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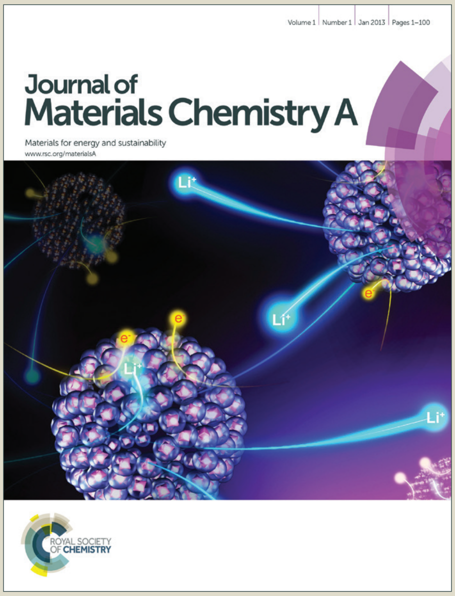
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ARTICLE TYPE

Highly Efficient Imide Functionalized Pyrrolo[3,4-c]pyrrole-1,3-dione-Based Random Copolymer Containing Thieno[3,4-c]pyrrole-4,6-dione and Benzodithiophene for Simple Structured Polymer Solar Cells

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As an effort to improve the photovoltaic properties of highly efficient large band gap (2.11 eV) alternating copolymer, P(BDT-TDPPDT), comprising electron rich benzodithiophene (BDT) and novel electron accepting pyrrole-based imide functionalized 4,6-bis(thiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,3-dione (TDPPDT) derivatives, we incorporated a relatively strong electron accepting thiophene-based imide functionalized thieno[3,4-c]pyrrole-4,6-dione (TPD) unit in its main chain via the random copolymerization between BDT, TDPPDT and TPD units to give polymer P1. The incorporation of TPD unit shows significant improvement in the optoelectrical and photovoltaic properties. P1 exhibits lower optical band gap (1.91 eV) and deeper lowest unoccupied molecular orbital (LUMO) energy level compared with those of P(BDT-TDPPDT). The hole mobility of P1 was 3.66×10^{-4} $cm^2V^{-1}s^{-1}$ and the PSC made with a simple device structure of ITO/PEDOT:PSS/P1:$PC_{70}BM$(1:2.25 wt%)+3 vol%/Al gave a maximum power conversion efficiency (*PCE*) of 7.03% with high photovoltaic parameters such as a open-circuit voltage (V_{oc}) of 0.87 V, a short-circuit current (J_{sc}) of 11.52 mA/cm^2 and a fill factor (*FF*) of 70%. Interestingly, P1-based PSCs exhibit high incident photon to current efficiency (*IPCE)* of maximum 78% at 410 nm and over 70% response in between 370 nm–590 nm. The *PCE* achieved in this study is the highest value reported so far among PSCs made with random copolymers.

1. Introduction

A numerous novel structured electron donating π–conjugated polymers[1] and electron accepting fullerene derivatives[2] have been developed in the recent years with the aim of improving the power conversion efficiency (*PCE*) of polymer solar cells (PSCs). The PSCs prepared with a large band gap polymer such as P3HT,[3a,3b] PCDTBT[3c-e] or PBnDT-FTAZ,[3f,3g] (E_g ~ 1.9–2.0 eV), as an electron donor and fullerene derivative as an electron acceptor offered a *PCE* of in the range of 6–8%[3] and the PSCs prepared with a suitable low band gap polymer as an electron donor and fullerene derivative as an electron acceptor provided the improved *PCE* in the range of 8–9%.[4] On the other hand, the tandem PSCs consisting of the front cell made from the blends of large band gap P3HT:ICBM and the rear cell prepared from the blends of low band gap:$PC_{70}BM$ gave a maximum *PCE* up to 11.5%.[5] Previous attempts of preparing tandem PSCs with different large and low band gap polymers have shown a maximum *PCE* in the range of 8–9.5%.[6] In this instance, the *PCE* of tandem PSCs is expected to be improved further by replacing P3HT with other large band gap polymer which produces higher *PCE* than P3HT because the front cell *PCE* is crucial for the overall device performances of tandem PSCs.

Recently, we reported a high solar to electrical energy converting large band gap polymer, P(BDT-TDPPDT) (Fig. 1), containing electron rich benzodithiophene (BDT) and electron deficient 4,6-bis(thiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (TDPPDT) units for PSCs.[7] Interestingly, the PSC made with P(BDT-TDPPDT) and $PC_{70}BM$ gave a *PCE* of 6.74% with a short-circuit current (J_{sc}) of 10.94 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.86 V, and a fill factor (*FF*) of 0.71. Though the band gap (~2.11 eV) of P(BDT-TDPPDT) is higher than that of the most successful large band gap polymer, P3HT (~1.90 eV), the overall *PCE* is 3% higher with greatly improved V_{oc} and *FF* compared to the results obtained for the PSCs made with P3HT and $PC_{60}BM$ or $PC_{70}BM$.[3a] Also, the incident photon to current efficiency (*IPCE*) of the P(BDT-TDPPDT)-based PSC is 6% higher than that of the P3HT based PSC.[5] Those unique properties made P(BDT-TDPPDT) as a promising large band gap

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polymer. In an attempt to improve the *PCE* of the P(BDT-TDPPDT)-based single layer PSC further, we intended to lower the polymer band gap because shifting the absorption band of P(BDT-TDPPDT) towards the low energy part of the solar spectra is expected to offer higher J_{sc} and *PCE*. The easy way to lower the band gap of polymer is just incorporating another strong electron acceptor unit in polymer chain. Interestingly, polymer PBDTTPD (shown in Fig. 1) comprising electron rich BDT and electron deficient 5-octylthieno[3,4-c]pyrrole-4,6-dione (TPD)[8] displayed very good opto-electrical (E_g ~ 1.73 eV) properties and high photovoltaic performances.[4c,8] Both of the thiophene and pyrrole based imide functionalized polymers such as PBDTTPD and P(BDT-TDPPDT) produce high *PCE* even though their band gap is very much different. We expect that the incorporation of TPD units in the main chain of P(BDT-TDPPDT) lowers the band gap of the final polymer significantly, and consequently, the improved absorption of the new polymer might offer higher *PCE* than P(BDT-TDPPDT).

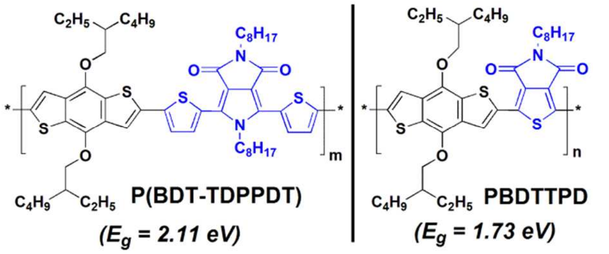

Fig. 1 Chemical structures of P(BDT-TDPPDT) and PBDTTPD.

2. Experimental section

2.1 Materials and Instruments

The required monomers such as 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b‘]dithiophene (BDT) and 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD) and necessary reagents and solvents such as tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3), tri(o-tolyl)phosphine (P(o-tol)$_3$) and chlorobenzene were received from Sigma-Aldrich. On the other hand, monomer 4,6-bis(5-bromothiophen-2-yl)-2,5-dioctylpyrrolo[3,4-c]pyrrole-1,3(2H,5H)-dione (TDPPDT) was prepared via the procedure we reported.[7] The ^{1}H NMR spectroscopy of P1 was recorded by using Varian Mercury Plus spectrometer (300 MHz). The molecular weight of P1 was determined by GPC (Agilent 1200 Infinity Series separation module) with chloroform as the eluent and the GPC was calibrated against the polystyrene standard. The TGA and DSC analysis of the polymer were performed on TA instrument Q600-0825 and TA instrument Q200-1968 at a heating and cooling rate of 10 °C/min under nitrogen at the Korea Basic Science Institute. A JASCO V-570 spectrophotometer was used to record the absorption spectra of the polymer, and cyclic voltammetry (CV) of the polymer was conducted using a CH Instruments Electrochemical Analyzer. CV was carried out on the polymer film on a platinum working electrode in an acetonitrile solution containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), Ag/AgCl as a reference electrode and platinum wire as a counter electrode. The CV instrument was calibrated with the ferrocene/ferrocenium ion (Fc/Fc^+) redox couple as an external standard. AFM was performed using a Seiko Instruments apparatus (SPI 3800N-SPA 400).

2.2 Synthesis of polymer

Synthesis of P1. A flame dried three necks round bottom flask containing a solution of monomers BDT (0.31 g, 0.40 mmol), TDPPDT (0.14 g, 0.20 mmol) and TPD (0.09g, 0.20 mmol) in chlorobenzene (20 mL) was purged well with argon for 30 min. Subsequently, Pd_2dba_3 (21 mg) and P(o-tol)$_3$ (45 mg) were added and the entire mixture was heated under reflux in argon for 36 h. The solution was cooled to RT and the solution was added drop wise to methanol (250 mL) with constant stirring. The precipitated polymer was allowed to settle. The precipitates were filtered and washed with methanol (50 mL) and acetone (50 mL). The polymer was then subjected to Soxhlet extraction with methanol and acetone for 24 h. The resulting polymer was dissolved in chloroform (20 mL) and filtered. The polymer was again precipitated by adding methanol (250 mL). The precipitates were filtered and dried under vacuum to afford pure polymer P1 as a dark brown color solid. Yield: 0.32 g (97%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.27-9.00 (m, 8H), 3.00-4.40 (m, 14H), 0.60-2.40 (m, 105H). The m:n ratio of P1 is calculated to be 1:1 from the NMR spectra and the yield obtained for P1.

2.3 Fabrication and characterization of PSCs

The PSCs were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure; ITO-coated glass substrate/poly(3,4-ethylenedioxythiophene) (PEDOT:PSS)/P1: $PC_{70}BM$/Al. The ITO-coated glass substrate was first cleaned with a detergent, ultrasonicated in acetone and isopropyl alcohol, and then dried overnight in an oven. PEDOT:PSS (Baytron PH) was spin-cast from an aqueous solution to form a 40 nm thick film. The substrate was dried for 10 min at 140 °C in air and then transferred to a glove box to spin-cast the charge separation layer. A solution containing a mixture of P1:$PC_{70}BM$ (1:2.00, 1:2.25 and 1:2.50 wt%) in chlorobenzene (CB) was then spin-cast on top of the PEDOT/PSS layer. For the samples with additive materials, a 1,8-diiodoctane (DIO) additive was added to the solution of P1:PC70BM in CB with a volume ratio of 97:3 (CB:DIO). The film with a thickness of 85 nm was dried for 30 min at room temperature (RT) in a glove box. An aluminium (Al, 100nm) electrode was then deposited by thermal evaporation in a vacuum of approximately 3×10^{-6} Torr. The current density-voltage (*J–V*) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit. The solar cell performance was measured with an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 Wm^{-2}. The spectral mismatch factor was calculated by comparing the solar simulator spectrum with the AM 1.5 spectrum at RT.

2.4 Fabrication and characterization of OFETs

OFETs were fabricated on highly n-type-doped silicon (Si) substrates with a 200 nm layer of thermally grown silicon oxide (SiO_2). All Si substrates were activated by an UV-ozone treatment for 30 min and treated with an octadecyltrichlorosilane (OTS) self-assembled monolayer. The n-type doped Si substrate functions as a gate electrode and the SiO_2 layer acts as a gate dielectric. The P1 solution in a CB solvent with a concentration of 5 mg/ml was spin-cast on top of the Si substrate with a spin speed of 2000 rpm and then dried at room temperature (RT) for

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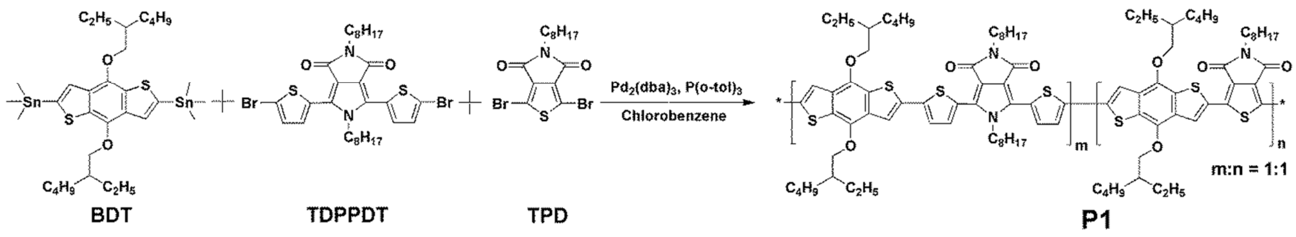

Scheme 1 Synthetic route to the synthesis of P1.

30 minutes. The source and drain electrodes (Au, 70 nm) were deposited on top of the P1 layer by thermal evaporation in a vacuum of approximately 2 x 10^{-6} Torr. The channel length (L) and channel width (W) of the device was 50 µm and 3.0 mm, respectively. The output and transfer characteristics of the OFETs were measured using a Keithley semiconductor parametric analyzer (Keithley 4200). All preparation processes and the characterization of OFETs were performed inside a N_2-atmosphere glove box. The mobility (µ) was determined using the following equation in the saturation regime:

$$I_{DS,sat} = (\mu W C_i/2L)\,(V_{GS}-V_T)^2$$

Where C_i is the capacitance per unit area of the SiO_2 dielectric (Ci = 15 nF cm^{-2}) and V_T is the threshold voltage.

3. Results and discussion

3.1 Synthesis and structural characterization

We prepared a new random copolymer namely P1 via the random copolymerization of distannyl derivative of BDT with dibromo derivative of TPD and TDPPDT as shown in Scheme 1. The number and weight average molecular weights (M_n and M_w) of P1 were 1.82×10^4 g/mol and 8.59×10^4 g/mol, respectively, with the polydispersity (*PDI*) of 4.73. Though polymer P1 shows high molecular weights, the solubility was excellent in chlorobenzene and dichlorobenzene.

The thermal properties of P1 were studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis and their corresponding curves are presented in Fig 2. The 5% weight loss temperature of P1 was estimated to be 340 °C from the TGA curve and the glass transition temperature (T_g) calculated from the DSC curve was 117 °C. We could not observe any other exothermic and endothermic peaks such as melting (T_m) or crystallization (T_c) peak while heating or cooling between 0–350 °C. The 5% weight loss temperature and T_g of P1 were identical to or only slightly different from those of P(BDT-TDPPDT) (340 °C and 113 °C, respectively)[7] and PBDTTPD (380 °C and 138 °C, respectively),[8] indicating that P1 has the thermal stability similar to that of P(BDT-TDPPDT) or PBDTTPD.

3.2 Optical and electrochemical properties

The absorption spectra of polymers P(BDT-TDPPDT), PBDTTPD and P1 spin-cast on glass plate are shown in Fig 3a. The maximum absorption (522 nm) of P1 is 28 nm red shifted in film state compared with that of P(BDT-TDPPDT). Based on the onset absorption wavelength of 648 nm as the film state, the optical band gap (E_g) of P1 was estimated to be 1.91 eV. The band gap of P1 is 0.2 eV lower and 0.18 eV higher compared with those of P(BDT-TDPPDT)[7] and PBDTTPD,[8] respectively.

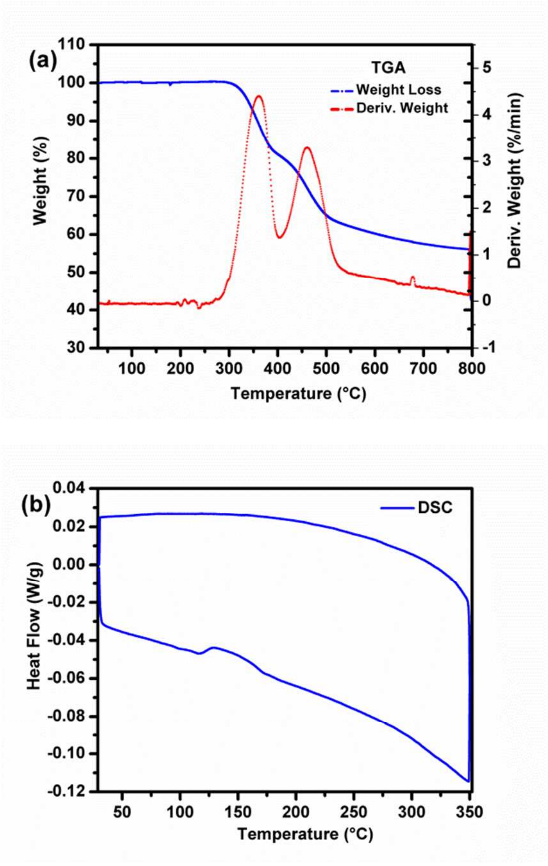

Fig. 2 (a) TGA and (b) DSC curves of P1.

The incorporation of relatively strong electron accepting TPD unit into the P(BDT-TDPPDT) main chain is expected to enhance the electron pulling ability from the donor (D) to acceptor (A) unit compared with that in P(BDT-TDPPDT), but decrease the electron transfer from D to A unit compared with that in PBDTTPD due to the random incorporation of TPD unit. In this

Table 1 Comparison of Polymerization Results and Thermal, Optical and Electrochemical Properties of P1 with those of P(BDT-TDPPDT).

Polymer[a]	M_w[b] (g/mol)	PDI[b]	T_d[c] (°C)	T_g[d] (°C)	λmax in solution (nm)[e]	λmax as film (nm)[f]	$E_{g,\,opt}$ (eV)[g]	HOMO (eV)[h]	LUMO (eV)[i]
P(BDT-TDPPDT)	2.15 x 10^4	1.59	340	113	464	494	2.11	–5.39	–3.28
P1	8.59 x 10^4	4.73	340	117	526	522	1.91	–5.39	–3.48

[a] Data for P(BDT-TDPPDT) are quoted from reference 7. [b] Weight average molecular weight (M_w) and polydispersity (PDI) of the polymer were determined by GPC using polystyrene standards. [c] 5 % weight loss temperature measured by TGA under N_2. [d] Glass transition temperature measured by DSC under N_2. [e] Measurements in chloroform solution. [f] Measurements in thin film were performed on the glass substrate. [g] Band gap estimated from the onset wavelength of the optical absorption in thin film. [h] The HOMO level was estimated from cyclic voltammetry analysis. [i] The LUMO level was calculated from HOMO and E_g values.

instance, the absorption band of random copolymer P1 is located in between the respective alternating polymers, P(BDT-TDPPDT) and PBDTTPD. The recently reported random polymer also displayed similar trends.[9]

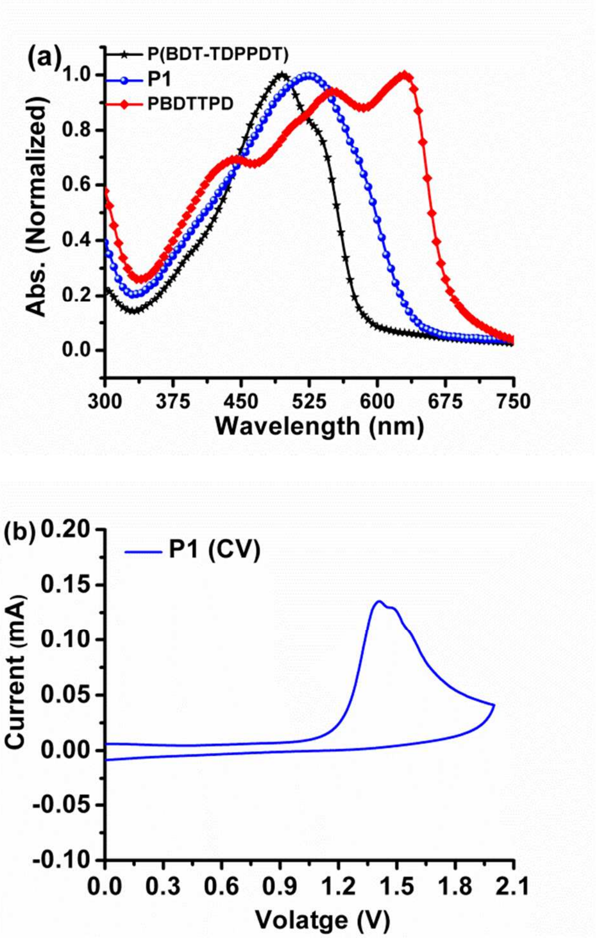

Fig. 3 (a) Absorption spectra of P1, P(BDT-TDPPDT) and PBDTTPD in film state and (b) CV spectra of P1.

The onset oxidation ($E_{ox\ onset}$) potential of P1 was estimated to be 1.15 eV from the cyclic voltammogram shown in Fig 3b. The highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energy levels of P1 were calculated to be –5.39 eV and –3.48 eV, respectively, with the use of $E_{ox\ onset}$ and E_g values. These results suggest that the inclusion of TPD unit in P(BDT-TDPPDT) main chain lowers the LUMO level by 0.2 eV, but does not alter the HOMO level of P(BDT-TDPPDT).[7a] The HOMO levels of alternating polymers P(BDT-TDPPDT) and PBDTTPD were found to be very similar (~ –5.40 eV),[7a,8b] but the LUMO level of PBDTTPD was found to be lower by ~ 0.4 eV than that of P(BDT-TDPPDT) due to the strong electron accepting ability of TPD unit compared to that of TDPPDT unit. Consequently, the presence of TPD unit in the random polymer P1 main chain does not alter the HOMO level, but notably lowers the LUMO level and the LUMO level of P1 was found to be located in between the LUMO levels of P(BDT-TDPPDT) and PBDTTPD. The molecular weight, absorption maximum and HOMO/LUMO levels of P1 are summarized in Table 1.

3.4 Photovoltaic properties

Fig. 4(a) shows the structure of the PSC device together with the molecular structures and an energy level diagram of the component materials. ITO forms the bottom electrode and the PEDOT:PSS layer on top of ITO serves a buffer layer for matching the energy levels of ITO and the components of the BHJ. The BHJ consists of a composite of P1 as an electron donor and the $PC_{70}BM$ as an electron acceptor. Under irradiation, generated holes and electrons in the BHJ layer are collected at the ITO and the Al electrode, respectively.

The typical current density-voltage (*J–V*) curves of the PSCs made from three different P1:$PC_{70}BM$ blend ratios (1:2.00 wt%, 1:2.25 wt% and 1:2.50 wt%) with 1,8-diiodoocatne (3 vol%, DIO) as a processive additive are displayed in Fig 4b and the *J–V* measurements were performed under one sun of simulated AM 1.5G solar irradiation (1000 Wm^{-2}). The maximum *PCE* for the PSC device prepared from the 1:2.25 wt% blends was 7.03% with V_{oc} of 0.87 V, a J_{sc} of 11.52 mA/cm^2 and a *FF* of 70%. It is worth to note that the further increase or decrease of the $PC_{70}BM$ content in the photoactive layer notably diminishes the photovoltaic parameters. The three PSC device results are summarized in Table 2. We also measured the *J–V* curve of PSCs prepared without DIO for 1:2.25 wt% blend ratio to understand the importance of processive additive and the respective *J–V* curve and device results are also included in Fig 4b and Table 2, respectively. The device results obtained for the PSCs made with and without DIO evidenced that the processive additive is quite important to achieve high photovoltaic performances for pyrrolo[3,4-c]pyrrole-1,3-dione-based polymers. The photovoltaic parameters such as V_{oc} and *FF* obtained for P1-based

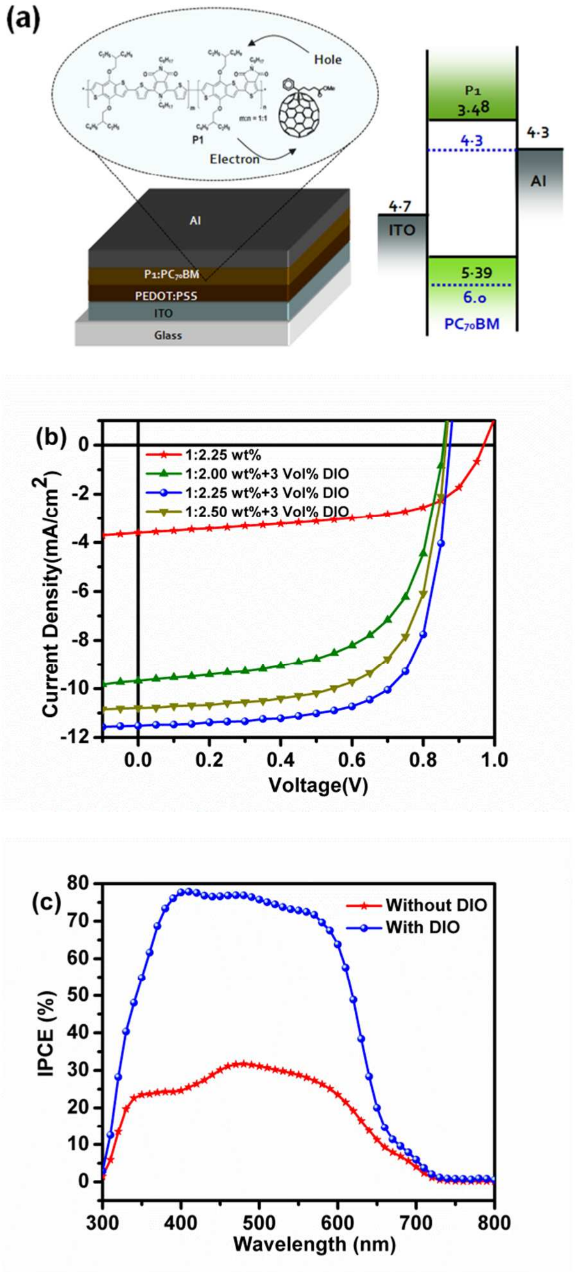

Fig. 4 (a) device structure and energy level diagram. (b) *J-V* characteristics of the PSCs prepared with three different P1:$PC_{70}BM$ blend ratios (1:2.00 wt%, 1:2.25 wt% and 1:2.50 wt%) with 1,8-diiodoocatne (3 vol%, DIO), and without DIO for 1:2.25 wt% blend. (c) *IPCE* spectra of PSCs made with (3 vol%)/without DIO for 1:2.25 wt% blends

Table 2. Photovoltaic Properties of the PSCs.

Weight Ratio	DIO	Jsc (mA/cm^2)[a]	Voc (V)[b]	FF (%)[c]	PCE$_{max}$ (%)[d]	PCE$_{avg}$ (%)[e]
1:2.25 wt%	no	3.60	0.97	59	2.04	1.84$\pm$(0.20)
1:2.00 wt%	3 vol%	9.67	0.85	61	5.06	4.88$\pm$(0.18)
1:2.25 wt%	3 vol%	11.52	0.87	70	7.03	6.89$\pm$(0.14)
1:2.50 wt%	3 vol%	10.80	0.86	66	6.14	6.02$\pm$(0.12)

[a] Short-circuit current density. [b] Open-circuit voltage. [c] Fill factor. [d] Highest value. [e] Average values.

PSCs are quite similar to those of PSCs made from P(BDT-TDPPDT) due to their similar HOMO level and hole mobilities but the improved J_{sc} of P1-based PSCs due to the wider and red shifted absorption of P1 enhances the overall device performances up to 7.03%.

The higher J_{sc} value obtained of the PSCs made with P1 compared with that of P(BDT-TDPPDT) was confirmed by using incident photon to current efficiency (*IPCE*) spectra. The *IPCE* spectra of the PSCs prepared with/without DIO for 1:2.25 wt% blends are presented in Fig 4c and the device made with DIO shows higher *IPCE* maxima than that of the device prepared without DIO. The PSC made with DIO displayed *IPCE* maximum of 78% at 410 nm with more than 70% *IPCE* response from 370 nm to 590 nm while the PSC made without DIO showed lower *IPCE* maximum of 32% at 480 nm. The increased *IPCE* maxima and response for the PSC made with DIO soundly evidenced its higher J_{sc} values. The maximum *IPCE* value was found to be 2% higher compared with that of the PSC device prepared with P(BDT-TDPPDT) and the spectral region was extended up to 700 nm.[7]

The higher J_{sc} of the PSCs made with DIO than that of the device made without DIO was confirmed further with the atomic force microscopy (AFM) images shown in Fig 5. The phase and tapping mode AFM images (a, a* and b, b*, respectively) of the films prepared without DIO showed large clusters (350 and 450 nm) of $PC_{70}BM$ while the films made with DIO (images c, c* and d, d*, respectively) represented well defined nanoscale phase separation. The surface roughness of the films made with DIO (roughness ~ 0.17 deg and 2.33 nm, respectively) is very much lower than the films prepared without DIO (roughness ~ 3.76 deg and 9.97 nm, respectively). It is obvious that the large clusters of $PC_{70}BM$ are liable for the recombination of photo-generated excitons before they reach the interfaces, which leads to the loss in *J*sc and FF for the device made without DIO. On the other hand, the very nice nanoscale phase separation and smooth surface of the photoactive layer prepared with DIO enhance the exciton dissociation and charge transport, resulting in a considerable increase in J_{sc}, *FF* and *PCE*. These results suggest that the surface morphology of the films made from P1 is very much improved by using DIO additive. In addition, it is better to note that the film made from P1:$PC_{70}BM$ blend with DIO showed smoother surfaces (rms roughness ~ 0.17 deg and 2.33 nm, respectively, for phase and tapping mode) than that of the film made from P(BDT-TDPPDT):$PC_{70}BM$ blend (rms roughness ~ 0.52 deg and 5.60 nm, respectively, for phase and tapping mode).[7a] Those results indicate that the incorporation of TPD unit in polymer main chain notably lowers the photoactive layer surface roughness and consequently expected to improve the charge transport and collection which leads higher *PCE*.

The preliminary organic field effect transistors (OFETs) studies for P1 show that it exhibits p-type semiconductor behaviour and the field-effect mobility was calculated to be $3.66x10^{-4}$ $cm^2V^{-1}s^{-1}$ with a current on/off ratio of $1.48x10^5$ and a threshold voltage of −6.72 V from the transfer characteristics shown in Fig 6. The mobility of P1 is found to be quite similar to that of P(BDT-TDPPDT) for the devices prepared under identical preparation condition.[7] The overall device performances of P1 were found to be improved compared with those of their respective alternating polymers such as P(BDT-TDPPDT)[7] and PBDTTPD[8] with the use of DIO additive.

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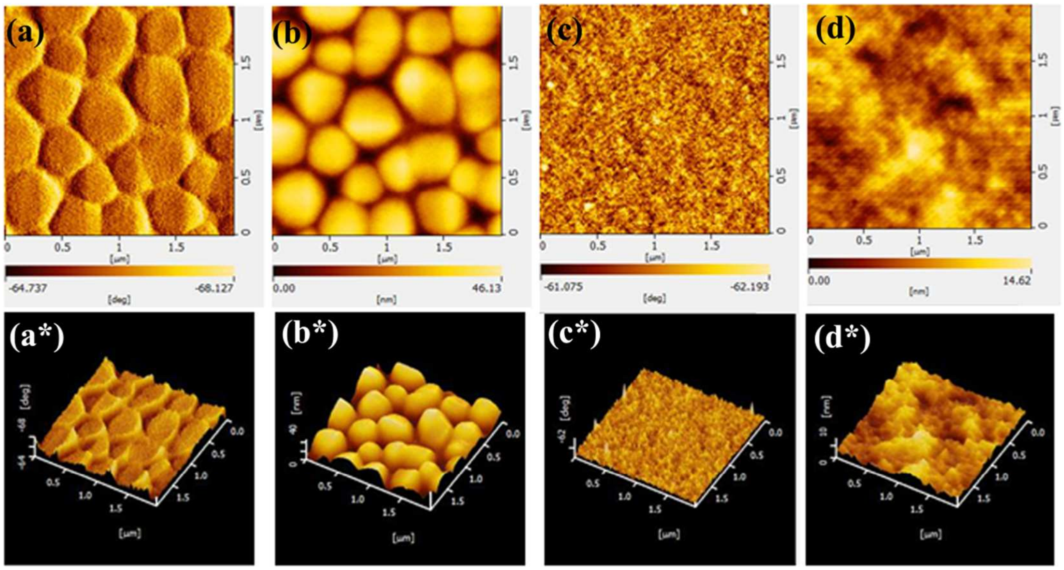

Fig. 5 AFM images of P1:PC70BM (1:2.25 wt%) blends without (images a, a* and b, b*) and with (images c, c* and d, d*) DIO. Images a, a* and c, c* were obtained from phase mode, whereas images b, b* and d, d* were obtained from tapping mode.

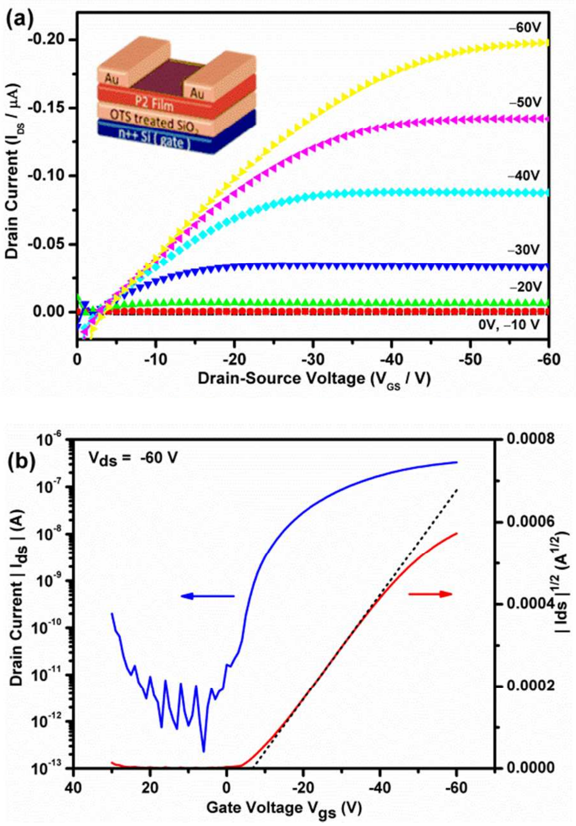

Fig. 6 (a) typical current-voltage characteristic (drain-source current, I_{DS}, versus drain-source voltage, V_{DS}) at different voltage and (b) I_{DS} and $I_{DS}^{1/2}$ versus V_{GS} plots at V_{DS} of –60 V for a P1-based OFET device.

Polymer P1 is the most efficient random copolymer among the so far reported highly efficient random copolymers for PSCs.[10] Though the band gap of P1 is lower than that of P(BDT-TDPPDT), it is still higher than those of other highly efficient low band polymers.[4] We expect that the incorporation of DFBT,[4a] TT[4b] or DKPP[6] unit in P(BDT-TDPPDT) instead of TPD might offer broad absorbing low band gap polymer (~1.4–1.7 eV), and consequently, expected to give higher *PCE* than P1. Currently, we are in the attempt of preparing those random polymers.

4. Conclusions

In this study, we demonstrated the possibility of increasing the *PCE* of pyrrolo[3,4-c]pyrrole-1,3-dione-based large band gap (~2.11 eV) polymer, P(BDT-TDPPDT), via the incorporation of thieno[3,4-c]pyrrole-4,6-dione (TPD) unit in the polymer main chain by random copolymerization. The inclusion of TPD unit in the P(BDT-TDPPDT) main chain decreases the band gap as well as improves the surface morphology of photoactive layer of the resulting random polymer (P1) and consequently, the PCE of the PSC prepared from P1 was improved to 7.03%. This is the highest value reported so far among PSCs made with random copolymers. This study proves that random copolymers also produce high PCE. In addition, P1 is also expected to be a promising large band gap candidate for the front cell in the preparation of effective tandem PSCs.

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A random copolymer showing a record PCE of 7.03% was prepared via the random copolymerization of benzodithiophene, pyrrolo[3,4-c]pyrrole-1,3-dione and thieno[3,4-c]pyrrole-4,6-dione units.