

Efficient polymer solar cells based on a broad bandgap
D–A copolymer of “zigzag” naphthodithiophene and
thieno[3,4-*c*]pyrrole-4,6-dione†Cite this: *J. Mater. Chem. A*, 2013, **1**,
1540Received 18th November 2012
Accepted 10th December 2012

DOI: 10.1039/c2ta01143c

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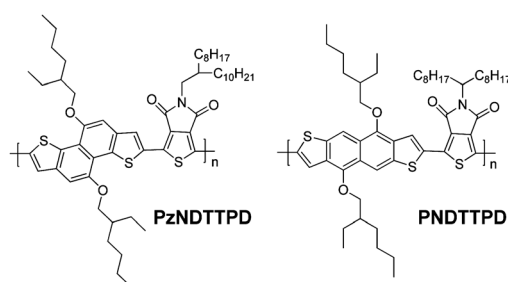
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A promising broad bandgap copolymer, PzNDTTPD, based on a rigid planar “zigzag” naphthodithiophene unit, was designed and synthesized. The BHJ solar cells based on PzNDTTPD:PC₇₁BM blends afforded a power conversion efficiency of 5.3% with a high V_{oc} over 0.9 V.

Solution-processed polymer solar cells (PSCs) have attracted considerable attention over previous decades due to their potential application in flexible, lightweight, and low-cost large-area devices through roll-to-roll printing.^{1–3} Significant progress has been made in this field through the design and synthesis of new materials, optimized fabrication processing techniques, and engineered new device architectures.⁴ To date, the power conversion efficiencies (PCEs) of single junction PSCs have reached more than 8% using a bulk hetero-junction (BHJ) architecture, in which a blended film of an electron donor conjugated polymer and an electron acceptor fullerene acts as the active BHJ layer.⁵ However, the inherent disadvantages of conjugated materials, such as narrow absorption range and relatively low carrier mobility, limit the further improvement of device efficiency.

Tandem solar cells, especially a typical double-junction cell, in which a front cell with a large-bandgap material and a rear cell comprising a low-bandgap material are connected in series, provide an effective way to harvest a broader spectrum of solar radiation.⁶ Very recently, a new world record efficiency of 10.7%

for small molecule tandem solar cells was reported by the company Heliatek, indicating that tandem structure may be a promising approach to further improve device performance.⁷ Compared with a single-junction device, the open-circuit voltage (V_{oc}) of the tandem structure is equal to the sum of the open-circuit voltage of two individual cells, while the short circuit current density (J_{sc}) is limited by the current density of the lower cell. At present, most research on tandem PSCs has focused on the development of low-bandgap (<1.5 eV) materials with the aim of minimizing the overlap of absorption spectra between the front and rear cells and obtain a high current in the rear cell, while poly(3-hexylthiophene) (P3HT) was the most commonly used large-bandgap material in the tandem solar cells. However, the higher highest occupied molecular orbital (HOMO) energy level (*ca.* −4.76 eV) of P3HT results in lower V_{oc} of the front cell, which limits the V_{oc} enhancement of tandem PSCs.⁸ Thus, it is necessary to explore new broad band gap polymer materials with higher V_{oc} for high efficiency tandem PSCs.



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† Electronic supplementary information (ESI) available: Experimental details including the polymer synthesis, the fabrication and characterization of the polymer solar cells, measurements, and instruments. See DOI: 10.1039/c2ta01143c

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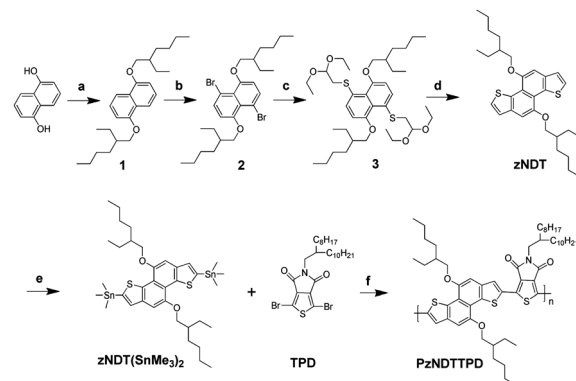
In search of broad band gap polymers with deep HOMO levels and high efficiency, a newly reported building block-naphthodithiophene (NDT) – attracted our attention.⁹ With two thiophenes fused at the end of naphthalene, the extended π -conjugation system and the highly rigid planar backbone of NDT are expected to afford strong intermolecular orbital overlap and electron-donating properties which could thereby enhance charge separation, transport, and energy level

tunability. Up to now, NDT-based low-bandgap PSCs and solution-processed small molecule solar cells have reached a PCE of more than 5% and 4%, respectively.¹⁰ As most fused aromatics, NDT contains different isomers, including linear- and angular-shaped ("zigzag") analogues (zNDT). Recent studies indicate that the shapes of NDT and the related curvature of the polymer chains have a large impact on HOMO levels and charge mobility of conjugated polymers. For example, Takimiya *et al.* have discovered that NDTs of angular shapes showed lower HOMO levels and larger band gaps than their linear counterparts. Also, when compared with linear NDT, they found that zNDT units show more delocalized HOMOs along the whole backbone and a higher ordered structure, which is beneficial to promote the efficient HOMO overlaps and facilitate the efficient charge carrier transport.¹¹ All those reports give us inspiration to employ zNDTs for constructing new efficient photovoltaic polymers with deep HOMO energy levels.

Herein, we designed and synthesized a new donor-acceptor (D-A) copolymer, PzNDTTPD, by using electron rich 4,9-bis-(2-ethylhexyloxy)naphtho[1,2-*b*:5,6-*b'*]dithiophene as a donor unit and thieno[3,4-*c*]pyrrole-4,6-dione (TPD) as an acceptor unit. TPD was chosen as an acceptor unit due to its rigidly fused, coplanar structure and strong electron-withdrawing properties, which make it a potential acceptor unit for increasing intramolecular/intermolecular interactions and/or lowering HOMO energy levels when incorporated into polymeric backbones.¹² In addition, unlike previously reported zNDT-based polymers, in this work, zNDT functionalized with 2-ethylhexyloxy groups was introduced into polymer for the first time to achieve the solubility and thin film uniformity required in solution processed PSCs. The resulting polymer possesses a broad bandgap of 2.04 eV and a deep HOMO energy level of -5.38 eV. As a result, the PSCs with PzNDTTPD as a donor and PC₇₁BM as an acceptor demonstrated a PCE of 5.26%, with a high V_{oc} of 0.91 V, a J_{sc} of 9.03 mA cm^{-2} and a fill factor (FF) of 0.64 compared to the reported linear NDT-TPD-based copolymer PNDTTPD with a PCE of 4.0% and a V_{oc} of 0.69 V under the illumination of AM1.5G, 100 mW cm^{-2} .^{10d} Also, the PCE of 5.26% is the highest efficiency ever reported for PSCs based on a polymer donor with a band gap over 2.0 eV, revealing a promising potential for application in tandem PSCs.

The synthetic route of the relevant monomers and copolymer is illustrated in Scheme 1. The detailed procedure is described in the ESI.† The polymer possessed good solubility in common organic solvents, and exhibited good thermal stability up to 372°C (with 5% weight loss) (see Fig. S1 in ESI†). The molecular weight was measured by gel permeation chromatography (GPC) analysis. PzNDTTPD has a number-average molecular weight (M_n) of 20.7 kDa, with a polydispersity index (PDI) of 2.75.

Fig. 1a shows the absorption spectra of PzNDTTPD in dilute chloroform solution and in the solid state. The absorption of the thin film is almost the same as that in solution with a peak at $\sim 578 \text{ nm}$ and a vibronic shoulder at $\sim 535 \text{ nm}$ which indicates a similar rigid-rod conformation in both states. The absorption at the long wavelength direction drops sharply with an absorption edge at $\sim 609 \text{ nm}$, corresponding to a band gap (E_g) of 2.04 eV. Cyclic voltammetry (CV) was used to measure



Scheme 1 Synthetic route of the copolymer PzNDTTPD. Reagents: (a) KOH, TBAB, H_2O , ethylhexylbromide, RT then 80°C ; (b) NBS, CH_3CN , 0°C then RT; (c) *n*-BuLi, bis(2,2-diethoxyethyl) disulfide, THF, -78°C then RT; (d) PPA, chlorobenzene, reflux; (e) *n*-BuLi, Me_3SnCl , THF, -78°C then RT; (f) $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-tol})_3$, chlorobenzene, 135°C .

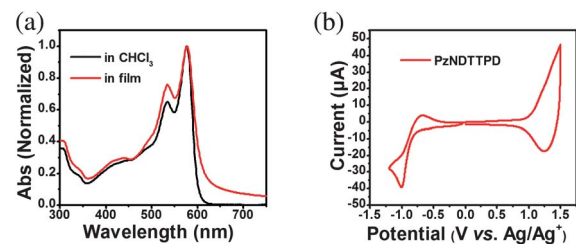


Fig. 1 (a) Normalized UV-Vis absorption spectra of PzNDTTPD in diluted chloroform solution and as a solid thin film. (b) Cyclic voltammograms of PzNDTTPD films on a platinum electrode in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ acetonitrile solution at a scan rate of 100 mV s^{-1} . The ferrocene/ferrocenium redox couple is used as a standard (-4.8 eV).

oxidation and reduction potentials of the polymers (Fig. 1b).¹³ PzNDTTPD presents one reversible p-doping (with the onset oxidation potential $E_{ox} = 0.58 \text{ V vs. Fc/Fc}^+$) process and one reversible n-doping (with the onset reduction potential $E_{red} = -1.37 \text{ V vs. Fc/Fc}^+$). The HOMO and LUMO levels of the polymers were calculated from E_{ox} and E_{red} , respectively, where $\text{HOMO} = -e(E_{ox} + 4.80) \text{ (eV)}$ and $\text{LUMO} = -e(E_{red} + 4.80) \text{ (eV)}$. The calculated HOMO is -5.38 eV , LUMO is -3.43 eV , and the electrochemical bandgap (E_g^{ec}) of PzNDTTPD is 1.95 eV which well matches its optical bandgap of 2.04 eV. In comparison with PNDTTPD, PzNDTTPD exhibits a deeper HOMO level, which is helpful to get a higher V_{oc} in PSCs.

The photovoltaic properties of PzNDTTPD were investigated by fabricating the PSC devices with a structure of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al, where PzNDTTPD was used as the donor and PC₇₁BM was used as the acceptor in the photoactive layer of the devices. The active layer was prepared by spin-coating the blend solution of polymer and PC₇₁BM in *o*-dichlorobenzene. The effective area of the device is 4 mm^2 . The characterization of the current density-voltage ($J-V$) curves under the illumination of AM1.5G, 100 mW cm^{-2} was done in an inert nitrogen atmosphere and the external quantum efficiencies (EQEs) of the devices without encapsulation were

Table 1 The photovoltaic performance of the PSCs based on PzNDTTPD:PC₇₁BM with different weight ratios under the illumination of AM1.5G, 100 mW cm⁻²

D–A ratio	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1.5 : 1	4.45	0.93	45	1.86
1.5 : 1 ^a	7.36	0.95	63	4.40
1 : 1	5.28	0.93	54	2.65
1 : 1 ^a	9.03	0.91	64	5.26
1 : 2	5.46	0.92	45	2.26
1 : 2 ^a	7.92	0.93	52	3.83

^a 1% DIO additive (v/v).

measured in air. A more detailed description of the device fabrication process is available in the ESI.†

The device performance data are presented in Table 1. We optimized the device performance of the PSCs by changing the weight ratio of PzNDTTPD to PC₇₁BM from 1.5 : 1 to 1 : 2. It can be seen that the PSC with the weight ratio of PzNDTTPD : PC₇₁BM of 1 : 1 showed the best photovoltaic performance with a V_{oc} of 0.93 V, a J_{sc} of 5.28 mA cm⁻² and a FF of 0.54, leading to a PCE of 2.65%. The device performance dramatically changed after the addition of 1% (v/v) DIO (diiodooctane) and a PCE of 5.26% was obtained. The change of PCEs is mainly due to the improved J_{sc} and FF, which can be attributed to the better polymer–fullerene phase separation and stronger intermolecular packing in films by using the solvent additives.¹⁴ As shown in the atomic force microscopy (AFM) images (see Fig. S2 in ESI†), the formation of nanoscale fine networks between donor and acceptor materials facilitates both the exciton dissociation and charge transport in the blend film. This is consistent with the large improvement of photocurrent from 5.28 mA cm⁻² to 9.03 mA cm⁻² in the devices. To evaluate the photoresponse of PzNDTTPD and calibrate the J_{sc} data, external quantum efficiencies (EQE) of the devices with or without DIO were measured (Fig. 2b). The device showed a relatively high photo-conversion efficiency over the whole wavelength range of 400–600 nm, with monochromatic EQE values around 50–60%. The J_{sc} calculated by integrating the EQE curve with an AM1.5G reference spectrum is within 10% error compared to the corresponding J_{sc} obtained from the J – V curves.

In conclusion, a new broad band gap polymer, PzNDTTPD, was designed and synthesized. In spite of a narrow absorption range, a high PCE of ~5.3% was still achieved by using

o-dichlorobenzene with 1% DIO as the solvent to make solution for a spin-coating process of the active layers, which suggests that 4,9-bis(2-ethylhexyloxy)naphtho[1,2-*b*:5,6-*b'*]dithiophene should be a useful electron-rich building unit in a copolymer donor material for efficient PSCs. Compared with the classic photovoltaic material P3HT, PzNDTTPD shows a deeper HOMO level and a broader band gap; a V_{oc} of more than 0.9 V is also the highest reported value for PSCs with a band gap over 2.0 eV, indicating that PzNDTTPD may be a more promising candidate than P3HT for the high-bandgap material used in tandem PSCs.

This work was supported by the Beijing Natural Science Foundation (2122047).

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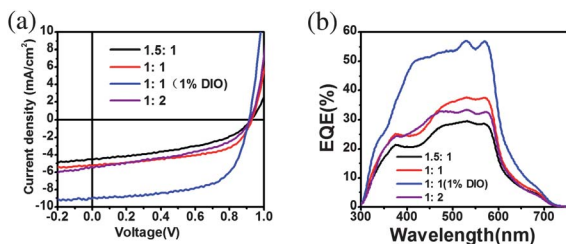


Fig. 2 (a) J – V curves of the PzNDTTPD/PC₇₁BM device under the illumination of AM1.5G, 100 mW cm⁻². (b) External quantum efficiency curve of the PzNDTTPD/PC₇₁BM device.

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