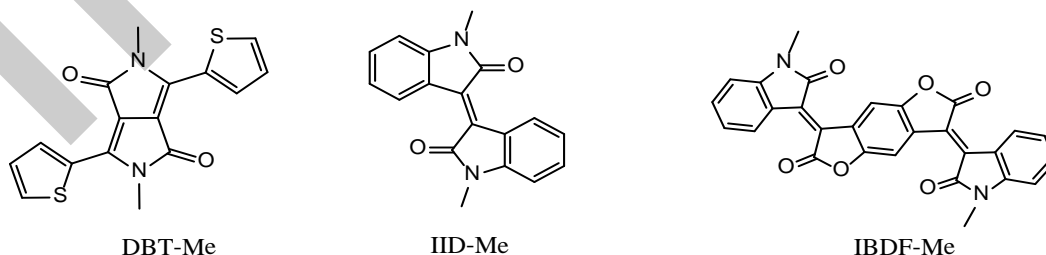


Novel stable (3*E*,7*E*)-3,7-bis(2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b'*]difuran-2,6(3*H*,7*H*)-dione based donor-acceptor polymer semiconductors for n-type organic thin film transistors[§]

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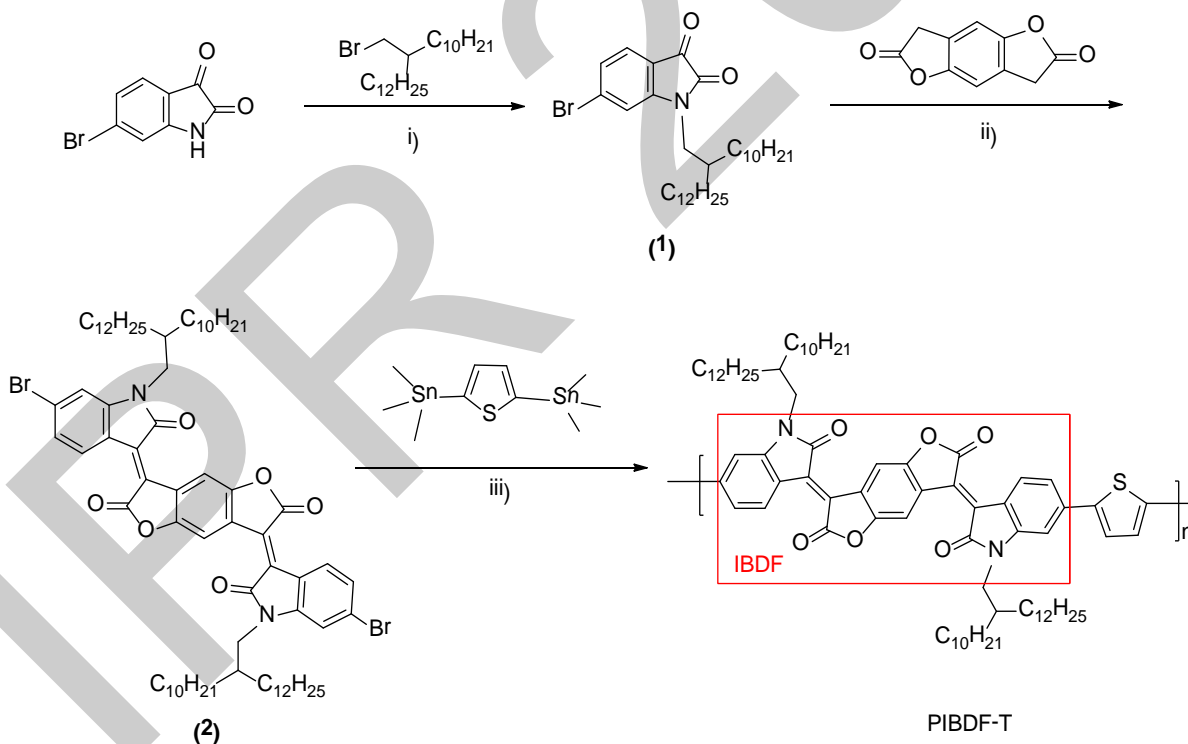
Conjugated polymers represent a new class of semiconducting materials for printed organic thin film transistors (OTFTs).¹ Compared with traditional semiconducting materials, they are solution-processable, light-weight, low-cost and mechanically robust. However, the commercialization of organic electronics is limited by their rather low charge carrier mobility compared with traditional inorganic semiconductors. It has been proven that combining electron donating and electron accepting building blocks in the main backbone of the polymer is one of the most promising strategies to increase the intermolecular interaction, thus increasing charge carrier mobility.² Diketopyrrolopyrrole (DPP)³ and isoindigo (IID)⁴ based donor-acceptor copolymers are examples of semiconducting polymer materials exhibiting charge carrier mobility close to or even greater than $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. With a great number of donors commercially or synthetically available, significant progress has been achieved in the preparation of hole transporting, p-type semiconducting polymers for OTFTs with hole mobility close to that of amorphous silicon.⁵ However, n-type, electron transporting semiconductors has lagged behind their p-type counterparts with much less acceptors available. In this study, we have prepared an electron-accepting building block, 3,7-bis(1-(2-decyltetradecyl)-2-oxoindolin-3-ylidene)benzo[1,2-*b*:4,5-*b'*]difuran-2,6(3*H*,7*H*)-dione (IBDF) and a IBDF-based n-type donor-acceptor copolymer, PIBDF-T.



Scheme 1. Structure of DBT-Me, IID-Me and IBDF-Me.

Before the synthesis was started, computer simulation was performed on IBDF-Me DBT-Me and IID-Me to study the coplanarity of IBDF building block and to compare the energy levels of the molecule. The optimized structure of IBDF-Me suggested that the molecule is highly coplanar, and the predicted HOMO/LUMO energy levels are much lower than the values predicted for DBT-Me and IID-Me, indicating that IBDF is a potential acceptor for D-A copolymers.

The preparation of PIBDF-T is outlined in Scheme 2. Compound 6-bromo-1-(2-decyltetradecyl)indoline-2,3-dione (**1**) was prepared from 6-bromoindoline-2,3-dione via N-alkylation. Substitution of the branched (-decyltetradecyl) group was designed for better solubility purpose. Compound (**1**) was then reacted with benzodifurandione, which was prepared via established synthesis route,⁶ to afford (3E,7E)-3,7-bis(6-bromo-1-(2-decyltetradecyl)-2-oxindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione (**2**) monomer. PIBDF-T was prepared via Stille-coupling polymerization of IBDF monomer and 2,5-bis(trimethylstannyl) thiophene.



Scheme 2. The synthetic route to IBDF-based polymers PIBDF-T: i) K₂CO₃/DMF/70 °C; ii) TsOH/acetic acid/115 °C; iii) Pd₂(dba)₃/P(o-tol)₃/chlorobenzene, 130 °C.

The polymer has been fully characterized. Thermal gravimetric analysis (TGA) suggested that the polymer is thermal stable up to 385 °C. The optical band gap of the polymer was determined from onset wavelength in UV-Visible spectrum (Figure 1) to be 1.36 eV. The cyclic voltammograms (CV) of **PIBDF-T** (Figure 2) indicated that this polymer is stable towards both oxidation and reduction processes. The HOMO and LUMO energy levels were extracted from the oxidation and reduction onset potentials to be -5.79 eV and -4.11 eV, respectively. Tightly packed grains of ~50 nm are observed in atomic force microscopy (AFM) images of the polymer thin film spin coated on DTA modified SiO₂/Si wafer substrates; however, X-ray diffraction (XRD) analysis of the polymer films suggested poor crystallinity.

The device performance of PIBDF-T has been evaluated on bottom-gate, bottom-contact OTFTs (Table 1). Devices encapsulated with PMMA showed typical n-type channel transistor characteristics, with the highest electron mobility of $5.4 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ($I_{\text{on/off}} = 6.4 \times 10^3$) recorded for the polymer film annealed at 200 °C. To our surprise, OTFT devices characterized in air exhibit ambipolar charge transport behaviour with balanced electron/hole mobility up to $8.2 \times 10^{-3}/1.0 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Table 1. Summary of OTFT device performance using **PIBDF-T** as the channel layers. ^a

Encapsulation with ~500 nm PMMA	Annealing temperature	Charge transport	Mobility, $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$I_{\text{on}}/I_{\text{off}}$
Yes	100 °C	n-type	$\mu_n = 1.5\text{-}2.2 \times 10^{-3}$	$\sim 10^3$
	150 °C	n-type	$\mu_n = 2.4\text{-}3.0 \times 10^{-3}$	$\sim 10^3$
	200 °C	n-type	$\mu_n = 4.2\text{-}5.4 \times 10^{-3}$	$\sim 10^3\text{-}10^4$
	250 °C	n-type	$\mu_n = 0.9\text{-}1.5 \times 10^{-3}$	$\sim 10^3$
No	150 °C	ambipolar	$\mu_n = 5.5\text{-}8.2 \times 10^{-3}$ $\mu_h = 0.8\text{-}1.0 \times 10^{-2}$	$\sim 10^3$ $\sim 10^4$
	200 °C	ambipolar	$\mu_n = 8.4\text{-}9.0 \times 10^{-3}$ $\mu_h = 4.7\text{-}4.9 \times 10^{-3}$	$\sim 10^3$ $\sim 10^2\text{-}10^3$
	250 °C	ambipolar	$\mu_n = 1.2\text{-}1.4 \times 10^{-3}$ $\mu_h = 2.5\text{-}3.3 \times 10^{-3}$	$\sim 10^4$ $\sim 10^6$

^a The devices were annealed in a glove box on a hotplate at the selected temperature for 15 min under

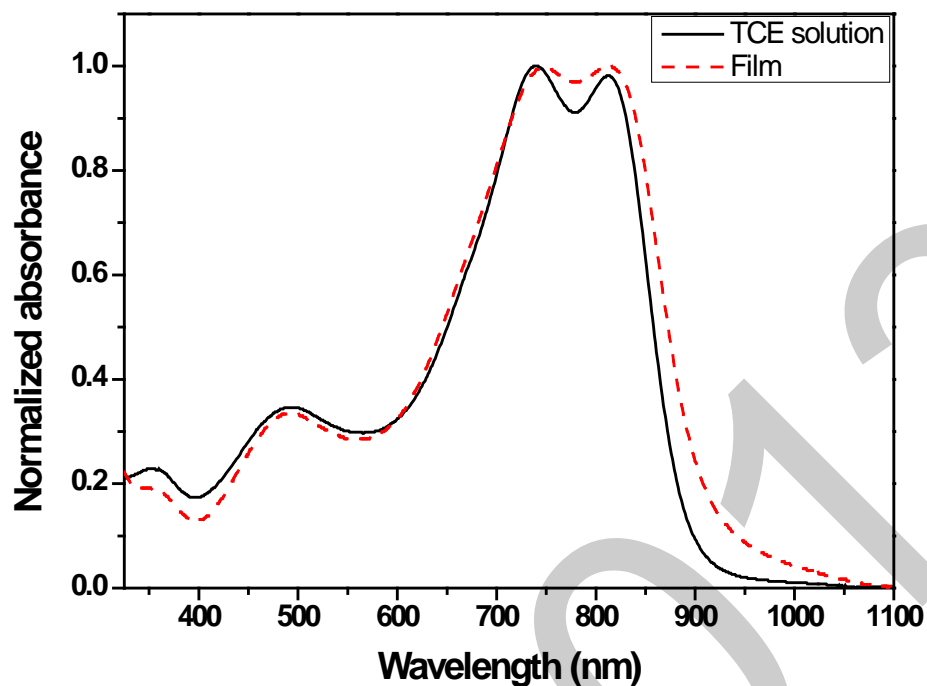


Figure 1. UV-vis-NIR absorption spectra of PIBDF-T in tetrachloroethane (TCE) and in thin film.

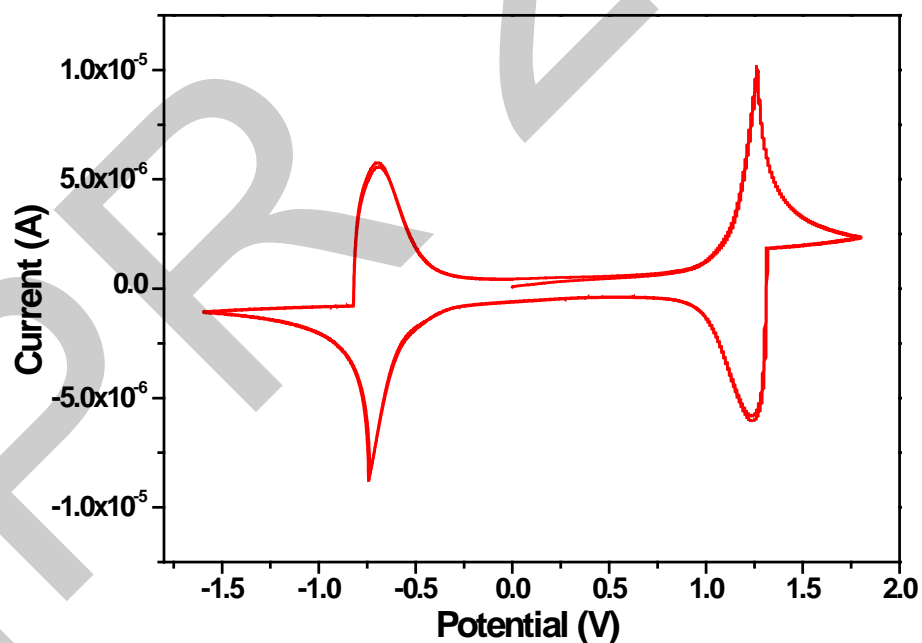


Figure 2. Cyclic voltammograms (two cycles) of a PIBDF-T thin film showing two oxidative and reductice cycles at a scan rate of 0.05 Vs^{-1} . The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile.

§ This work is published in *Chem. Commun.* **2013**, DOI: 10.1039/c3cc40531a.

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Novel stable (3E,7E)-3,7-bis(2-oxoindolin-3-ylidene)benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione based donor-acceptor polymer semiconductors for n-type organic thin film transistors

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IPR Symposium
May 8, 2013

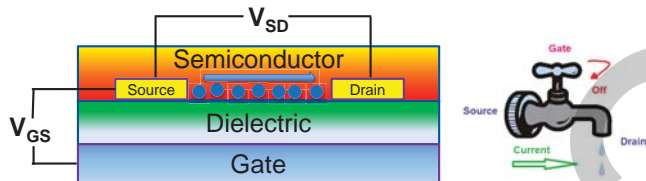
Introduction

- Three building blocks of printed electronics: organic thin film transistors (OTFT), organic light-emitting diode (OLED), and organic photovoltaic (OPV).
- Printed organic electronics: Electronic devices in which circuits (organic semiconductor) are developed with printing techniques.
- Why organic semiconductors? Flexible, light weight, mechanically robustness, low-cost, large-area production
- Challenge: low mobility

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1. Neuvo, Y., & Ylönen, S. (eds.), *Bit Bang – Rays to the Future*. Helsinki University of Technology (TKK), MIDE, Helsinki University Print, Helsinki, Finland, 63-102

Organic Thin Film Transistors

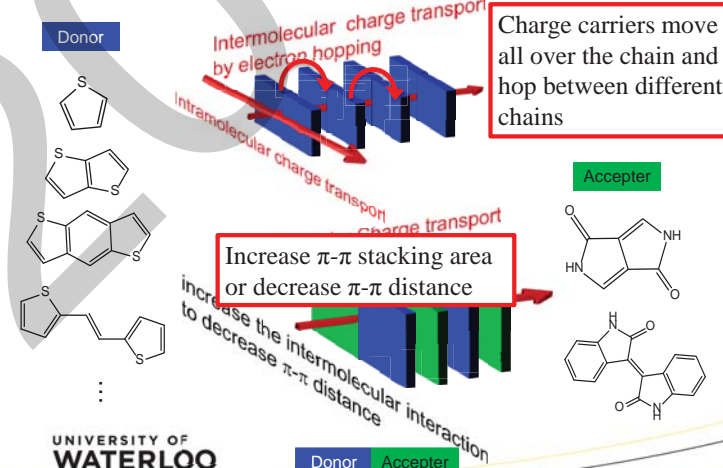


- Composed of source, drain and gate electrodes, a dielectric (insulating) layer, and a organic semiconducting layer.
- Act as "switches" that can turn current on and off based upon an applied voltage.
- Semiconductor:
 - n-type transport electrons (negative charge)
 - p-type transport holes (positive charge)
 - Ambipolar transport both electrons and holes.

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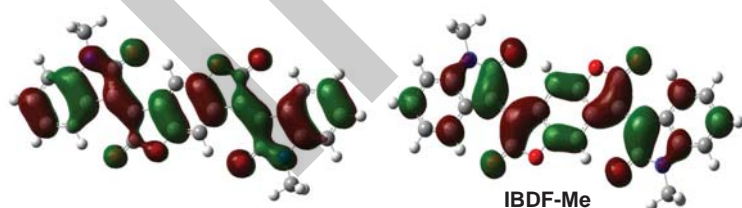
Polymer semiconductors



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3. Li, Y., Singh, S. and Sonar, P., *Adv. Mater.* 2010, 22, 4862; 4. Li, Y., Sonar, P., Singh, S., Zeng, W. and Seb, M., *Chem. Commun.* 2011, 2011, 5. Sonar, P. et al., *Energy Environ. Sci.* 2011, 4, 2011

New Electron Acceptor—IBDF

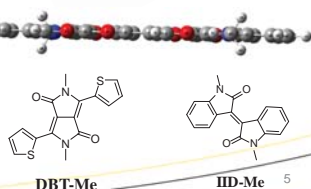


b:4,5-b'difuran-2,6(3H,7H)-dione (IBDF)

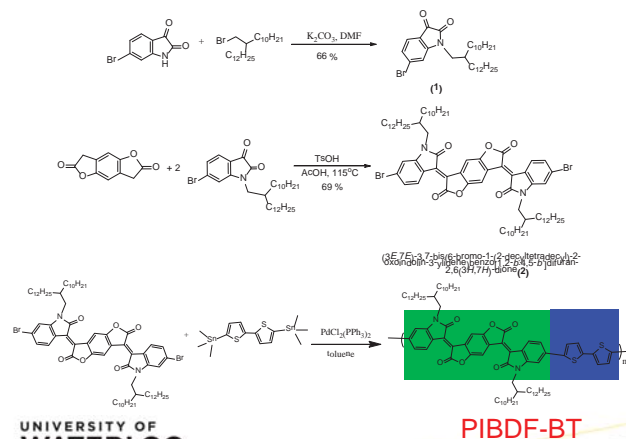
HOMO

LUMO

Predicted value	E_{HOMO} (eV)	E_{LUMO} (eV)
IBDF-Me	-5.97	-3.59
DBT-Me	-5.16	-2.75
IID-Me	-5.70	-2.76



Synthesis of IBDF monomer

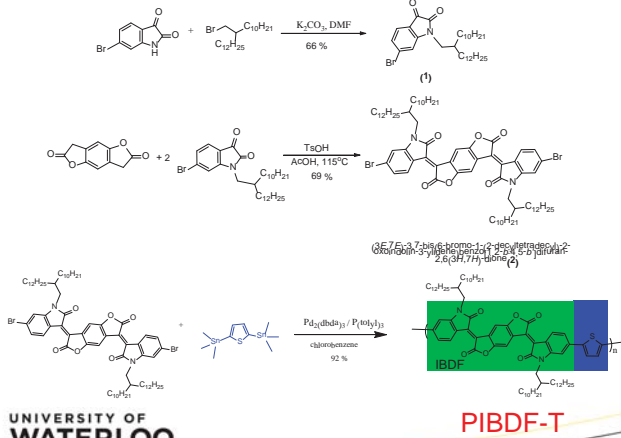


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PIBDF-BT

6. Wood, Colburn, Cox, and Garland, *J. Am. Chem. Soc.* 1944, 66, 1540; 7. Nesvadba, P., Jandke, L., *USP*

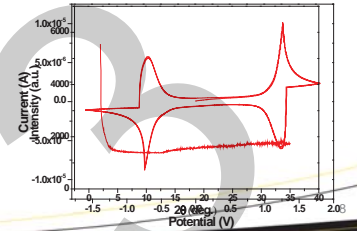
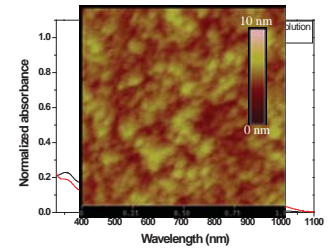
Synthesis of IBDF monomer



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Characterization of PIBDF-T

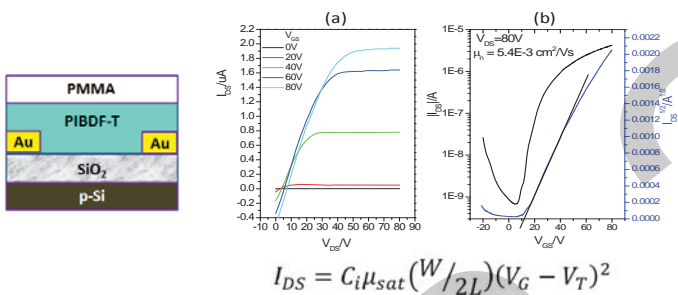
M_n	34,200
M_w	50,100
Decomposition temperature	385 °C
Optical band gap	1.36 eV
E_{HOMO}	-5.79 eV
E_{LUMO}	-4.43 eV



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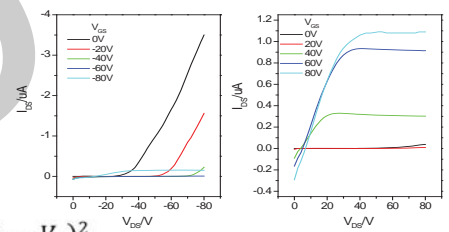
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Device Performance of PIBDF-T



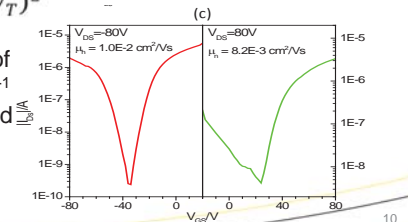
Annealing temperature	Charge transport	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	I_{on}/I_{off}
100 °C	n-type	$\mu_n = 1.5\text{-}2.2 \times 10^{-3}$	$\sim 10^3$
150 °C	n-type	$\mu_n = 2.4\text{-}3.0 \times 10^{-3}$	$\sim 10^3$
200 °C	n-type	$\mu_n = 4.2\text{-}5.4 \times 10^{-3}$	$\sim 10^3\text{-}10^4$
250 °C	n-type	$\mu_n = 0.9\text{-}1.5 \times 10^{-3}$	$\sim 10^3$

Device Performance of PIBDF-T



$I_{DS} = C_i \mu_{sat} \left(\frac{W}{2L} \right) (V_G - V_T)^2$

The electron/hole mobilities of $8.2 \times 10^{-3}/1.0 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the polymer films annealed at 150 °C



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Device Performance of PIBDF-T

Encapsulation with ~500 nm PMMA	Annealing temperature	Charge transport	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	I_{on}/I_{off}
Yes	100 °C	n-type	$\mu_n = 1.5\text{-}2.2 \times 10^{-3}$	$\sim 10^3$
	150 °C	n-type	$\mu_n = 2.4\text{-}3.0 \times 10^{-3}$	$\sim 10^3$
	200 °C	n-type	$\mu_n = 4.2\text{-}5.4 \times 10^{-3}$	$\sim 10^3\text{-}10^4$
	250 °C	n-type	$\mu_n = 0.9\text{-}1.5 \times 10^{-3}$	$\sim 10^3$
No	150 °C	ambipolar	$\mu_n = 5.5\text{-}8.2 \times 10^{-3}$	$\sim 10^3$
			$\mu_p = 0.8\text{-}1.0 \times 10^{-2}$	$\sim 10^4$
	200 °C	ambipolar	$\mu_n = 8.4\text{-}9.0 \times 10^{-3}$	$\sim 10^3$
			$\mu_p = 4.7\text{-}4.9 \times 10^{-3}$	$\sim 10^2\text{-}10^3$
	250 °C	ambipolar	$\mu_n = 1.2\text{-}1.4 \times 10^{-3}$	$\sim 10^4$
			$\mu_p = 2.5\text{-}3.3 \times 10^{-3}$	$\sim 10^6$

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Summary

- The copolymer of IBDF and thiophene, **PIBDF-T**, showed good solution processability and exhibited characteristic n-type semiconductor performance in encapsulated OTFTs with electron mobility as high as $5.4 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ even though the polymer films are rather disordered. The non-encapsulated devices exhibited ambipolar charge transport behaviour with balanced electron/hole mobilities up to $8.2 \times 10^{-3}/1.0 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.
- Our preliminary results demonstrated that IBDF is potentially a promising electron acceptor building block for polymer semiconductors.

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