

A high mobility conjugated polymer based on dithienothiophene and diketopyrrolopyrrole for organic photovoltaics†

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Received 18th January 2012, Accepted 13th February 2012

DOI: 10.1039/c2ee21149a

A new low bandgap conjugated polymer (PDTTDP) comprising dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) and diketopyrrolo[3,4-*c*]pyrrole (DPP) showed an outstanding hole mobility of 0.60 cm² V⁻¹ s⁻¹ in organic field effect transistors without post-treatment, and a promising power conversion efficiency of 6.05% with PC₇₁BM in organic photovoltaics.

Semiconducting conjugated polymers (SCPs) have attracted great interest because of their potential applications to electronic devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaics (OPVs).¹ They have particularly several advantages such as solution processability, light weight, and flexibility over inorganic and small-molecule semi-conducting materials. Although remarkable advances in hole mobility of SCPs have been achieved,² their hole mobilities are not satisfactory yet as compared to inorganics and small organic molecules. To increase the mobility of SCPs, fused aromatic ring moieties (*e.g.*, π -extended heteroarenes: thieno[3,2-*b*]thiophene,³ benzo[1,2-*b*:4,5-*b'*]dithiophene,⁴ naphtho[1,2-*b*:5,6-*b'*]dithiophene,⁵ and indaceno[1,2-*b*:5,6-*b'*]dithiophene^{6a}) have been introduced into the conjugated polymer backbone. Since the π -extended heteroarene structure has

highly planar nature and also affords strong π - π interaction with a large overlapping area between polymer chains, charge carriers are expected to transport effectively not only along the polymer chain but also through intermolecular hopping in the π - π direction.^{6b}

The introduction of the electron donor-acceptor (D-A) structure into a polymer backbone is another promising approach to improve the charge carrier mobility, because the D-A structure in SCPs induces intermolecular interaction, leading to an increased molecular ordering through the self-assembly of rigid backbones of SCPs.⁷ It has recently been reported that SCPs based on the D-A structure exhibited the hole mobility over 0.1 cm² V⁻¹ s⁻¹.⁸ The SCPs with a D-A structure have also been very promising active materials for OPVs, not only because the energy levels can be easily tuned by a proper combination of D and A units, but also because they exhibit low bandgap.⁹

Recently, diketopyrrolo[3,4-*c*]pyrrole (DPP) has emerged as an important building block of active layer materials for the optoelectronic applications including both OFETs and OPVs. Particularly, SCPs based on DPP exhibited high hole mobilities up to 1.0 cm² V⁻¹ s⁻¹ in OFETs¹⁰ and promising power conversion efficiencies (PCEs) of 4.5–5.5% in OPVs¹¹ when DPP is copolymerized with electron-rich monomers such as thiophene, naphthalene and benzene, and very recently 6.5% PCE was achieved by SCPs based on furan-attached DPP.^{11d}

Meanwhile dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) has also received considerable attention as an electron-donating unit for synthesis of SCPs.^{12a-d} Due to highly extended heteroarene structure of DTT, DTT-based semi-conductors exhibited high crystallinity, charge carrier mobility and excellent environmental stability.^{12e,f} However, high performance has not been achieved in OFETs and OPVs, although recent reports showed the possibility to use DTT as

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ee21149a

Broader context

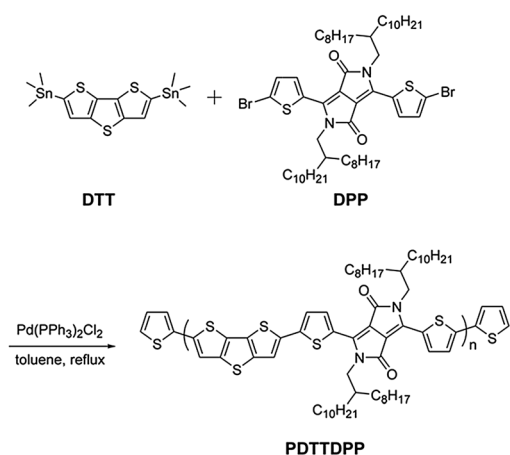
The semiconducting conjugated polymers (SCPs) based on a donor-acceptor structure are an emerging class of materials for high performance organic electronics such as organic field effect transistors (OFETs) and organic photovoltaics (OPVs). The incorporation of highly fused aromatic building block in the polymer backbone is the most powerful strategy to gain not only high mobility but also low band gap of the SCPs. A novel SCP, PDTTDP, which is composed of DPP and highly fused DTT, has shown high mobility in OFETs and a promising power conversion efficiency in OPVs. This work has also demonstrated that the use of optimum solvent mixture is a key for the formation of an ideal morphology of the active layer and thus achieving the best performance in bulk heterojunction OPVs.

a building block for synthesis of SCPs.¹³ Li *et al.*^{14a} have recently reported the synthesis of a SCP, PDTT–T–DPP, composed of DTT, thiophene, and DPP. However, the hole mobility ($8.7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) of the polymer was much lower than expected, although it showed a PCE over 5%.

In this communication, we report synthesis of a novel low bandgap SCP, PDTTDPP, which has a D–A structure with dithieno[3,2-*b*:2',3'-*d'*]thiophene (DTT) as an electron donating unit and DPP as an electron accepting unit, and its application to OFET and OPV. The PDTTDPP synthesized in this study showed a high hole mobility of $0.60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in OFETs and a promising PCE of 6.05% in OPVs with PC₇₁BM without post-treatment. It should be noted here that during preparation of this manuscript, Patil *et al.*^{14b} reported the synthesis of PDTTDPP and its OPV application. However, the molecular weight of their polymer was 5000 g mol^{-1} and the PCE of their polymer was less than 1%.

The PDTTDPP was synthesized *via* the Stille coupling reaction of DTT and DPP in anhydrous toluene with a catalytic amount of Pd(PPh₃)₂Cl₂, as shown in Scheme 1. After Soxhlet extraction and precipitation, PDTTDPP was obtained as a dark purple solid with the number average molecular weight of $101\,000 \text{ g mol}^{-1}$ and the polydispersity of 5.20. Details of synthesis of monomers, polymerization, and their characterizations are given in the ESI†. PDTTDPP is very soluble in common organic solvents such as tetrahydrofuran, chloroform (CF), toluene, chlorobenzene (CB), and *o*-dichlorobenzene (DCB). The UV-Vis absorption spectrum of PDTTDPP in CF solution shows the maximum absorption (λ_{max}) at 802 nm and the absorption onset (λ_{onset}) at 1015 nm, while the thin film spectrum exhibits slightly extended λ_{onset} at 1055 nm, as shown in Fig. 1. When the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of PDTTDPP film were measured by cyclic voltammetry, as shown in Fig. 1b, the HOMO and LUMO levels of PDTTDPP were -5.19 eV and -3.80 eV , respectively. Thus the electrochemical bandgap ($E_{\text{g,elec}}$) was 1.39 eV , which agrees well with the optical bandgap ($E_{\text{g,opt}}$) of 1.22 eV . The LUMO level difference (0.3 eV) between PDTTDPP (-3.80 eV) and PCBM (-4.10 eV) is sufficient for charge separation at the interface between the donor and the acceptor.^{15,16}

The crystal structure of the PDTTDPP thin film was studied by the grazing incidence wide angle X-ray scattering (GIWAXS). To examine the effect of annealing temperature on the molecular



Scheme 1 Synthetic route to PDTTDPP.

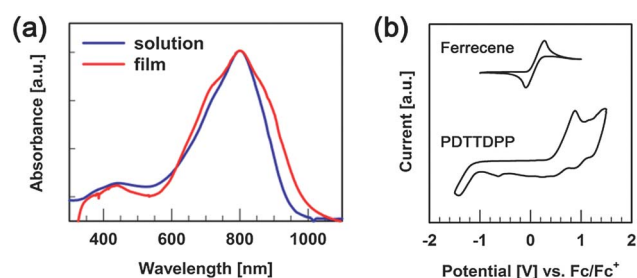


Fig. 1 (a) UV-Vis absorption spectra in chloroform (blue) and solid film (red) of PDTTDPP, and (b) cyclic voltammograms of ferrocene and PDTTDPP.

packing, PDTTDPP thin films were thermally annealed at $150 \text{ }^\circ\text{C}$ and $250 \text{ }^\circ\text{C}$. The GIWAXS pattern of the as-cast PDTTDPP thin film showed an intense but broad diffraction peak at $q_z = 0.31 \text{ \AA}^{-1}$, corresponding to the (100) reflection of the polymer crystal with an interlayer spacing of 20.3 \AA , as shown in Fig. 2. When the PDTTDPP thin film was annealed at $150 \text{ }^\circ\text{C}$ for 1 h, the intensity of (100) reflection was slightly increased and the (200) reflection peak was more distinctly grown, indicating the improvement of edge-on orientation. When the annealing temperature was further increased up to $250 \text{ }^\circ\text{C}$, the (300) and (400) reflection peaks became more discernible. The interchain distance was not significantly changed with the annealing temperature, because the peak positions of (100), (200) and (300) reflections remain unchanged, although the high temperature annealing enhanced the crystallinity of PDTTDPP. Furthermore, the high crystallinity of the as-spun PDTTDPP thin film and its relatively low sensitivity to annealing temperature indicate that the polymer chains readily form a layered structure with edge-on

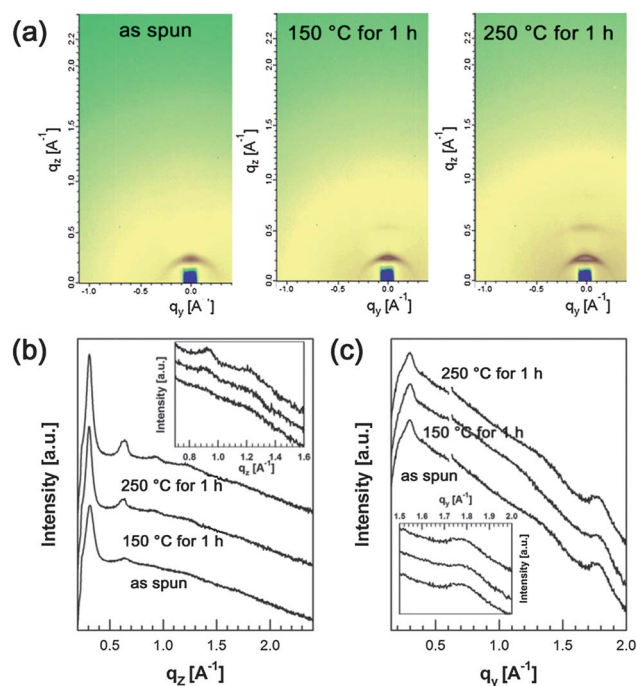


Fig. 2 2-D GIWAXS pattern images (a), out-of-plane (b) and in-plane (c) line cuts of the GIWAXS pattern of PDTTDPP thin films with different annealing temperatures. The insets of (b) and (c) show the scattering peaks more distinctly.

stacking on the substrate as the solvent evaporates, owing to the aforementioned strong intermolecular π - π stacking and intermolecular D-A interaction.

Since the GIWAXS reveals that the edge-on packing of PDTTDPP along the (100) axis normal to the film surface is predominant, this molecular orientation facilitates the charge carrier transport through the direction parallel to the dielectric layer in OFETs.

For measurement of the hole carrier mobility of PDTTDPP, OFETs with the configuration of bottom-gate and top-contact device ($W = 3000 \mu\text{m}$, $L = 100 \mu\text{m}$, Au electrode) were fabricated using heavily *n*-doped conductive silicon wafer with a layer of 250 nm SiO_2 . The PDTTDPP film with 30 nm thickness was spin coated from CB solution and then inverse-transferred to the octadecyltrichlorosilane-treated SiO_2 surface. The hole carrier mobility was evaluated from the transfer curve of source-drain current vs. gate voltage (I_{DS} vs. V_{G}) in a well-resolved saturation regime, as shown in Fig. 3.^{3b,10b,c} The OFETs made of as-spun PDTTDPP exhibited a typical behavior of a p-channel transistor with an average hole carrier mobility of $0.60 \pm 0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (the highest value = $0.68 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $I_{\text{on}}/I_{\text{off}} \approx 10^5$ to 10^6 , $V_{\text{th}} = -1 \text{ V}$) which is one of the highest hole mobilities of as-spun SCPs. When the sample was thermally annealed at 150 and 250 °C for 1 h, the hole mobility was slightly increased up to 0.70 and 0.75 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Particularly, SCPs processed without post-treatment (thermal annealing) have advantages because they do not require a time-consuming step for device fabrication, and furthermore a flexible plastic material, which allows roll-to-roll mass production, can be used as the substrate of device.¹⁷

High mobility of SCPs provides a significant benefit for high efficiency bulk heterojunction OPVs when the SCPs are used as electron donor materials, because electron mobility is usually higher than hole mobility in most of the BHJ solar cells, which may cause low fill factor.¹⁸ The photovoltaic properties of PDTTDPP were measured in a device configuration of ITO/PEDOT:PSS/PDTTDPP:PC₇₁BM/LiF/Al. The devices were optimized by varying the solvent (CF, DCB, diiodooctane (DIO)) and the blend ratio of PDTTDPP to PC₇₁BM (see Fig. 4 and Table 1). When CF was used as a solvent, photovoltaic devices showed very low PCEs less than 1% (see Fig. S7 and Table S1†). However, when the blend with 1 : 1.5 ratio of PDTTDPP to PC₇₁BM was spin-coated from a mixed solvent of CF and DCB (4 : 1 v/v), the PCE over 4% was achieved. This is because DCB has higher boiling point than CF, which allows polymer chains more time to self-assemble and to phase separate from PC₇₁BM. To further optimize the performance of OPVs, a small amount of DIO was added into the solution of PDTTDPP and PC₇₁BM, because it has been known that DIO promotes phase separation of polymer from PCBM in the bulk heterojunction active

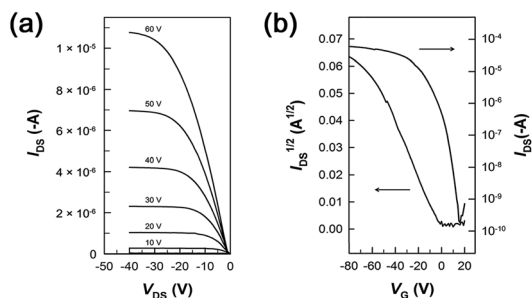


Fig. 3 Output (a) and transfer (b) characteristics of OFETs based on a PDTTDPP thin film.

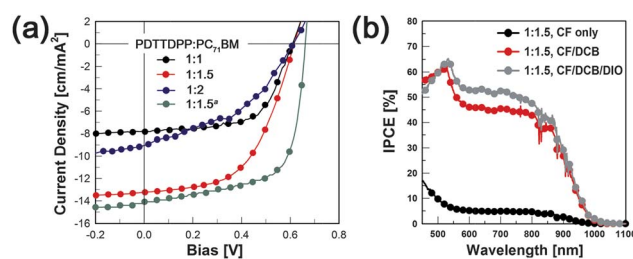


Fig. 4 (a) J - V curves and (b) IPCE spectra of OPVs based on PDTTDPP with different weight ratios of PC₇₁BM cast from different solvents. ^a2.5 vol% of DIO was added to the solution.

layer due its high boiling point which selectively dissolves PCBM. The solar cell device cast from a mixed solvent of CF, DCB, and 2.5 vol% of DIO exhibited a promising PCE of 6.05% (an average of 10 devices) with a high J_{SC} of 13.7 mA cm^{-2} , V_{OC} of 0.66 V and FF of 66.1%, which is one of the highest PCEs among DPP-based SCPs, to the best of our knowledge (see Fig. 3a and Table 1). The OPV device of PDTTDPP showed relatively high photo-conversion efficiency over 50% throughout the wavelength range of 400–800 nm (Fig. 4b). The J_{SC} calculated from integration of the IPCE under an AM 1.5G was 13.1 mA cm^{-2} which is consistent well with the J_{SC} value obtained from the J - V measurement, considering that the IPCE was measured in the range of 450–1000 nm. It should be mentioned here that thermal annealing did not improve the performance of OPV due to the formation of PCBM agglomeration accompanied with macro-phase separation of the active layer (see Fig. S11†).

Morphologies of the active layers cast from different solvent and different blend ratios of PDTTDPP to PC₇₁BM were observed by transmission electron microscopy (TEM), as shown in Fig. 5 and S10†. The active layer cast from CF showed very smooth surface without distinct phase separation between the polymer and PC₇₁BM while the active layer cast from DCB showed large aggregates of PDTTDPP, due to higher boiling point of DCB compared to CF. The mixed solvent of CF and DCB promotes self-assembly of PDTTDPP to some extent and thus clear phase separation. Furthermore, the addition of a small amount (2.5 vol%) of DIO to the mixed solvent induces nano-scale phase separation, as shown in Fig. 5d. The use of high-boiling-point additives has been known to promote the packing of the polymer by suppressing excessive crystallization of the PCBM.¹⁹ The blend ratio of PDTTDPP to PC₇₁BM is also an important parameter for the morphology and device performance.¹⁹ When the blend ratio was 1 : 1.5, an interconnected network structure was well developed particularly for the blend prepared in a mixed solvent of CF/DCB/DIO (see Fig. S10†). The

Table 1 Photovoltaic properties with different ratios of PDTTDPP to PC₇₁BM

Ratio (PDTTDPP: PC ₇₁ BM)	Solvent	V_{OC} /V	$J_{\text{SC}}/ \text{mA cm}^{-2}$	FF (%)	PCE (%)
1 : 1	CF/DCB	0.61	8.8	41.4	2.28
1 : 1.5		0.62	13.4	55.5	4.42
1 : 2		0.61	7.9	62.1	2.94
1 : 1.5 ^a	CF/DCB/DIO	0.66	13.7	66.1	6.05

^a 2.5 vol% of DIO was added to the solution.

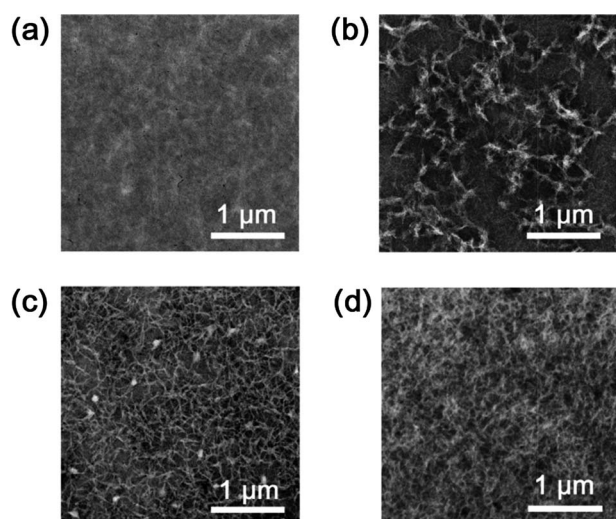


Fig. 5 TEM images of PDTTDPP:PC₇₁BM thin films with a weight ratio of 1 : 1.5 cast from (a) CF, (b) DCB, (c) CF/DCB (4/1), and (d) CF/DCB (4/1) with 2.5 vol% of DIO.

nano-scale phase separation with interconnected network was also evidenced by the space charge limited current (SCLC) hole mobility (see ESI†). The active layer cast from the mixture of CF/DCB/DIO showed the highest SCLC hole mobility of $5.33 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the active layers cast from CF and CF/DCB were 1.68×10^{-3} and $3.39 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, indicating that the active layer cast from the mixed solvent of CF/DCB/DIO forms an interconnected network more effectively than others. In short, a proper choice of solvent can also control the active layer morphology, which affects both exciton dissociation and charge carrier transport.

In conclusion, we have demonstrated that a novel low bandgap polymer PDTTDPP, which is composed of an electron-rich extended heteroarene unit (DTT) and an electron-deficient unit (DPP), can be used as a p-type conjugated polymer for both OFETs and OPVs. The strong intermolecular π - π stacking of PDTTDPP contributes to achieve the high hole mobility of $0.60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in OFETs without post-treatment. The PDTTDPP also shows a low bandgap of 1.22 eV due to strong intra-molecular charge transfer between DTT and DPP. Consequently, the high hole mobility and broad light absorption of PDTTDPP achieve a PCE of 6.05% with $J_{\text{SC}} = 13.7 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.66 \text{ V}$, and $\text{FF} = 66.1\%$. This work clearly demonstrates that the extended heteroarene unit (DPP) is a promising building block in the molecular design of new SCPs for high performance organic electronics.

Acknowledgements

The authors thank the Ministry of Education, Science and Technology (MEST), Korea for financial support through the Global Research Laboratory (GRL) and the World Class University (WCU) programs. T. P. R. and F. L. would also like to acknowledge the support of the US Department of Energy through the Energy Frontier Research Center.

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