 3.25° (Figure 4b), indicating the films are relatively amorphous. The AFM images of the films are shown in Figure 4c,d. **IIDDT** shows crystalline fibrillar intercalating networks,[13] likely the result of the strong intermolecular $\pi-\pi$ interactions, which were also observed in other high-performance OFET materials.[2c,5c] In contrast, the films of **IIDT** are more amorphous without obvious crystallized zones. Therefore, the difference in crystallinity between **IIDDT** and **IIDT** may explain the largely different device performances.

In summary, we have synthesized two donor−acceptor copolymers, **IIDDT** and **IIDT**, in which an isoindigo core is incorporated into the backbone of polythiophene. The polymers are obtained in three steps with high yields, which is important for practical low-cost applications. Both polymers show similar photophysical and electrochemical properties. However, they exhibit completely different OFET performance. **IIDDT** exhibits a high μ up to 0.79 cm^2 V^{-1} s^{-1} and an on/off ratio $\sim 10^7$, which is among the highest field-effect performance from polymers. It is
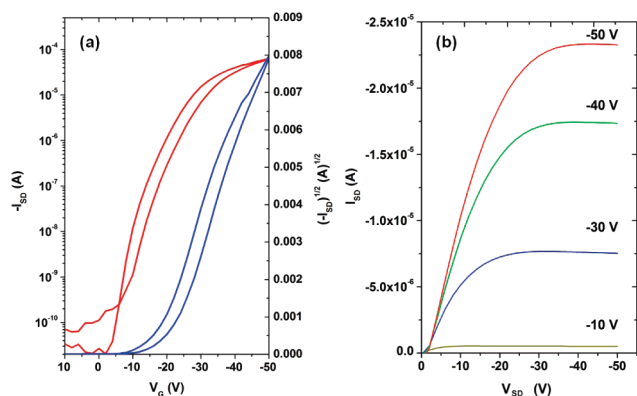
Figure 3. (a) Transfer and (b) output characteristics of an **IIDDT** device (spin-cast from TCE solutions, 4 mg/mL) at $V_{DS} = -50$ V ($L = 60$ μm, $W = 3.0$ mm) after 150 °C annealing.
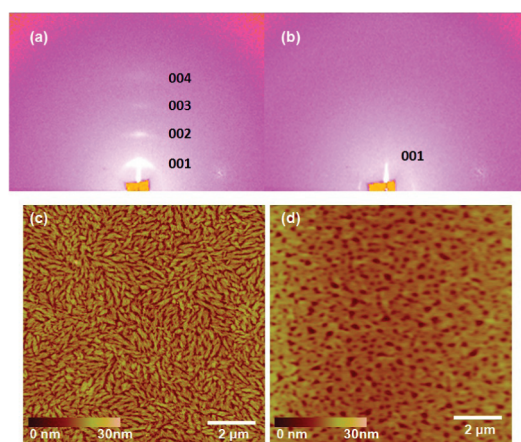

Figure 4. 2D-GIXD patterns of (a) **IIDDT** and (b) **IIDT**. Tapping-mode AFM height images of the (c) **IIDDT** and (d) **IIDT** films spin-cast from TCE solution (4 mg/mL).

notable that these devices show very good stability in ambient and high-humidity conditions, owing to their low-lying HOMO levels. Moreover, these polymers have good solubility in many common solvents, which is crucial for their environmentally friendliness[14] and printing fabrication.[2]

■ ASSOCIATED CONTENT

⑤ Supporting Information. Monomers/polymers synthesis, characterization, and device fabrication details. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(9) See Supporting Information, Figure S1, for the unnormalized spectra of the thin films.

(10) This can be understood from the absorptions of the films, in which the further aggregation of **IIDT** can only be achieved by thermal annealing; in contrast, **IIDDT** seems more planar than **IIDT** and so can form ordered packing as spin-cast. Furthermore, the isoindigo core may have steric hindrance in **IIDT**.

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