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 cm² 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. 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. Although significant progress has been achieved in vacuum-deposited small molecules, polymeric OFET materials with high mobility are still challenging.

Several polythiophene-based OFETs were reported with mobility (μ) >0.5 cm² V⁻¹ s⁻¹ and an on/off ratio >10⁶, comparable to the values for amorphous silicon; however, their stability still must be improved for practical application. An effective approach to improve the stability is to introduce electron-deficient aromatic rings into the backbone of polythiophene to lower the HOMO level. Recently, Reynolds and coworkers reported the synthesis of a series of small molecules and polymers containing an isoindigo unit, which showed potential for application in photovoltaic devices. 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 cm² 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-ido-2-octyldodecane to give 4 in 74% yield. A Stille-coupling polymerization between 4 and bis(trimethylstannanyl)iodophenone or 5,5'-bis(trimethylstannanyl)-2,2'-bithiophene, Pd₂(dba)₃, P(o-tol), PhMe, 110°C, 48 h; for IIDDT, 95%; for IIDT, 96%.

Figure 1 shows the absorption spectra of IIDDT and IIDT in CHCl₃ (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

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Table 1. Polymer Molecular Weights and OFET Performances

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n/M_w$</th>
<th>PDI</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$I_{on}/I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIDT</td>
<td>19,800/39,100</td>
<td>2.0</td>
<td>$0.019 (0.015)^a$</td>
<td>$\sim 10^4$</td>
</tr>
<tr>
<td>IIDDT</td>
<td>87,900/185,800</td>
<td>2.1</td>
<td>$0.1-0.2^a$</td>
<td>$\sim 10^6$</td>
</tr>
</tbody>
</table>

$^a$ 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, 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, 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 $\mu$ 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, C$_2$ symmetry, and high molecular weight of IIDDT. The polymer also exhibited good transfer curves with a small hysteresis. The 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 ($R_{hh} = 60\%$) 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$\theta = 3.58^\circ$, corresponding to a d-spacing of 19.88 Å ($X = 1.240$ Å) (Figures 4a and 5e). 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 3.2$^\circ$ (Figure 4b), indicating the films of IIDT are much less crystalline. The AFM images of the films are shown in Figure 4c,d. IIDDT shows crystalline fibrillar intercalating networks, likely the result of the strong intermolecular $\pi-\pi$ interactions, which were also observed in other high-performance OFET materials. 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 $\mu$ up to 0.79 cm$^2$ V$^{-1}$ s$^{-1}$ and an on/off ratio $\sim 10^4$, which is among the highest field-effect performance from polymers. It is
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 and printing fabrication.

■ ASSOCIATED CONTENT

Supporting Information. Monomers/polymer 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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■ REFERENCES


(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.


(13) The crystalline zones are also identified by optical microscopy using a polarized incident light.