

Improved Charge Transport and Absorption Coefficient in Indacenodithieno[3,2-b]thiophene-based Ladder-Type Polymer Leading to Highly Efficient Polymer Solar Cells

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The development of donor-acceptor (D-A) based bulk-heterojunction (BHJ) polymer solar cells (PSCs) has made significant progress in the past decade. In particular, power conversion efficiency (PCE) of 8–9% in a single junction device has been demonstrated.^[1–5] Among various materials developed for BHJ devices, the multifused-ring conjugated polymers are particularly interesting due to their superior optical and electrical properties.^[6–20] The highly fused aromatic/heteroaromatic units enhance effective conjugation of the polymer backbone to facilitate electron delocalization. Moreover, the covalently rigidified adjacent units could prevent rotational disorder to reduce reorganization energy, which results in enhanced charge carrier mobilities.^[21–23] To date, numerous fused-ring, ladder type donor systems have been developed since the first report of thiophene-phenylene-thiophene (TPT) (also called indacenodithiophene (IDT)), based polymers by Ko et al.^[6–8]

The PSC performance of one of the IDT based polymers, PIDT-BT, has been shown to reach 6.4% after careful solvent annealing.^[24] This has inspired vigorous efforts to modify the IDT backbone, such as changing the bridging atoms or side-chains to improve polymer packing for better charge transport or light absorption.^[9,12,25–27] Larger fused-rings by extending the IDT backbone,^[10,11,16,18,19,28–30] increasing the number of aromatic rings, or changing the sequence of tethered aromatic units on the backbone all have been tried and generated a wide variety of multiple fused-ring systems.^[17,20] For example, Cheng et al. have reported a novel seven-ring system by fusing a fluorene unit and two thiophene units together. Through proper side-chain modifications, the PCE of devices made from these

polymers can be significantly increased from 2.8% to ≈7% with an open-circuit voltage (V_{oc}) of 0.83 V.^[16,19] These findings proved that the extension of the ladder-type donor unit is a promising approach of improving the light-conversion efficiency of polymers.

To take advantage of desirable properties generated from these ladder-type polymers, we have focused on derivatizing IDT-based polymers.^[31–38] By copolymerizing IDT with different acceptor units, we could fine-tune optoelectronic properties and energy levels of the targeted polymers to achieve high efficiency. For example, the PIDT-PhanQ based device (Figure S1, Supporting Information) has shown a high PCE of 6.2% without using any additives or post-solvent/thermal annealing.^[36] Due to its amorphous nature, the morphology of PIDT-PhanQ/fullerene derivative based BHJ blends is quite insensitive to the processing conditions. This is an important characteristic that may help simplify the roll-to-roll processing of PSCs, hence, it is worthwhile to explore their structure/property relationships to further improve performance.

From the literature, the introduction of fluorine (F) substituents on D-A conjugated polymers has minor effect on their optical properties but affects significantly their energy levels due to its strong electronegativity. This has led to decreased HOMO and LUMO energy levels to result in higher V_{oc} values.^[39–41] From our systematic study of F-substituted PIDT-benzothiadiazole (BT) polymers, it was shown that the introduction of two F atoms to a BT unit lowered the HOMO energy level without really affecting its absorption characteristics (Figure S1, Supporting Information).^[34] By utilizing a fullerene surfactant modified silver electrode, the performance of the PIDT-DFBT could reach ≈6% with a large V_{oc} of 0.97 V. However, the short-circuit current density (J_{sc}) and fill factor (FF) of PIDT-DFBT are still quite low compared to those of several state-of-the-art polymers and there is ample room for further improvement.

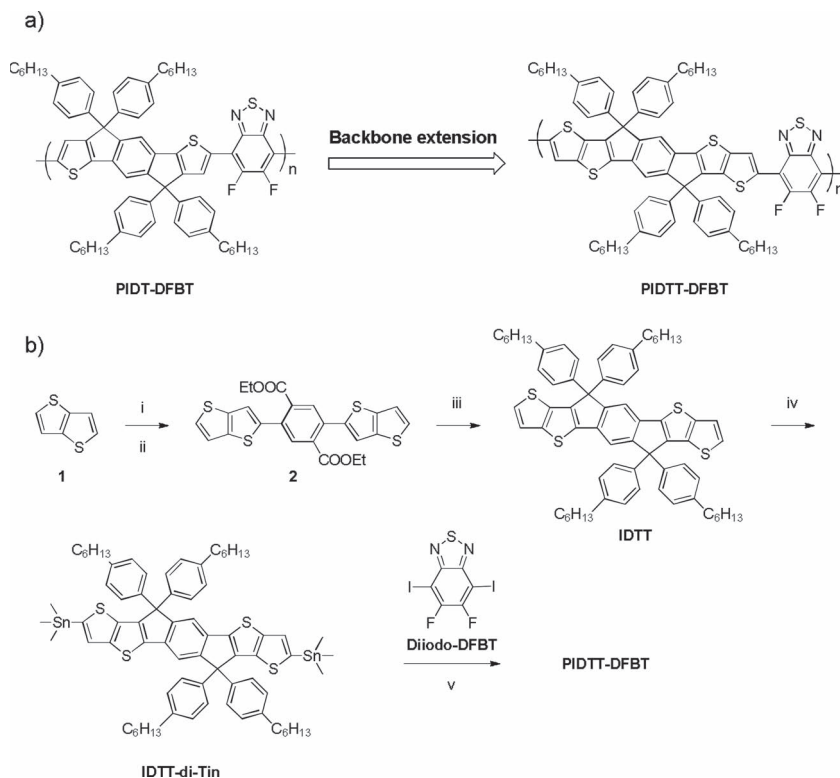
In order to enhance charge mobility and performance of the fused-ring polymers, the IDT unit is further extended by incorporating two thieno[3,2-b]thiophene (TT) units. TT has been widely utilized to improve charge mobility of polymers^[11,42–44] because it can simultaneously extend the effective conjugation length of a polymer and improve its coplanarity. The extended IDT system with two outward TT units replacing the thiophene moieties on IDT was designed to form a novel seven-ring indacenodithieno[3,2-b]thiophene (IDTT) donor unit, as shown in **Scheme 1**. It was then copolymerized with DFBT to form PIDTT-DFBT. The chemical structures of PIDT-DFBT and PIDTT-DFBT and the synthetic route used to make IDTT

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DOI: 10.1002/adma.201203246



Scheme 1. a) Chemical structures of PIDT-DFBT and PIDTT-DFBT. b) Synthetic route of the PIDTT-DFBT polymer: (i) BuLi, -78°C then ZnCl_2 , THF, 0°C ; (ii) 2,5-dibromoterephthalate, $\text{Pd}(\text{PPh}_3)_4$, THF, reflux; (iii) 4-hexyl-1-bromobenzene, BuLi, THF then AcOH, H_2SO_4 , reflux; (iv) BuLi, -78°C then Me_3SnCl , RT; (v) $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-tol})_3$, toluene, reflux.

are depicted in Scheme 1.^[45] The detailed synthetic conditions and relevant physical properties of PIDT-DFBT can be found in our previous work,^[34] and the syntheses of PIDTT-DFBT are described in the Supporting Information.

The Pd-catalyzed coupling between diethyl 2,5-dibromoterephthalate with 2-thienothiophenyl zinc chloride (generated in situ through transmetalation of 2-thienothiophenyl lithium with ZnCl_2) afforded the doubly coupled product **2** in 83% yield. After the double nucleophilic addition and acid-promoted intramolecular annulation, IDTT could be isolated in 65% yield. It was further lithiated and quenched with trimethyltin chloride to afford the IDTT-di-Tin. Finally, PIDTT-DFBT was obtained by copolymerizing IDTT-di-Tin with diiodo-DFBT.

The resulting polymer can be readily dissolved in chlorinated solvents, such as chlorobenzene (CB) and dichlorobenzene (DCB) but has a slightly poorer solubility in chloroform (CHCl_3). The number-average molecular weight (M_n) of PIDTT-DFBT was 24 kDa with a polydispersity index (PDI) of 2.58. No distinct thermal transitions could be detected between RT and 280°C by DSC measurements, similar to that observed for PIDT-DFBT, which indicates that PIDTT-DFBT possesses a similar amorphous nature.

The UV-vis absorption spectra of both polymers in DCB solution and in thin film are shown in Figure 1a,b. They possess quite similar absorption characteristics due to their proximate polymer backbone. However, the short wavelength peaks at $\approx 410\text{ nm}$ is red-shifted to 427 nm for PIDTT-DFBT due to

its more extended IDTT donor. The thin film absorption maxima (λ_{max}) of these two polymers are all around 650 nm and the optical bandgaps extracted from their absorption band edges are the same around 1.78 eV . The relatively high intensity of the longer wavelength absorption peaks of these two polymers indicates that strong intramolecular charge transfer (ICT) exists between the IDT/IDTT and DFBT units.

Interestingly, the absorption coefficients of PIDTT-DFBT in both solution and thin film are slightly higher than those of PIDT-DFBT (Figure 1a,b). Since the absorption coefficient of D-A conjugated polymer is dependent on the orbital overlaps between HOMO and LUMO wave functions,^[46,47] quantum-chemical calculations were conducted to probe detailed information about oscillator strength, optimized geometry, and wave-function distribution of these polymers. The calculated oscillator strengths are shown in Figure 1c. The higher oscillator strength calculated for IDTT-DFBT than IDT-DFBT confirms the experimentally observed higher absorption coefficient. Meanwhile, its dominant long-wavelength peak also shows strong ICT between IDTT and DFBT units. Figure 1d presents the adopted planar conformation with extremely small torsion angles of $<4.5^{\circ}$ for both polymers, showing very nice coplanarity of these ladder-type polymers.

The detailed torsion angles along the conjugated backbones in the optimized conformations are shown in Figure S2 and Table S1 in the Supporting Information.

The distribution of molecular orbital wave-function of two oligomers (shorter analog of these two polymers) are presented in Figure 2. For both oligomers, the HOMO wave functions are well delocalized along the donor and acceptor units while their LUMO wave functions are more localized at the acceptor parts. Notably, a more extended delocalization of the HOMO was observed for IDTT-DFBT compared to IDT-DFBT. This increased orbital overlap between HOMO and LUMO of the IDTT-DFBT system contributes to the enhanced absorption coefficient.^[47] This effect could be even more pronounced in their polymers.

The electrochemical study of these two polymers was conducted by using cyclic voltammetry (CV) to measure their energy levels; the corresponding redox curves are shown in Figure S3 (Supporting Information). The HOMO and LUMO energy levels for PIDT-DFBT and PIDTT-DFBT are -5.46 and -3.56 , and -5.30 and -3.50 eV , respectively. The up-shifted PIDTT-DFBT HOMO level is expected due to its more electron-rich TT units on the backbone. The estimated electrochemical bandgaps coincide well with the optical bandgaps measured for these polymers.

Bottom gate and top-contact field-effect transistors (FET) were also fabricated to evaluate the effect of structural modification of polymers on their charge mobility. The corresponding

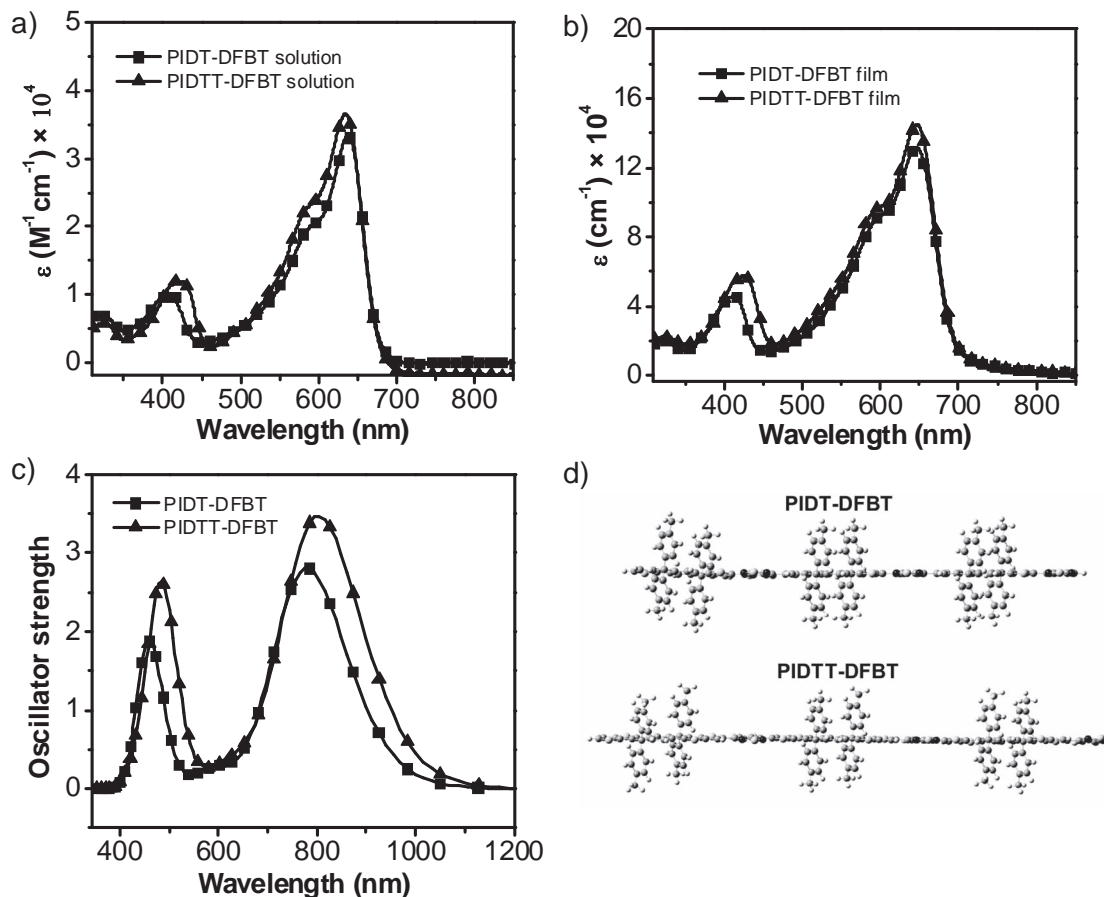


Figure 1. UV-vis spectra of PIDT-DFBT and PIDTT-DFBT: a) in dichlorobenzene solution and b) in a thin film. c) DFT-calculated oscillator strength of the analog trimer model of the studied polymers. d) Planar geometries of IDT-DFBT and IDTT-DFBT trimers (side view).

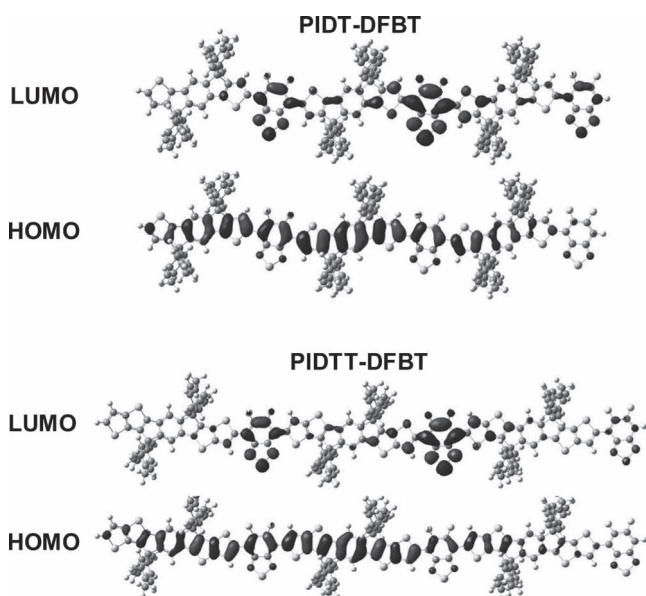


Figure 2. DFT-calculated HOMO and LUMO wave functions of the geometry optimized structures (B3LYP/6-31G*) of the analog trimer model of the studied polymers.

transfer curves are shown in Figure S4 (Supporting Information) and relevant parameters are summarized in Table 1. Both polymers clearly exhibit ambipolar behavior. The calculated saturation hole and electron mobilities ($\mu_{\text{sat,h}}$, $\mu_{\text{sat,e}}$) for PIDT-DFBT and PIDTT-DFBT are 2×10^{-3} and 8×10^{-3} , and 2×10^{-2} and $2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Both hole and electron mobilities of PIDTT-DFBT increase quite significantly compared to those obtained for PIDT-DFBT. This enhancement supports the design concept that the extension of the effective conjugation length and planarity improve both chain packing and charge transport. The high $\mu_{\text{sat,h}}$ and $\mu_{\text{sat,e}}$ of PIDTT-DFBT are important for achieving high efficiency PSCs.

The performance of PIDT-DFBT in a PSC was first investigated using a conventional device configuration with a similar ITO/PEDOT:PSS/polymer:PC₇₁BM (1:3)/Ca/Al device structure

Table 1. FET characteristics of PIDT-DFBT and PIDTT-DFBT.

Polymer	$\mu_{\text{sat,h}}$ [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	$I_{\text{on}}/I_{\text{off,h}}$	$\mu_{\text{sat,e}}$ [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]	$I_{\text{on}}/I_{\text{off,e}}$
PIDT-DFBT	$\approx 2 \times 10^{-3}$	2×10^3	$\approx 8 \times 10^{-3}$	$\approx 10^3$
PIDTT-DFBT	$\approx 2 \times 10^{-2}$	5×10^4	$\approx 2 \times 10^{-2}$	6×10^4

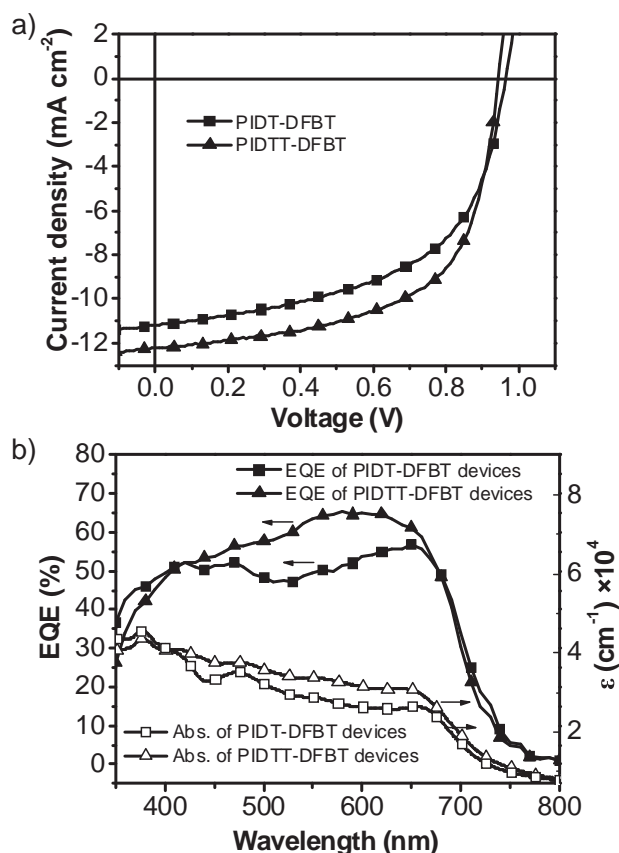


Figure 3. a) Characteristic J - V curves for the BHJ solar cells derived from PIDT-DFBT and PIDTT-DFBT. b) EQE and absorption spectra for the BHJ devices derived from PIDT-DFBT and PIDTT-DFBT.

to that reported previously.^[34] It showed a decent performance of 5.10% with a large V_{oc} of 0.92 V. The device performance could be improved to 5.97% by utilizing surfactant-modified Ag cathode to further increase V_{oc} to 0.97 V.^[38] This optimized device configuration is illustrated in Figure S5 (Supporting Information), where the device configuration consists of ITO/PEDOT:PSS/polymer:PC₇₁BM (1:3)/Bis-C₆₀/Ag. The detailed device fabrication is described in the Supporting Information.

Figure 3a shows the J - V curves of the devices measured under the 100 mW cm⁻² AM 1.5 illumination condition. The performance of these devices is summarized in Table 2. Due to enhanced charge mobility, the PIDTT-DFBT polymer is expected to show better device performance than PIDT-DFBT. Indeed, the PIDTT-DFBT device shows a much improved PCE of 7.03% with a V_{oc} of 0.95 V, a J_{sc} of 12.21 mA cm⁻², and a FF of 0.61. The increased J_{sc} and FF apparently are the results

of the slightly enhanced light-harvesting ability and charge mobility of PIDTT-DFBT than PIDT-DFBT.

To verify the improved J_{sc} , the external quantum efficiency (EQE) of polymer/PC₇₁BM devices were measured and is shown in Figure 3b. The J_{sc} values calculated from the EQE curves under the standard AM 1.5G conditions match well with those obtained from the J - V measurements. Figure 3b also shows the extinction spectra of polymer/PC₇₁BM blends. Similar to that observed for thin film absorption of polymers, the PIDTT-DFBT blend with PC₇₁BM exhibited slightly higher intensity than that from the blend of PIDT-DFBT/PC₇₁BM. The increased absorption coefficient coincides well with the increased EQE, indicating its contribution to the increased J_{sc} . In addition, a relatively smooth and featureless thin film morphology could be observed in the atomic force microscopy (AFM) images of these polymer blends (Figure S6, Supporting Information), which also indicates their amorphous nature.

Because charge mobility is crucial for achieving high efficiency devices, the one-order higher $\mu_{sat,h}$ of PIDTT-DFBT compared to PIDT-DFBT is another important reason that may contribute to the enhanced J_{sc} and FF. In addition to charge mobility measured by using the FET method, the space-charge-limited-current (SCLC) method was also conducted for the polymer/PC₇₁BM BHJ films. The detailed fabrication and analysis are described in the Supporting Information (Figure S7). The hole and electron mobilities ($\mu_{SCLC,h}$, $\mu_{SCLC,e}$) of PIDT-DFBT and PIDTT-DFBT are 4×10^{-5} and 3×10^{-4} , and 1×10^{-4} and 4×10^{-4} cm² V⁻¹ s⁻¹, respectively. These results also showed that PIDTT-DFBT has higher and more balanced charge mobility than PIDT-DFBT in the BHJ films. The only drawback is the slightly lower V_{oc} of PIDTT-DFBT than PIDT-DFBT due to up-shifted HOMO level mentioned above. Nevertheless, the performance of the PIDTT-DFBT device is among the best reported in multiring systems so far without using any additives or post-solvent/thermal treatments.^[39,40]

In conclusion, a novel seven-ring ladder-type donor (IDTT) was designed and synthesized by substituting the two outward thiophenes of IDT donor with two thieno[3,2-b]thiophenes. The copolymerization of IDTT with DFBT resulted in a polymer with longer effective conjugation and better planarity to improve charge mobility. Since the absorption coefficient of D-A conjugated polymers is dependent on the orbital overlaps between HOMO and LUMO wave functions, quantum-chemical calculations were conducted to provide detailed information about oscillator strength, optimized geometry, and wave-function distribution of these polymers. The PSC device derived from PIDTT-DFBT showed an improved PCE of 7.03% with a large V_{oc} of 0.95 V without using any additives or post-solvent/thermal annealing processes. This proves the effectiveness of using a multifused-ring donor to enhance the performance of PSCs.

Table 2. Photovoltaic characteristics of PIDT-DFBT and PIDTT-DFBT.

BHJ layer	V_{oc} [V]	J_{sc} [mA/cm ²]	FF	PCE [%]
PIDT-DFBT/PC ₇₁ BM	0.97	11.20	0.55	5.97
PIDTT-DFBT/PC ₇₁ BM	0.95	12.21	0.61	7.03

Experimental Section

Materials: All chemicals, unless otherwise specified, were purchased from Aldrich and used as received. Diiodo-DFBT was synthesized according to a previously reported procedure.^[39]

Synthesis of Monomers and Polymers: *Synthesis of Compound 2.* To a stirred solution of thieno[3,2-b]thiophene (421 mg, 3.0 mmol) in dry

THF (10 mL) was added dropwise to a 2.41 M solution of *n*-butyllithium in hexane (1.24 mL, 3.0 mmol) at -78°C under argon atmosphere. After being stirred for 30 min at -78°C , the resulting solution was warmed to -35°C and stirred for another 15 min. Then anhydrous zinc chloride (409 mg, 3.0 mmol) in dry THF (10 mL) was added to the mixture. The mixture was stirred for 1 h at 0°C and then the cooling bath was removed. Diethyl 2,5-dibromoterephthalate (456 mg, 1.2 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (69 mg, 0.06 mmol) were added directly. The reaction mixture was refluxed overnight. Upon completion, the reaction mixture was filtered over celite, extracted with ethyl acetate and then dried over anhydrous Na_2SO_4 . The product was purified by silica gel chromatography to afford a light yellow solid (496 mg, 83%). ^1H NMR (300 MHz, CDCl_3 , δ): 7.89 (s, 2H), 7.40 (d, $J = 5.4$ Hz, 2H), 7.29 (s, 2H), 7.28 (d, $J = 5.4$ Hz, 2H), 4.25 (q, $J = 7.2$ Hz, 4H), 1.13 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 167.4, 142.0, 139.9, 139.3, 134.1, 133.8, 132.1, 127.4, 119.4, 119.3, 61.8, 13.8. HRMS (MALDI) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{24}\text{H}_{18}\text{O}_4\text{S}_4\text{Na}$, 520.9980; found, 520.9993.

Synthesis of IDTT: To a solution of 4-hexyl-1-bromobenzene (930 mg, 3.9 mmol) in THF (10 mL) at -78°C was added *n*-BuLi (1.54 mL, 3.9 mmol, 2.5 M in hexane) and the mixture was kept at -78°C for 1 h. A solution of compound **2** (400 mg, 0.80 mmol) in THF (10 mL) was then added slowly. After this addition, the mixture was stirred at room temperature overnight and then poured into water and extracted twice with ethyl acetate. The combined organic phase was dried over Na_2SO_4 . After removing the solvent, the crude product was charged into three-neck flask. Acetic acid (20 mL) and concentrated H_2SO_4 (0.4 mL) were added and the mixture was refluxed for 3 h. Then the mixture was poured into water and extracted with ethyl acetate. The resulting crude compound was purified by silica gel column using a mixture of hexane/DCM as the eluent to give a light yellow solid (530 mg, 65%). ^1H NMR (300 MHz, CDCl_3 , δ): 7.50 (s, 2H), 7.28 (d, $J = 5.1$ Hz, 2H), 7.25 (d, $J = 5.1$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 8H), 7.07 (d, $J = 8.4$ Hz, 8H), 2.55 (t, $J = 7.8$ Hz, 8H), 1.60–1.53 (m, 8H), 1.35–1.29 (m, 24H), 0.86 (t, $J = 6.3$ Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 153.2, 145.9, 143.2, 141.7, 141.6, 140.3, 136.1, 133.8, 128.4, 128.1, 126.3, 120.3, 116.9, 62.9, 35.6, 31.7, 31.2, 29.2, 22.6, 14.1. HRMS (MALDI) m/z : M^+ , calcd for $\text{C}_{68}\text{H}_{74}\text{S}_4$, 1018.4673; found, 1018.4695.

Synthesis of IDTT-di-Tin: To a solution of IDTT (187 mg, 0.18 mmol) in THF (10 mL) at -78°C was added *n*-BuLi (0.2 mL, 0.5 mmol, 2.5 M in hexane). After the addition, the mixture was kept at -78°C for 1 h and then warmed up to RT for another 30 min. After cooling back to -78°C again, trimethyltin chloride (0.55 mL, 0.55 mmol, 1 M in hexane) was added dropwise. The resulting mixture was stirred overnight at room temperature. It was then poured into water and extracted with hexane. After drying over Na_2SO_4 , the solvent was removed and ethanol was added. The precipitation was collected and dried as a solid (222 mg, 90%). ^1H NMR (300 MHz, CDCl_3 , δ): 7.46 (s, 2H), 7.30 (s, 2H), 7.19 (d, $J = 8.4$ Hz, 8H), 7.07 (d, $J = 8.4$ Hz, 8H), 2.55 (t, $J = 7.8$ Hz, 8H), 1.61–1.55 (m, 8H), 1.35–1.27 (m, 24H), 0.86 (t, $J = 6.3$ Hz, 12H), 0.37 (s, 18H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 153.0, 145.4, 143.7, 143.2, 141.5, 140.5, 140.3, 139.3, 136.2, 128.4, 128.1, 127.4, 116.8, 62.9, 35.6, 31.7, 31.2, 29.2, 22.6, 14.1, -8.1.

Polymerization of PIDTT-DFBT: IDT-di-Tin (378 mg, 0.28 mmol) and DFBT (113 mg, 0.27 mmol) were charged in a 50 mL three-neck flask under argon. After adding toluene (5 mL), the mixture was degassed by three freeze/pump/thaw cycles to remove O_2 . Then $\text{Pd}_2(\text{dba})_3$ (12.8 mg, 5 mol%) and $\text{P}(\text{o-tol})_3$ (34 mg, 0.11 mmol) were added and the mixture was degassed once more. Then the mixture was heated at 120°C for 3 days. After cooling to RT, the mixture was poured into methanol. The precipitate was collected and washed by Soxhlet extraction sequentially with acetone, hexane, and chloroform. The remained solid in the filter was collected and dried (319 mg, 96%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.67 (s, 2H), 7.56 (s, 2H), 7.26 (m, 8H), 7.13 (m, 8H), 2.57 (m, 8H), 1.55 (m, 8H), 1.30 (m, 24H), 0.85 (m, 12H). Molecular weight: $M_n = 24$ kDa, PDI = 2.58.

General Characterization Methods: UV-vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. The ^1H and ^{13}C NMR spectra were collected on a Bruker AV 300 and 500 spectrometer

operating at 300 and 125 MHz in deuterated chloroform solution with TMS as the reference, respectively. High-resolution mass spectroscopy (HRMS) measurements were performed on a Bruker Apex-Qe FT/ICR from the Medicinal Chemistry Department at University of Washington. Gel permeation chromatography (GPC) measurements were performed on GPC Model 120 (DRI, PLBV400HT) viscometer against polystyrene standards in chlorobenzene at 60°C . Thermal transitions were measured on a TA Instruments Q20-1066 differential scanning calorimeter with a heating rate of $10^{\circ}\text{C min}^{-1}$. Cyclic voltammetry of the polymer film was conducted in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate using a scan rate of 100 mV s^{-1} . ITO, Ag/AgCl and Pt mesh were used as the working electrode, reference electrode and counter electrode, respectively. AFM images using tapping mode were taken on a Veeco multimode AFM with a Nanoscope III controller.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Y.-X.X. and C.-C.C. contributed equally to this work. This work was supported by the AFOSR (FA9550-09-1-0426), the Office of Naval Research (N00014-11-1-0300), and AOARD (FA2386-11-1-4072). A. K.-Y. Jen thanks the Boeing-Johnson Foundation for the financial support. C.-C. Chueh thanks the National Science Council of Taiwan (NSC100-2917-I-564-031) for financial support. The authors thank Dr. Joshua Davies for his useful suggestions.

Received: August 7, 2012

Revised: August 27, 2012

Published online: September 24, 2012

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