Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2012, 22, 1504

www.rsc.org/materials

PAPER

Swapping field-effect transistor characteristics in polymeric diketopyrrolopyrrole semiconductors: debut of an electron dominant transporting polymer[†]

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Received 14th September 2011, Accepted 2nd November 2011 DOI: 10.1039/c1jm14549e

A fact-finding study on thiophenyl diketopyrrolopyrrole (**TDPP**)-containing polymers for electronically convertible transport characteristics in organic field effect transistors (OFETs) is presented. In the subject of this consideration, a **TDPP**-based polymer with bis-benzothiadiazole (**BisBT**) units that serve as powerful electron-deficient building blocks, namely **PDTDPP–BisBT**, is prepared in order to achieve an n-channel transistor. The resulting polymer shows n-channel dominant ambipolar OFET characteristics and its electron mobility $(1.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ is found to be one order of magnitude higher than the hole mobility. Besides, the **PDTDPP–BisBT** OFET performance is independent of film-deposition conditions due to its completely amorphous microstructure, supported by the atomic force microscopy (AFM) and X-ray diffraction (XRD) analyses. Herein, we report an intriguing discovery in sync with our previous studies that **TDPP**-based polymers can function as a p-type, n-type, or ambipolar organic semiconductor in accordance with the degree of electron affinity of the comonomers.

1. Introduction

Stimulated by the need for low-cost, flexible, and solution-processed electronics, complementary integrated circuits from both p- and n-channel organic field-effect transistors (OFETs) are widely viewed to be the linchpin of next generation electronic devices because of their low power consumption, easy patterning technique, and large noise margin.^{1,2} Considering a key prerequisite for inexpensive device assembly by spin-coating, casting, or printing, polymeric materials are obvious candidates for satisfactory OFETs and practicable logic circuits since they enable ink formulation with tuned rheological properties.^{3,4} As far as solution-processable polymeric semiconductors are concerned, impressive progress has been achieved in developing p-type conjugated polymers such as P3HT, F8T2, PBTTT, and PQT of which OFETs exhibit hole mobilities (μ_h) of $\cong 0.01-1$ cm² V⁻¹ s⁻¹ with good ambient stability.⁵⁻⁷ However, solutionprocessable n-type polymers remain largely elusive.⁸⁻¹¹ To the best of our knowledge, only few studies have been reported focusing on polymers based on naphthalene,¹²⁻¹⁴ and perylene diimide^{12,15,16} as well as the ladder-polymer BBL.¹⁷ In spite of much effort in synthesizing novel n-type polymers,^{18,19} the development of polymers having appreciable electron mobilities that are soluble in conventional organic solvents and air-stable under ambient conditions has met limited success.²⁰

To pioneer an innovative new material that validates favorable properties of charge carrier mobilities for either electrons or holes, an original diketopyrrolopyrrole (**DPP**)-based materialsdesign methodology is devised to evaluate structural modification options. Herein, we demonstrate a new family of readily processable n-type dominant polymers with an extended optical absorption toward the IR region, namely poly[3,6-dithien-2-yl-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione-5',5''diyl-*co*-4,4'-bis-(2,1,3-benzothiadiazole)-7,7'-diyl] (**PDTDPP– BisBT**), that integrates both **DPP** and bis-benzothiadiazole (**BisBT**) units as powerful electron-deficient building blocks (Fig. 1).

2. Experimental

2.1. Materials and instruments

All starting materials were purchased either from Aldrich or Acros and used without further purification. All solvents are of ACS grade unless otherwise noted. Anhydrous THF was

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[†] Electronic supplementary information (ESI) available: Cyclic voltammograms of **PDTDPP-TPA** and **PDTDPP-BT**, DFT calculations of the polymers consisting of two units, and spectral data for **PDTDPP-BisBT**. See DOI: 10.1039/c1jm14549e



Fig. 1 Molecular structure of PDTDPP–BisBT.

obtained by distillation from sodium/benzophenone prior to use. Anhydrous toluene was used as received. 3,6-Dithien-2-yl-2,5dihydropyrrolo[3,4-c]pyrrole-1,4-dione,21 2-decyltetradecylbromide,²² 3,6-dithien-2-yl-2,5-di(2-decyltetradecanyl)-pyrrolo [3,4-c]pyrrole-1,4-dione,²³ 7,7'-dibromo-4,4'-bis(2,1,3-benzothiadiazole)²⁴ were prepared according to established literature procedures. ¹H NMR and ¹³C NMR spectra were recorded on a VNMRS 600 (Varian, USA) spectrometer using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard and MALDI-MS spectra were obtained from Ultraflex III (Bruker, Germany). UV-Vis spectra were taken on a Cary 5000 (Varian USA) spectrophotometer. Number-average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with Agilent 1200 HPLC Chemstation using a series of monodisperse polystyrene as standards in THF (HPLC grade) at 308 K. Cyclic voltammetry (CV) measurements were performed on Solartron SI 1287 with a three-electrode cell in a 0.1 M tetra-n-butylammonium hexafluorophosphate $(n-Bu_4NPF_6)$ solution in acetonitrile at a scan rate of 50 mV s⁻¹ at room temperature under argon. A silver wire, a platinum wire and a platinum disk were used as the reference electrode, counter electrode and working electrode respectively. The Ag/Ag⁺ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard, whose oxidation potential is set at -4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO $(eV) = -(E_{(ox)}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$. The LUMO levels of polymers were obtained from the equation LUMO $(eV) = -(E_{(red)}^{onset} - E_{(ferrocene)}^{onset} + 4.8).$

Synthesis of 3,6-di(2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)thien-5-yl)-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1, 4-dione (1). To a solution of 3,6-dithien-2-yl-2,5-di(2-decyltetradecanyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (1 g, 1.0 mmol) and 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxoborane (0.42 g, 0.46 ml, 2.5 mmol) in THF (30 ml) under argon at -40 °C was slowly added LDA solution (1.28 ml, 2.5 mmol) for 5 minutes. The resulting mixture was stirred for 1 hour at 0 °C and then quenched with 200 ml of water. The compound was extracted in CHCl₃, washed, and dried over MgSO₄. The solvent was evaporated under reduced pressure. The crude product was washed with MeOH (200 ml) three times. Isolated yield = 1.0 g (79%) as a thick viscous dark purplish oil. ¹H NMR (CDCl₃, 600 MHz): δ ppm 8.91 (d, J = 3.17, 2H), 7.71 (d, J = 3.17, 2H), 4.05 (m, 4H), 1.91 (m, 2H), 1.36 (s, 24H), 1.27–1.20 (m, 80H), 0.87–0.86 (m, 12H). ¹³C NMR (CDCl₃, 150 MHz): δ ppm 161.71, 140.48, 137.62, 136.11, 135.63, 108.70, 84.55, 46.24, 37.77, 31.91, 31.27, 30.01, 29.80, 29.68, 29.66, 29.64, 29.62, 29.57, 29.35, 29.33, 26.32, 24.75, 22.67, 14.10. MALDI-TOF MS (*m*/*z*) 1225.68 (M⁺). Anal. Calcd for C₇₄H₁₂₆B₂N₂O₆S₂: C, 72.52; H, 10.36; N, 2.29. Found: C, 72.40; H, 10.59; N, 2.57.

Synthesis of poly[3.6-dithien-2-yl-2.5-di(2-decyltetradecanyl)pyrrolo[3,4-c]pyrrole-1,4-dione-5',5"-diyl-co-4,4'-bis-(2,1,3-benzothiadiazole)-7,7'-diyl] (PDTDPP-BisBT). A mixture of 1 (200 mg, 0.16 mmol), 7,7'-dibromo-4,4'-bis(2,1,3-benzothiadiazole) (69 mg, 0.16 mmol), and tris(dibenzylidenacetone)dipalladium(0) (10 mg, 0.011 mmol) was taken in a Schlenk flask. To this, tri(o-tolyl)phosphine (5 mg, 0.016 mmol) and K_3PO_4 (220 mg) in toluene (5 ml) with demineralized water (1 ml) were added and the reaction mixture was heated at 95 °C under vigorous stirring for 72 h. The crude product was poured into a mixture of methanol (300 ml) and water (100 ml). The resulting solid was filtered off and subjected to sequential Soxhlet extraction with methanol (1 d), acetone (1 d) and hexane (1 d) to remove low molecular weight fraction of the materials. The residue was extracted with chloroform to give dark purplish product after precipitating again from methanol and drying in vacuo. Isolated vield of polymer PDTDPP-BisBT = 100 mg (50%). GPC analysis $M_{\rm n} = 57\ 000\ {\rm kg\ mol^{-1}},\ M_{\rm w} = 199\ 500\ {\rm kg\ mol^{-1}},\ {\rm and}$ PDI = 3.5 (against PS standard, see ESI[†] for GPC curve). ¹H NMR (CDCl₃, 600 MHz) (see ESI[†] for full NMR spectroscopy).

2.2. OFET device preparation and measurement

All FETs were fabricated on heavily n-type doped silicon (Si) wafers with a 200 nm thick thermally grown SiO₂ layer. FETs were fabricated in the top contact geometry. The n-type doped Si substrate functioned as the gate electrode and the SiO₂ layer functioned as the gate dielectric. The semiconducting layer was spin-cast from solution at 2500 rpm. All solutions were prepared at 5 mg/ml concentration in chlorobenzene. Prior to deposition of semiconducting layer, the SiO₂ surface was modified with polypropylene-co-1-butene (PPcB) to remove hydroxyl group from the SiO₂ surface. After semiconducting layer deposition, the films were dried on a hot plate stabilized at 80 °C for 30 minutes. The semiconducting layer deposition was carried out in a controlled atmosphere glove box filled with N_2 . Source and drain electrodes were deposited by thermal evaporation using a shadow mask. The thickness of source and drain electrodes was 50 nm. Channel length (L) and channel width (W) were 50 μ m and 2.0 mm, respectively. Electrical characterization was performed under N₂ atmosphere using a Keithley semiconductor parametric analyzer (Keithley 4200). The electron mobility (μ) was determined using the following equation in the saturation regime:

$$I_{\rm ds} = (\mu W C_{\rm i}/2L)(V_{\rm gs} - V_{\rm T})^2,$$

where C_i is the capacitance per unit area of the SiO₂ dielectric ($C_i = 15 \text{ nF cm}^{-2}$) and V_T is the threshold voltage.

3. Results and discussion

3.1. Synthetic strategies and chemical characterization

The 3,6-(2-thiophenyl)-substituted diketopyrrolopyrrole (thiophenyl DPP) unit has a well-conjugated structure, which leads to strong π - π interaction,²⁵ and the lactam part makes the **DPP** unit exhibit a high electron-withdrawing effect, and hence the DPP segment possesses high electron affinity.²⁶ Although significant progress has been made for application of thiophenyl DPP-containing materials in both organic photovoltaic cells (OPVs) and OFETs, all OFETs reported in the literature based on these materials have shown either good p-channel properties or ambipolar transport characteristics.^{23,27-32} Besides, it has been recently reported that ambipolar transistors, integrated CMOSlike inverters, and ring oscillators with poly(diketopyrrolopyrrole-terthiophene) are used as semiconductors.³³ Thus, the thiophenyl DPP-based polymers without exception have been applied as donor layers in OPV devices.^{27,30,34} Independently, we found that thiophenyl DPP-based polymer, PDTDPP-TPA (see Fig. 2) bearing electron-rich triphenylamine (TPA) building blocks, exhibits high hole mobility.35 What is more, in our earlier study, is that the replacement of TPA group in PDTDPP-TPA by electron-deficient benzothiadiazole (BT) moiety resulted in an excellent ambipolar polymeric semiconductor PDTDPP-BT.23 From such observations, we have designed a copolymer PDTDPP-BisBT consisting of bis-benzothiadiazole (BisBT) and thiophenyl **DPP** segments to possess an extended π electron affinity system along the main chain, which would further strengthen electron charge carrier transport and be anticipated to afford n-channel OFETs.

The thiophenyl **DPP** as a starting compound was synthesized according to the literature procedure.²¹ To overcome the solubility issue, we chose long branched alkyl side chains, 2-decyl-tetradecyl groups to substitute **DPP** at the nitrogen atoms. And then, we treated the thiophenyl **DPP** containing two 2-decylte-tradecyl solubilizing groups with lithium diisopropylamine (LDA) solution at low temperature (-40 °C), followed by the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, to generate the corresponding diboronic ester **1** with

a yield of 79%. As shown in Scheme 1, the thiophenyl **DPP** units were incorporated into the polymer backbone by a 1 : 1 copolymerization with a 4,4'-bis(2,1,3-benzothiadiazole) comonomer,²⁴ affording **PDTDPP–BisBT**. The resulting polymer is readily soluble in all organic solvents tested at room temperature due to the long branched side chain substitutions. The number-average molecular weight (M_n) of **PDTDPP–BisBT** is 57 000 kg mol⁻¹ with a polydispersity index of 3.5, as determined by using GPC with a polystyrene standard calibration.

To access a good deal of information of the electronic structure of the polymer, the photophysical properties of **PDTDPP– BisBT** were investigated by UV-vis-NIR absorption spectroscopy in dilute chloroform and as spin-coated film on quartz substrate (Fig. 3). In solution, **PDTDPP–BisBT** shows an absorption band centered at 780 nm with a vibronic absorption shoulder at 865 nm which is associated with molecular rigidity imposed molecular connectivity in the solution measurement, indicating the rigid-rod nature of the polymer main backbone, as a result of the coplanar structure and strong polarity of the **DPP**



Scheme 1 Synthetic route to PDTDPP-BisBT. Reagents and conditions: (i) LDA, THF, -40 °C under Ar, 24 h, 79%; (ii) Pd₂(dba)₃/P-(o-Tol)₃, K₃PO₄, toluene/H₂O, 95 °C for 72 h, 50%.



Fig. 2 Chemical structures of thiophenyl DPP-based polymers.



Fig. 3 (a) UV-vis-NIR absorption spectra of **PDTDPP–BisBT** in dilute CHCl₃ solution and thin film on quartz plate.

units. The absorption maximum is larger than our earlier reported polymer **PDTDPP–TPA** ($\lambda_{max} = 500-700$ nm).³⁵ A rationale for the relatively wider optical bandgap of **PDTDPP–TPA** (1.65 eV) is the minimized coplanarity in the polymer backbone as a result of 3D propeller-like TPA units as well as the weakness of intramolecular charge transfer (ICT) compared to **PDTDPP–BisBT**.

The absorption spectrum of PDTDPP-BisBT in the film is almost identical to that in solution and no significant bathochromic shift is revealed. This observation is in contrast to most DPP-based polymers, in which there are strong red-shifts from the solutions to the films since they have the fused **DPP** ring units for coplanarity, aggregation, and reducing π -stacking.^{21,29,36} This is most likely attributed to the two bulky side chains impeding a planar conformation of the DPP segment. In addition, we cannot rule out that steric interaction between the adjacent BT units in the BisBT segment can produce twisting around their interring bonds, which probably leads to reduced π -conjugated electronic structure along the chain.³⁷ This assumption is supported by a previous report on the single crystal X-ray structure of a **BisBT** derivative that showed a nonplanar anti-conformation with strong twist angles of about 43-54° between the two BT units.²⁴ As a consequence of the severe torsion between the two BT units, despite the relatively stronger electron accepting character of the BisBT versus the BT, the optical bandgap of **PDTDPP-BisBT** is 1.27 eV, which is slightly higher than that of PDTDPP-BT (1.20 eV) containing single BT with the same set of DPP blocks.23

3.2. Electrochemical properties

Cyclic voltammetry (CV) was performed to determine the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels of the conjugated polymer. The CV curves were recorded referenced to an Ag/Ag⁺ (0.1 M of n-Bu₄NPF₆ in acetonitrile) electrode, which was calibrated by a ferrocene–ferrocenium (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level). As shown in Fig. 4a, **PDTDPP–BT** shows quasi-reversible oxidation/reduction processes. The corresponding LUMO energy is estimated at -3.77 eV from the onset reduction potential in cyclic voltammetry (CV). The LUMO value is noticeably deeper than those calculated in the



Fig. 4 (a) Cyclic voltammogram of **PDTDPP–BisBT** thin film on the Pt electrode in 0.1 M *n*-Bu₄NPF₆ acetonitrile solution at room temperature. (b) Energy level diagrams of thiophenyl **DPP** derivatives.

same manner for both **PDTDPP–TPA** $(-3.42 \text{ eV})^{35}$ and **PDTDPP–BT** $(-3.59 \text{ eV})^{23}$ while the HOMO energies of the three polymers reveal remarkable similarities within experimental error $(-5.07 \text{ eV} \text{ for$ **PDTDPP–TPA** $}, -5.07$ for **PDTDPP–BT**, and -5.04 for **PDTDPP–BisBT**), indicative of the identical thiophenyl **DPP** counterparts (see Fig. 4b). The discrepancy (0.01-0.27 eV) of the electrochemically and optically determined bandgaps could be due to the exciton binding energy of conjugated polymers, which can be 0.4–1.0 eV.^{38,39} Interestingly, the low-lying LUMO position is comparable to well-known n-type polymers containing rylene bisimides electronically conjugated along the backbone,^{12,14} approaching that of the polymer based on strongly electron-depleted naphthalene



Fig. 5 DFT-optimized geometries and charge-density isosurfaces for the HOMO and LUMO levels and the side views of thiophenyl **DPP**-based polymers.



Fig. 6 (a) Output and (b) transfer characteristics of PDTDPP–BisBT FET. The output transfer characteristics of PDTDPP–TPA (c) and PDTDPP– BT FETs (d) obtained from earlier works, respectively. Insets are chemical structures of thiophenyl DPP-based polymers and the schematic device.

diimide with the lowest LUMO of approximately -4.0 eV reported to date.^{13,16} The low-lying LUMO level for **PDTDPP–BisBT** is desirable to enable an electron-transporting semiconductor since the lower the LUMO energy, the lower the bias required to inject the carriers and the less susceptible are the electrons to trapping.¹⁶

3.3. DFT electronic structure calculation

To understand the position and energies of frontier orbitals for the conjugated polymers, density functional theory (DFT) calculations on their electronic states are performed using the Gaussian 03 package at the B3LYP/6-31G* (Fig. 5). Both **PDTDPP-TPA** and **PDTDPP-BT** data in this study are presented to help us better understand the changed electron-statedensity distributions of the HOMO and LUMO in the geometry optimized structures by changing comonomers in the thiophenyl **DPP**-based polymers. The alkyl chains in the polymers were replaced by methyl groups to reduce the time required for calculation.

The optimized geometry of PDTDPP-BT reveals a highly planar BT π core with negligible intramonomer torsion and both the PDTDPP-TPA and PDTDPP-BisBT are predicted to have large dihedral angles of the aromatic counterparts in the settlement of thiophenyl DPP units. As depicted on the top of Fig. 5a, the HOMO isosurface of PDTDPP-TPA is well delocalized along the conjugated chain whereas the LUMO is disconnected at TPA moiety, showing only p-type OFET reported in our previous study.35 Also, in the course of our earlier experiment for PDTDPP-BT, the charge delocalizations of both the HOMO and LUMO orbitals had been observed, resulting in an effective ambipolar behavior. In the case of PDTDPP-BisBT, to our surprise, the coefficients in the HOMO orbital are positioned only on the core **DTDPP** unit, but the effective coefficients in the LUMO are located on the entirely lateral axis π -system. Thereby, the nature of **PDTDPP–BisBT**



Fig. 7 Topographic AFM images of **PDTDPP–BisBT** film (a) at room temperature and (b) after annealing at 120 °C. (c) X-ray diffraction (XRD) patterns of **PDTDPP–BisBT** thin film.

OFETs is interesting considering the electron mobility achievable (*vide infra*).

3.4. OFET performance

PDTDPP-BisBT OFETs with top contact and a bottom gate were fabricated by spin-coating the polymer solution in the $SiO_2/n^{++}Si$ substrate covered by a polypropylene-co-1-butene (PPcB) layer. The PPcB layer was introduced as a passivation layer to remove the hydroxyl group which acts as trap sites of electrons (Fig. 6a). All fabrication and testing were performed in an inert nitrogen atmosphere. The PDTDPP-BisBT device reveals a bipolar feature with both p-type and n-type characteristics, such as a diode-like current increase at low gate bias with current saturation at high gate voltage in output curves (Fig. 6a) and V-shaped transfer curves with narrow off-state (Fig. 6b), which is similar to that of PDTDPP-BT with nearly balanced hole and electron mobilities.²³ In marked contrast, PDTDPP-BisBT predominately displays electron transport behavior. The saturated charge carrier mobility of PDTDPP-BisBT is calculated using the saturation current equation: $I_{ds} = (\mu W C_i/2L)(V_{gs} - V_T)^2$.⁴⁰ A linear fit is applied in the saturation region of the $I_{ds}^{1/2}$ versus V_{gs} curve of the polymer in order to calculate the mobility. An electron mobility (μ_e) as high as 1.3×10^{-3} cm² V⁻¹ s⁻¹ and hole mobility as high as $6.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are estimated for OFETs produced from PDTDPP-BisBT. Note that the electron mobility value is about one order of magnitude higher than the hole mobility. Apparently, this result is in accordance with the fact that **BisBT** has better electron transport ability than BT unit, which is in good agreement with both the aforementioned DFT study and the electrochemical behavior.

3.5. Film surface microstructure

For OFET based on **PDTDPP–BisBT**, the deviation from coplanarity caused by the interring bond between the two BT units can account for the relatively reduced performance in comparison with **PDTDPP–BT**. Both as-spun and annealed **PDTDPP–BisBT** film microstructures assessed by atomic force microscopy (AFM) and X-ray diffractions (XRD) studies (Fig. 7a–c), as evidenced by the absence of order diffraction peaks as well as detectable fibrillar structures, do not reveal the distinctive crystalline features associated with other **DPP**-based polycrystalline thin films.^{28,29} This is due to the combination of the strong twist between consecutive BT groups and the bulky branched side chains on the **DPP**. Therefore, one can conclude that **PDTDPP–BisBT** has poorly defined, randomly ordered lamellar structure, implying an amorphous π -conjugated

material with achievable reproducibility in the OFETs. An important point to pinpoint here is that thiophenyl **DPP**-containing polymers can function as a p-type, n-type, or ambipolar semiconductor depending on the counterpart comonomers.

4. Conclusions

In summary, we have demonstrated an approach to n-channel transistor development, where our previous results can guide materials design from initial conception to refinement of the final semiconductor structure. A narrow bandgap copolymer PDTDPP-BisBT comprised of a strong acceptor, BisBT, which is relatively stronger than BT, and thiophenyl DPP moieties is synthesized. The new polymer exhibits electron dominant ambipolar characteristics, resulting in charge-carrier mobility of up to 1.3×10^{-3} cm² V⁻¹ s⁻¹ for electrons, which is about one order of magnitude higher than that for holes. While the behavior of many high-performance semiconductors is sensitive to deposition conditions, PDTDPP-BisBT polymer film exhibits OFET performance predominately independent of fabrication conditions because of the amorphous morphology in the solid state as determined by AFM and XRD, evidenced by no scattering patterns and non-fibrillar structural features in both asspun and annealed films. This study together with our previous courses indicate that thiophenyl DPP-based polymers can operate on either p-type, n-type, or ambipolar semiconductor subjecting to tune the counterpart comonomers. As a result, this work can serve as a beacon to further improve mobility of thiophenyl DPP derivatives for either p-type, n-type, or ambipolar OFETs. Besides, we believe that this discovery has answered questions about effective electron transport capabilities of polymeric semiconductors. A preliminary investigation on allpolymers solar cells with PDTDPP-TPA as an electron donor and PDTDPP-BisBT as an electron acceptor is in progress.

Acknowledgements

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0002494) and the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (2010-0019408), (2010-0026916), (2009-0093818), and (2011-0009148). The first two authors contributed equally to this work.

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