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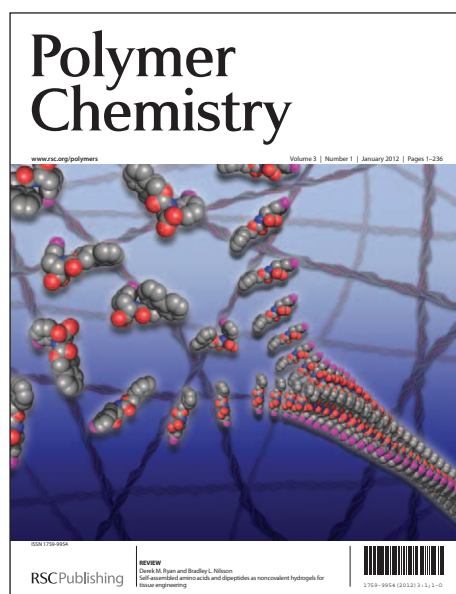
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ARTICLE TYPE

Design and Modification of Three Components Randomly Incorporated Copolymers for High Performance Organic Photovoltaic Application

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In this study we report the molecular design, synthesis, characterization, and photovoltaic properties of a series of diketopyrrolopyrrole (DPP) and dithienothiophene (DTT) based donor-acceptor random copolymers. The six random copolymers are obtained via Stille coupling polymerization using various concentration ratios of donor to acceptor in the conjugated backbone. Bis(trimethylstannyl)thiophene was used as the bridge block to link randomly with the two comonomers of 5-(bromothien-2-yl)-2,5-dialkylpyrrolo[3,4-c]pyrrole-1,4-dione and 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene respectively. The optical properties of these copolymers clearly reveal the change in absorption band through optimization of the donor-acceptor ratio in the backbone. Additionally, the solution processibility of the copolymers is modified through the attachment of different bulky alkyl chains to the lactam N-atoms of the DPP moiety. Applications of polymers as light-harvesting and electron-donating materials in solar cells, in conjunction with PCBM as acceptors, show power conversion efficiencies (PCEs) of up to 5.02%.

Introduction

Bulk heterojunction (BHJ) polymer solar cells, comprising interpenetrating networks of a donor polymer semiconductor and a fullerene derivative acceptor such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM), have attracted a great deal of attention by virtue of their easy solution processability, mechanical flexibility, and the low-cost large-area manufacturing.^[1] Organic photovoltaic (OPV) devices based on these materials are predicted to have a power conversion efficiency (PCE) of close to 10% based on some theoretical models if a suitable low band gap donor material has been developed.^[2] In order to obtain high-performance photovoltaic polymer materials, it is necessary to design and synthesize novel conjugated donor polymers with ideal characteristics such as broad absorption spectrum for efficient sunlight harvesting and high mobility for effective charge carrier transportation to the electrodes. Large short-circuit current density (J_{sc}), good fill factor (FF) and high open-circuit voltage (V_{oc}) are important parameters for getting high PCE in OPV devices and these factors can be achieved by modulating appropriate molecular energy levels with good charge carrier mobility of the semiconducting material.^[3]

Dithieno[3,2-b:2',3'-d]thiophene (DTT) is a classic condensed aromatic moiety that has been explored previously for making various class of electronically active or semiconducting materials.^[4] DTT based small molecules have been successfully reported and used for various applications such as organic light emitting diodes (OLEDs), non linear optics, photochromics,

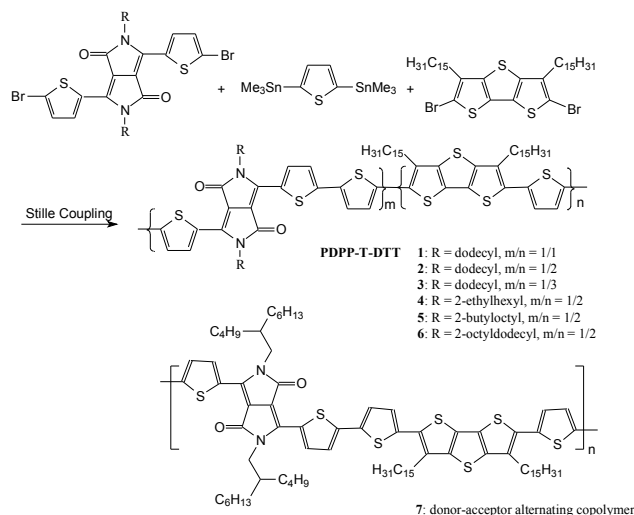
organic thin film transistors (OTFTs), and OPV.^[5,6] However, there are few reports on DTT-based semiconducting polymers, presumably due to their inherently poor solubility and processability.^[7,8] The introduction of long alkyl side-chains to the β -positions of DTT unit would be an excellent approach for making them easily solution-processable.^[9] We have recently synthesized one copolymer based on 3,5-dipentadecyldithieno[3,2-b;2',3'-d]thiophene, PBTDDT-15, which exhibited high OTFT mobilities of 0.06 cm²·V⁻¹·s⁻¹. In addition, blends of PBTDDT-15 and PC₇₁BM have achieved promising solar cell PCEs of up to 3.2%.^[9b,c] Considering the relatively narrow absorption spectrum of PBTDDT-15, which has an absorption onset of around 640 nm, the OPV results suggest that the dialkyl-substituted DTT would be a promising building block for donor polymers. Combining the electron-donating DTT moiety with an electron-accepting moiety can create a novel push-pull type copolymer with a lower band-gap and better photon-absorption characteristics. Such combination will also modulate the energy levels for further improvement in solar cell performances.

Among reported various push-pull based materials, recently diketopyrrolopyrrole (DPP)-based molecules and polymers are gaining significant attention in research community due to their excellent properties such as high stability, weather fastness, large extinction coefficient, and electron-deficient nature.^[10] 3,6-Dithien-2-yl-2,5-dialkylpyrrolo[3,4-c]pyrrole-1,4-dione (DTDPP) is one of the important segments which was significantly investigated for making interesting class of DPP based materials for various applications including unipolar, ambipolar OFETs to

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OPVs.^[11,12] Nguyen et al. and Janssen et al. successfully demonstrated the high performance OPV devices using DPP based molecular and polymeric donor materials with PCBM, respectively.^[13,14] Afterwards many alternating copolymers containing DTDPP with benzene, carbazole, fluorene, dibenzosilole, dithienosilole, benzodithiophene, dithieno[3,2-b;2',3'-d]pyrrole, dithienothiophene, and cyclopenta[2,1-b;3,4-b']-dithiophene as comonomer units have been developed for high performance OPV application by different research groups.^[15] Recently Sonar et al. and Janssen et al. demonstrated successful utilization of DPP based materials as acceptors for OPV applications.^[16]

Scheme 1. Synthetic route and structure of PDPP-T-DTT copolymers



In our study, we used a DTDPP unit as the acceptor block, and the dipentadecyl-substituted DTT unit as the donor segment. By combining DPP with DTT we expect to create a novel condensed aromatic push-pull conjugated backbone system with wide absorption spectrum and good charge transporting ability. Bis(trimethylstannyl)thiophene was used as the bridging unit to link the dibrominated monomers of 3,6-bis(5-bromothiophen-2-yl)-2,5-dialkylpyrrolo[3,4-c]pyrrole-1,4-dione and 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene through the Stille coupling polymerization. In contrast to most investigated donor-acceptor (D-A) type copolymers, which have been synthesized through alternating fashion, our copolymers are random by nature and the donor/acceptor blocks are incorporated randomly in the main conjugated backbone. This design strategy is beneficial because of easy tailoring in the comonomer (donor, acceptor or linking blocks) feed ratio, which controls the optical and electronic properties of the copolymer.^[17] In our previous communication, we reported a random D-A copolymer based on DPP and DTT moieties, which shows promising high power conversion efficiency.^[18] In this article a systematic exploration of the structure-property relationship was carried out on this type of random D-A copolymers. A series of copolymers PDPP-T-DTT have been consecutively designed and synthesized (Scheme 1). The copolymers 1-3 with different ratios of dodecyl chain attached DPP to DTT moieties were first prepared in this series and were found to have relatively poor solubility in common organic solvents, but being soluble only in chlorobenzene or dichlorobenzene. In spite of this, promising solar cell PCEs

greater than 3% were achieved for these polymers (*vide infra*). The best performance was offered by copolymer 2 which possesses balanced optical absorption from UV to near IR region, thus we set out to improve the solubility and processability of this kind of polymer by replacing straight dodecyl chain with the branched alkyl chains such as 2-ethylhexyl, 2-butylhexyl and 2-octyldodecyl, respectively. Polymers 4 to 6 which have different branched alkyl chains but same comonomer feed ratio (same as copolymer 2) were synthesized and further evaluated in OPV devices. The best OPV performance was demonstrated by copolymer 5, where a typical cell device of ITO/PEDOT-PSS/polymer:PC₇₁BM/Ca/Ag, under simulated AM1.5G conditions, exhibit V_{oc} of 0.584 V, J_{sc} of 12.76 mA cm⁻², and FF of 67.27%, resulting in a PCE of 5.02%. Our systematic study has demonstrated that the high OPV performance can be realized in randomly linked donor-acceptor copolymers. These results might open up new avenues to the material chemists on the new molecular design for high performance OPV polymers.

Experimental

Instrumentation and characterization

¹H NMR data were acquired on a Bruker DPX 400 MHz spectrometer. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10 °C min⁻¹). Thermogravimetric analysis (TGA) was carried out using a TGA Q500 instrument (heating rate of 10 °C min⁻¹). Molecular weight determinations were carried out in hot chlorobenzene solution on a Shimadzu Prominence CBM-20A series HPLC using Agilent PLGel 5 micrometer Mixed-C column (79911 GP-MXC) with polystyrene calibration standards. Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. A glassy carbon disk was used as working electrode, a platinum wire as counter electrode and a silver wire as reference electrode. Ferrocene was used for potential calibration. UV-Vis-NIR spectra were recorded on a Shimadzu model 2501-PC.

Organic Photovoltaic Device Fabrication

For the BHJ solar cell devices, polymer was dissolved in 1,2-dichlorobenzene (DCB) solution at a concentration of 8-10 mg mL⁻¹. Blends of polymer with PCBM were prepared in the concentration ratio from 1:1 to 1:5 in DCB. The patterned ITO glass substrates were first sonicated in a detergent bath for half an hour, followed by rinsing with de-ionized water for 20 min. This was succeeded by sonication in an acetone and iso-propanol bath for 15 min and 20 min respectively. The cleaning step was concluded by drying the substrates in an oven at 80 °C for at least an hour. The substrates were subjected to UV-ozone plasma treatment for 10 min before a 40 nm thick PEDOT:PSS was spin-coated onto the ITO surface. The polymer/PCBM solution was then spin-coated onto the PEDOT:PSS layer and left standing to dry for 2 hours. A 10 nm thick calcium layer, followed by 100 nm of silver, were deposited onto the blend layer via thermal evaporation to form the cathode. The active area of the device is 9 mm². Current density-Voltage ($J-V$) measurements were carried out in an inert environment (MBraun glovebox, N₂ atmosphere) under 1 Sun (AM1.5G) conditions using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA).

General synthetic procedure for PDPP-T-DTT

The monomers were weighed and added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glovebox where tris(dibenzylideneacetone)dipalladium(0) (2 mol%), tri(o-tolyl)phosphine (8 mol%) and anhydrous chlorobenzene (20 mL) were added.^[17] The vial was then stirred at 120 °C for 36 hours using an oil bath. The reaction mixture was poured into 200 mL of methanol and 10 mL of concentrated hydrochloric acid and stirred overnight to remove the stannylated end-groups. The subsequent purification processes depended on the solubility of the polymer. The polymers were subjected to soxhlet extraction with ethanol and hexanes for 24 h each. The polymers with R = n-C₁₂H₂₅, which had poor solubility, were then dissolved in hot chlorobenzene, precipitated into methanol and filtered to obtain the final product. All other polymers were subject to soxhlet extraction with chloroform and chlorobenzene (if necessary), precipitated into methanol and filtered to obtain the final product.

Copolymer 1: The title compound (80 mg, 75%) was obtained as black solids. ¹H-NMR (1,1,2,2-tetrachloroethane-d₄, 400 MHz, 120 °C) δ 8.85 (s, 2H), 7.43-7.25 (m, 6H), 4.17 (s, 4H), 3.08 (s, 4H), 1.95-1.93 (m, 8H), 1.58-1.38 (m, 84H), 0.98-0.96 (m, 12H). Anal. calcd. for C₈₄H₁₂₂N₂O₂S₇: C, 71.23; H, 8.68; N, 1.98. Found C, 71.20; H, 8.57; N, 1.90. *M_w/M_n* (GPC) = 53.4k/15.7k. *T_d* (TGA) = 414 °C.

Copolymer 2: The title compound (128 mg, 96%) was obtained as black solids. ¹H NMR (1,1,2,2-tetrachloroethane-d₄, 400 MHz, 120 °C) δ 8.87 (s, 2H), 7.44-7.17 (m, 10H), 4.18 (s, 4H), 3.08 (s, 8H), 1.94 (m, 12H), 1.57-1.38 (m, 132H), 0.98-0.96 (m, 18H). Anal. calcd. for C₁₂₆H₁₈₆N₂O₂S₁₁: C, 71.60; H, 8.87; N, 1.33. Found C, 71.83; H, 8.81; N, 1.37. *M_w/M_n* (GPC) = 69.4k/21.7k. *T_d* (TGA) = 417 °C.

Copolymer 3: The title compound (170 mg, 96%) was obtained as black solids. ¹H NMR (1,1,2,2-tetrachloroethane-d₄, 400 MHz, 120 °C) δ 8.87 (s, 2H), 7.43-7.25 (m, 14H), 4.18 (s, 4H), 3.08 (s, 12H), 1.95 (m, 16H), 1.57-1.38 (m, 180H), 0.97 (m, 24H). Anal. calcd. for C₁₆₈H₂₅₀N₂O₂S₁₅: C, 71.79; H, 8.96; N, 1.00. Found C, 71.41; H, 8.96; N, 1.02. *M_w/M_n* (GPC) = 52.9k/25.4k. *T_d* (TGA) = 400 °C.

Copolymer 4: The title compound (199 mg, 82%) was obtained from the chlorobenzene fraction as black solids. ¹H NMR (1,1,2,2-tetrachloroethane-d₄, 400 MHz, 120 °C) δ 8.87 (s, 2H), 7.43-7.25 (m, 10H), 4.12 (s, 4H), 3.07 (s, 8H), 2.03-1.94 (m, 12H), 1.56-1.32 (m, 48H), 1.02-0.97 (m, 24H). Anal. calcd. for C₁₁₈H₁₇₀N₂O₂S₁₁: C, 70.82; H, 8.56; N, 1.40. Found C, 70.32; H, 8.40; N, 1.38. *M_w/M_n* (GPC) = 63.8k/17.7k. *T_d* (TGA) = 401 °C.

Copolymer 5: The title compound was obtained in two fractions as black solids. Chloroform fraction: 87 mg (29%); chlorobenzene fraction: 194 mg (65%); total yield 94%. ¹H NMR (1,1,2,2-tetrachloroethane-d₄, 400 MHz, 120 °C) δ 8.85 (s, 2H), 7.42-7.26 (m, 10H), 4.11 (s, 4H), 3.06 (s, 8H), 2.08-1.94 (m, 12H), 1.56-1.26 (m, 64H), 0.97-0.95 (m, 24H). Anal. calcd. for C₁₂₆H₁₈₆N₂O₂S₁₁: C, 71.60; H, 8.87; N, 1.33. Found C, 71.95; H, 8.89; N, 1.37. *M_w/M_n* (GPC) = 52.4k/15.4k. *T_d* (TGA) = 374 °C.

Copolymer 6: The title compound (310 mg, 93%) was obtained from the chloroform fraction as black solids. ¹H NMR (1,1,2,2-tetrachloroethane-d₄, 400 MHz, 120 °C) δ 8.86 (s, 2H), 7.42-7.25 (m, 10H), 4.12 (s, 4H), 3.07 (s, 8H), 2.08-1.94 (m,

12H), 1.56-1.32 (m, 96H), 0.95 (m, 24H). Anal. calcd. for C₁₄₂H₂₁₈N₂O₂S₁₁: C, 72.95; H, 9.40; N, 1.20. Found C, 72.65; H, 9.35; N, 1.20. *M_w/M_n* (GPC) = 67.8k/29.1k. *T_d* (TGA) = 372 °C.

Results and Discussion

Synthesis and Characterization

Compounds 3,6-bis(5-bromothien-2-yl)-2,5-dialkylpyrrolo[3,4-c]pyrrole-1,4-dione^[16a], 2,6-dibromo-3,5-dipentadecyl-dithieno[3,2-b;2',3'-d]thiophene^[9b] and 2,5-bis(trimethylstannyl)thiophene^[19] were synthesized according to the previously reported procedures, respectively. The polymerization reactions were carried out using the Stille coupling protocol.^[20] Copolymers 1-4, which were relatively poorly soluble, were subjected to soxhlet extraction with ethanol and hexanes, the remaining polymers were removed from the extraction thimble, dissolved in hot chlorobenzene, and precipitated into methanol to obtain the final polymers in yields of 75% to 96%. Copolymer 5 showed better solubility, hence soxhlet extraction was continued with chloroform and chlorobenzene. Copolymer 5 was then obtained by precipitating the chlorobenzene fraction into methanol. Copolymer 6, being soluble in hot chloroform, was obtained by soxhlet extraction with chloroform. GPC analysis using chlorobenzene as the eluent showed that the polymers had moderate to high number-averaged molecular weights of between 15,400 to 29,100 g mol⁻¹. NMR and elemental analyses were carried out on the polymers to verify that the composition of the polymers corresponded with the monomer feed ratios. The elemental analyses on the polymers show a decrease in the nitrogen content of the polymers as the proportion of the DPP units decrease, which is consistent with the calculated values.

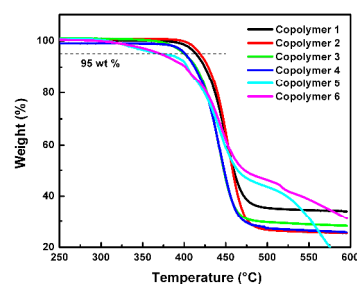


Figure 1. TGA scans of PDPP-T-DTT. The samples were heated at 10 °C min⁻¹ from room temperature to 600 °C and the weight losses were recorded. The 5% weight loss temperature was taken to be the sample's decomposition temperature.

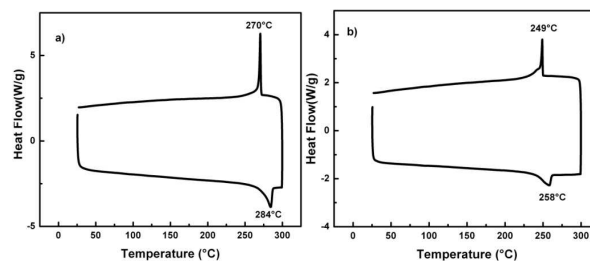


Figure 2. DSC scans of a) copolymer 5 and b) copolymer 6 showing their melting and recrystallization peaks. The samples were heated from room temperature to 300 °C and back to room temperature at a ramp rate of 10 °C min⁻¹.

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Thermal properties

In order to determine the thermal properties of the copolymers, differential scanning calorimetry (DSC) and thermogravimetry (TGA) analyses of copolymers have been carried out. All of the copolymers exhibited excellent thermal stability with 5% weight loss temperatures between 370 and 420 °C. By comparing the 5% weight loss temperatures of copolymers 2, 4, 5 and 6, in which the ratio between DPP and DTT moieties is the same but the attached alkyl chains to DPP are different, it can be observed that the thermal stability of the polymers decreased slightly as the bulk of the alkyl chains increased. DSC scans on the copolymers 1 to 4 revealed no clear thermal transitions from room temperature to 350 °C. Copolymers 5 and 6, however, had sharp melting peaks at 284 °C and 258 °C respectively (Figure 2), indicating that the bulky branched alkyl chains on DPP impact not only on the polymer solubility but also the polymer chains packing in the solid state.

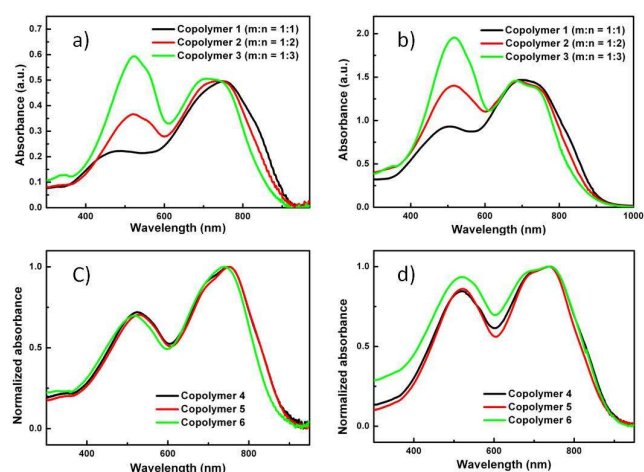


Figure 3. UV-Vis-IR spectra for PDPP-T-DTT. a) solution spectra of copolymers 1-3 in chlorobenzene, b) thin film spectra of copolymers 1-3, c) solution spectra of copolymers 4-6 in chlorobenzene, d) thin film spectra of copolymers 4-6.

Optical and electrochemical properties

The optical properties of the copolymers were studied by UV-Vis-NIR absorption spectroscopy. The solution and thin film absorption spectra for copolymers 1-6 are shown in Fig. 3. Two distinct absorption bands were observed, which can be attributed to the π - π^* transition from DTT segments (short wavelength region of 370~600 nm)^{9b} and D-A charge-transfer transition (long wavelength region of 600~910 nm). The solution and film spectra were similar, although the absorbance of all the polymers at the short wavelength region was relatively enhanced in the film. When the ratio of the DTT units in the copolymers 1-3 was increased, absorbance in the short wavelength region increased relative to that of the long wavelength region. In the film of copolymer 2, the absorption in the short wavelength region and the long wavelength region were almost equal; further increases in the DTT content caused the absorption in the short wavelength region to exceed that in the long wavelength region. For the copolymers 4-6, the absorption intensity at both short and long wavelength bands remain almost unchanged, showing that the attachment of different alkyl chains does not affect the electron delocalization along the polymer backbone. The optical band-

gaps of copolymers 1-6 were determined from their absorption onsets of around 910 nm, which corresponded to a band-gap of 1.37 eV. Compared with PBTDTT-15, the band-gaps of PDPP-T-DTT series are 0.56 eV lower due to the combination of DPP acceptor moiety with DTT donor moiety, this combination forms a push-pull conjugated system which results in hybridization of the highest occupied molecular orbital (HOMO) of the donor with lowest unoccupied molecular orbital (LUMO) of the acceptor.^[9b] The absorption onsets for all the copolymers are red-shifted by around 270 nm to near infrared region, indicating that these polymers have greater potential for effective photon harvesting.

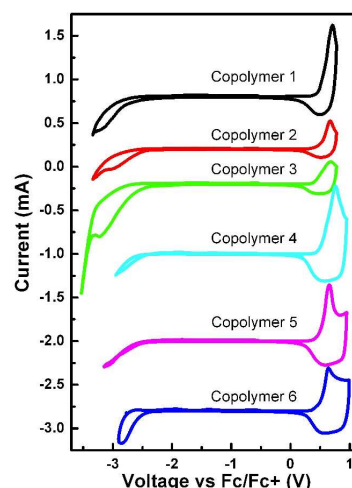


Figure 4. Cyclic voltammograms of PDPP-T-DTT. The ferrocene/ferrocenium couple was used as an internal reference and the oxidation onsets were used to calculate the HOMO values of the polymers.

Cyclic voltammetry experiments were performed in order to determine the HOMO and LUMO energy levels. All CV measurements were recorded in a 0.1 M tetrabutylammonium hexafluorophosphate solution in dry acetonitrile at a scanning rate of 100 mV·s⁻¹. The glassy carbon working electrode was coated with the polymer thin film by using a polymer solution in chlorobenzene. All the polymers had very similar oxidation onset potentials of around 0.35-0.45 V vs Fc/Fc⁺ (Figure 4), which translate to HOMO levels of between -5.15 eV and -5.25 eV.^[21] The polymer with the deepest HOMO level was copolymer 1 (m:n = 1:1) at -5.25 eV; increasing the DTT content caused the HOMO level to increase marginally to -5.24 eV for copolymer 2 (m:n = 1:2) and -5.19 eV for copolymer 3 (m:n = 1:3). Copolymers 4 to 6 had HOMO levels of between -5.15 to -5.18 eV, which was slightly higher than that of copolymer 2.

Photovoltaic properties

Photovoltaic devices with the structure of ITO/PEDOT:PSS/Polymer:PCBM blend/Ca/Ag were fabricated from blends of copolymers 1, 2 and 3 and PC₆₁BM according to the procedure described in Experimental section. Polymer:PC₆₁BM weight ratios ranging from 1:1 to 1:5 were used in order to see the effect of donor and acceptor concentrations on OPV performance. Active layers with thicknesses of around 120 nm were obtained by spincoating blend solutions. No thermal treatment was applied in the device fabrication process. The

results are shown in Figure 5 and the Table 1. From the results, it can be seen that the highest PCE was 2.06% for copolymer 1, 3.58% for copolymer 2, and 3.06% for copolymer 3. The best ratio of polymer to PC₆₁BM varied between the polymers, with copolymer 1 requiring a 1:4 ratio, copolymer 2 a 1:2 ratio and copolymer 3 a 1:1 ratio. For all 3 polymers, it was observed that an increase in the PC₆₁BM content resulted in a slight decrease in the V_{oc} . This has previously been observed for other donor polymers, such as MDMO-PPV, AFPO3, P3HTV and PF10TBT.^[22] The reduction in the V_{oc} correlated with the decrease in the energy of the charge transfer (CT) states with increasing PC₆₁BM concentrations.^[22c]

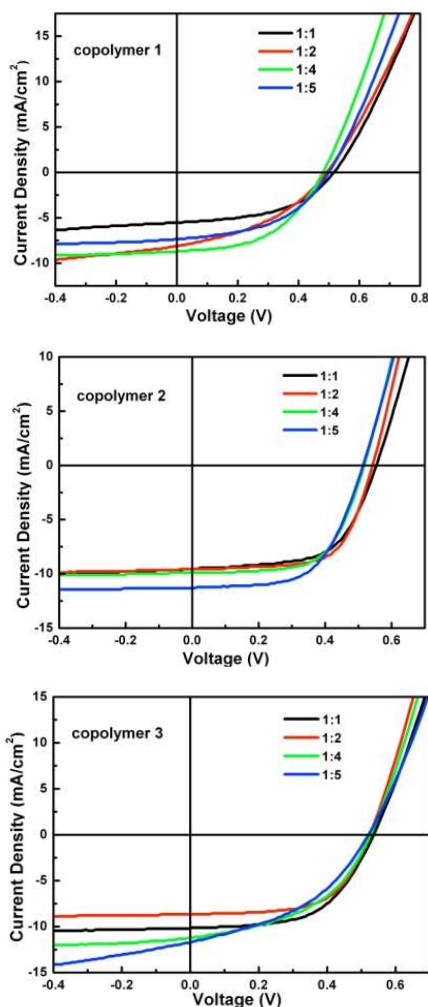


Figure 5. Current-voltage characteristics of PDPP-T-DTT:PC₆₁BM solar cells. Polymer:PC₆₁BM ratios of 1:1, 1:2, 1:4 and 1:5 were tested. The device structure was ITO/PEDOT:PSS/Polymer:PCBM blend/Ca/Ag and the device active area was 9 mm².

It is observed that copolymer 2 (m:n = 1:2) gave the best results among the three copolymers 1-3. Replacing PC₆₁BM by PC₇₁BM in blend with copolymer 2 resulted in a device with J_{sc} of 12.91 mA cm⁻², V_{oc} of 0.505 V, FF of 58.41% and PCE of 3.81%. The increase in PCE was due to an increase in the J_{sc} (12.91 vs 10.93 mA cm⁻² for the case of PC₆₁BM), which can be attributed to the better absorption properties of PC₇₁BM compared to PC₆₁BM.^[23] However, the general OPV performance does not improve much as we expect when compared to PBDTT-15. This is probably

due to the poor solubility of three copolymers 1-3. Thus copolymers 4, 5 and 6 were synthesized with different N-branched alkyl substituents (2-ethylhexyl, 2-butyloctyl and 2-octyldodecyl respectively) with the same 1:2 ratio in order to improve the processability of the polymer. It was observed that the solubility of copolymer 4 was similar with that of copolymer 2 and the solubilities of copolymers 5 and 6 were improved compared with copolymer 2.

Table 1: Device parameters of copolymer 1-3:PC₆₁BM solar cells

PDPP-T-DTT	Polymer:PCBM	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
1	1:1	5.54	0.517	48.93	1.41
	1:2	8.10	0.493	39.83	1.59
	1:4	8.71	0.480	49.33	2.06
	1:5	7.35	0.500	47.58	1.75
2	1:1	9.55	0.554	60.55	3.20
	1:2	10.93	0.536	61.00	3.58
	1:4	9.90	0.517	63.22	3.24
	1:5	11.28	0.514	59.25	3.44
3	1:1	10.17	0.536	56.21	3.06
	1:2	8.67	0.525	60.96	2.77
	1:4	11.24	0.527	46.52	2.75
	1:5	11.69	0.520	41.81	2.54

Copolymers 4, 5 and 6 were tested in solar cells utilising a 1:2 weight ratio blend of polymer to PC₇₁BM, and the results are shown in Figure 6 and Table 2. Comparing the performances of all the polymers in combination with PC₆₁BM, it is observed that cells with copolymer 4 had a low PCE of 3.07%. This could be attributed largely to a drop in the fill factor of the device, which we believe is due to reduced film quality stemming from its poor solubility. Cells utilising copolymer 5 had a slightly higher J_{sc} , V_{oc} and FF than those of the copolymer 2, resulting in an improved PCE of 4.39%. Furthermore, the substitution of PC₇₁BM for PC₆₁BM resulted in higher J_{sc} values and improved PCE of 5.02% for copolymer 5.

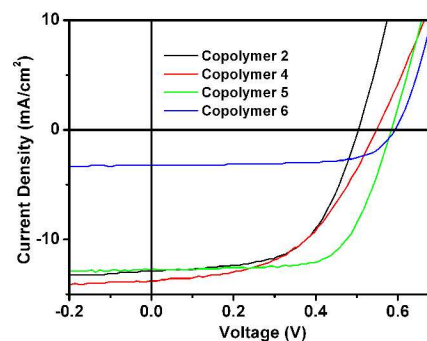


Figure 6. Current-Voltage characteristics of solar cells made from 1:2 blends of copolymers 2 (R = dodecyl), 4 (R = 2-ethylhexyl), 5 (R = 2-butyloctyl) and 6 (R = 2-octyldodecyl) and PC₇₁BM.

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Table 2: Device parameters of 1:2 blends of copolymers 4-6 with PC₆₁BM and PC₇₁BM

Copolymer:PCBM	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
4:PC ₆₁ BM	10.82	0.550	51.61	3.07
4:PC ₇₁ BM	13.75	0.548	50.33	3.79
5:PC ₆₁ BM	11.55	0.566	67.21	4.39
5:PC ₇₁ BM	12.76	0.584	67.27	5.02
6:PC ₇₁ BM	3.24	0.593	67.60	1.30

It is surprising that the performance of copolymer 6 in OPVs was much poorer although this polymer was much more soluble than their counterparts with shorter alkyl chains. Thus AFM studies (Figure 7) of the copolymer 5:PC₇₁BM and 6:PC₇₁BM devices were conducted to explore the cause of the poor performance for copolymer 6. It was observed that the domains in the copolymer 6:PC₇₁BM film were 50–150 nm in size. Such large domain sizes are detrimental for charge separation as there is a greater likelihood of excitons recombining before they reach an interface where charge separation can take place.^[24] The domains for the copolymer 5:PC₇₁BM film were much smaller at around 20 nm, leading to much better charge separation and a higher short circuit current.

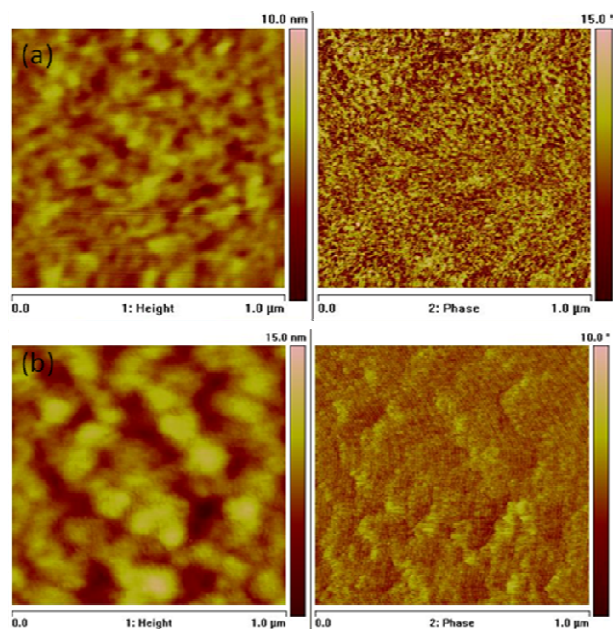


Figure 7. a) Height and phase AFM images of copolymer 5:PC₇₁BM film b) height and phase AFM images of copolymer 6:PC₇₁BM film.

Furthermore, for verifying the rationality of our strategy of donor-acceptor random copolymers for high efficient organic photovoltaic application, we intentionally prepared one donor-acceptor alternating copolymer based on DPP and DTT moieties (copolymer 7) as shown in Scheme 1.^[25] The Bottom-gate, top-contact thin film transistor (TFT) devices were fabricated from copolymer 5 and copolymer 7 respectively in order to investigate how the donor-acceptor linkage style affects its charge transport properties. The two copolymer both showed p-type transporting characteristic and good current on/off ratio above 10⁵ when measured in ambient conditions, the copolymer 7 presented much higher TFT performance over the copolymer 5 with saturation

hole mobility of 0.11 cm²/Vs. The hole mobility is at least one order of magnitude higher than that of copolymer 5 (ca. 8.7 × 10⁻³ cm²/Vs),^[17] this is likely to be due to the random linkage of DTT donor and DPP acceptor units along the polymer backbone, which reduces the molecular ordering of copolymer 5 compared to the alternating-linked copolymer 7. The solar cell devices were fabricated using a blend of copolymer 7 and PC₇₁BM with the same device structure as that for copolymer 5. Under the same measurement condition, however, the devices with the 1:2 ratio by weight of copolymer 7:PC₇₁BM provided the highest PCE of 3.44% with V_{oc} of 0.53 V, J_{sc} of 9.91 mA/cm², and FF of 65.65 %, less than the OPV performance of copolymer 5. This comparison confirms that high OPV performance can be obtained on a D-A randomly incorporated copolymer through the optimisation of donor/acceptor concentration ratio in the copolymer, opening a new design strategy for developing high efficiency OPV materials.

Conclusions

Currently, most low-band-gap polymers for OPV application are developed based on the strategy of alternating donor-acceptor along the polymer backbone. Our results in this study show that high OPV performance can also be obtained in a donor-acceptor randomly incorporated copolymer through the optimization of the ratio between donor and acceptor units in the main chain and solution processibility by attaching proper alkyl side chain, thus opening a new design strategy for developing high performance OPV materials. We note that the open circuit voltages of the cells in our current polymer system were close to 0.6 V, which could be a limitation on the performance of these cells. Thus, increasing the V_{oc} of these cells could be the key to achieving increased power conversion efficiencies. The design and synthesis of new monomer and polymer with low-lying HOMO level are in progress.

Notes and references

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