Synthesis and characterization of a thiazolo[5,4-*d*]thiazole-based copolymer for high performance polymer solar cells†

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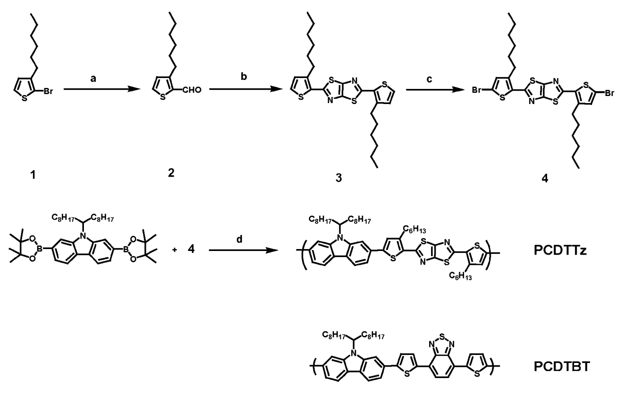
A highly processable, new semiconducting polymer, PCDTTz, based on alternating thiazolothiazole and carbazole units was synthesized. The new polymer exhibited a field-effect carrier mobility of up to 3.8 × 10^{-3} cm^2 V^{-1} s^{-1} and bulk heterojunction solar cells made from PCDTTz produced a power conversion efficiency of 4.88% under AM 1.5 G (100 mW cm^{-2}) conditions.

Polymer solar cells (PSCs) have attracted considerable attention over previous decades because of their unique advantages, which include low cost, lightweight, solution processability, and flexibility.[1–9] Despite considerable progress in this field, power conversion efficiencies (PCE) of PSCs must be further improved for commercialization. The decisive parameters that determine the efficiency of PSCs are the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and fill factor (FF). V_{OC} is limited by the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.[10] Among the various conjugated polymers, polyfluorene or polycarbazole derivatives have a deep HOMO level that increases the V_{OC} of the PSCs. However, these derivatives generally exhibit poor solubility, relatively low hole mobilities, and low molecular weights.[11,12] The J_{SC} and FF are directly limited by the charge carrier mobility. Higher charge carrier mobilities enable better carrier transport within an active layer without significant photocurrent loss due to recombination of opposite charges. High charge carrier mobilities also lead to high fill factors.[13] Recently, the thiazolothiazole unit has aroused interest as a semiconducting material with a high carrier mobility.[14–16] McCullough and coworkers reported the field-effect mobility of novel semiconducting polymers that incorporate thiazolothiazole fused rings into a polythiophene backbone, which showed a high charge carrier mobility of 0.14 cm^2 V^{-1} s^{-1}.[16] The use of the thiazolothiazole-fused ring ensures a rigid coplanar backbone and, therefore, a highly extended π-electron system with strong π-stacking.

Here, we report the application of a new carbazole-based polymer, poly[*N*-9″-hepta-decanyl-2,7-carbazole-alt-2,5-bis(3-hexylthiophene-2-yl)thiazolo[5,4-*d*]thiazole] (PCDTTz), in bulk heterojunction solar cells. Because the thiazolothiazole unit is an electron deficient fused ring, the backbone of the thiazolothiazole-based copolymer acts as a donor–acceptor system. The well-characterized thiazolothiazole moieties were introduced as a second bithiophene unit to improve the solubility of the resultant copolymer, which facilitated polymer characterization and photovoltaic device fabrication. The new copolymer semiconductor indeed exhibited a band gap of 2.07 eV, a field-effect carrier mobility of up to 3.8 × 10^{-3} cm^2 V^{-1} s^{-1}, and bulk heterojunction solar cells made from PCDTTz produced a power conversion efficiency of 4.88% under 100 mW cm^{-2} AM 1.5 G irradiation in ambient air. Although several widely investigated topics in PSCs research area is the development of small band gap (< 1.74 eV) conjugated polymers to match well with the solar spectrum,[17,18] organic semiconductors with a band gap of at least 2.0 eV are also required for efficient harvesting of solar energy over a broad spectral range in organic tandem solar cells.[19,20]

The PCDTTz polymer structure is shown in Scheme 1. PCDTTz was synthesized through a Suzuki coupling reaction using $Pd(OAc)_2$ as the catalyst and tricyclohexyl phosphine as the ligand. The properties of PCDTTz were compared to those of poly[*N*-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) reported by Blouin *et al.*,[21] prepared *via* the same synthetic procedure. The



Scheme 1 Synthesis of PCDTTz and molecular structure of PCDTBT. (a) Mg, THF, 70 °C for 5 h then DMF, room temperature; (b) dithiooxamide, DMF, reflux for 5 h; (c) NBS, chloroform, reflux for 3 h; (d) $Pd(OAc)_2$, tricyclohexyl phosphine, anhydrous toluene, tetraethyl ammonium hydroxide solution, reflux.

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† Electronic supplementary information (ESI) available: Experimental sections, physical properties, computation methodology: the charge-density isosurface of model compounds, electrochemical properties of PCDTTz and PCDTBT, transfer characteristics of FET fabricated using PCDTBT, the performance of the PSCs under various conditions, and AFM topography of films spin coated from PCDTBT/$PC_{71}BM$ and PCDTTz/$PC_{71}BM$. See DOI: 10.1039/c0cc03036h

weight average molecular weights (M_w) of the synthesized polymers PCDTTz and PCDTBT were determined by gel permeation chromatography (GPC), using a polystyrene standard in chloroform eluent, and were found to be 58 000 (PDI = 2.9) and 59 000 (PDI = 1.2), respectively. PCDTTz was readily soluble in common organic solvents, such as toluene, chloroform, and THF, whereas PCDTBT dissolved only in warm chloroform or warm chlorinated benzene, but remained dissolved when the temperature returned to room temperature. The thermal behavior of the copolymer under a nitrogen atmosphere was characterized by thermogravimetric analysis (TGA) and by differential scanning calorimetry (DSC). PCDTTz showed a high glass transition temperature (T_g; *ca.* 120 °C) and excellent thermal stability (5% degradation at 400 °C). Detailed description of the synthesis and characterization is provided in the ESI.†

The UV-Vis absorption spectra of the polymers, PCDTTz and PCDTBT, in chloroform and in thin films are shown in Fig. 1. In chloroform solvent, the spectrum of PCDTTz showed a λ_{max} of 487 nm, which was significantly blue-shifted relative to that of PCDTBT. The spectrum of PCDTBT displayed the two distinct absorption bands, which were characteristic of the push–pull units along the polymer backbone introduced by the low band gap polymers *via* intramolecular charge transfer (ICT) between the donor and the acceptor.[22] In contrast, PCDTTz presented a single broad absorption peak. To obtain further information about ICT electronic structure of the polymers, density-functional theory (DFT) calculation for the model compound was carried out using the DMol 3. Fig. S3 (ESI†) shows the calculated molecular orbitals of the model compounds. As shown in Fig. S3 (ESI†), the HOMO and LUMO of PCDTTz were delocalized over the π-conjugation systems, whereas in the case of PCDTBT, the HOMO was delocalized over the polymer backbone, and the LUMO was highly localized on the benzothiadiazole (BT) unit. Pure PCDTBT thin films presented two absorption bands at 396 and 577 nm and an absorption onset at 660 nm. Pure PCDTTz showed an absorption band with a peak at 518 nm and an absorption onset at 600 nm, which corresponded to a band gap of 2.07 eV. The energy level of the polymer was investigated by cyclic voltammetry (CV). The HOMO energy levels of PCDTBT and PCDTTz were calculated to be −5.45 and −5.31 eV, by using the ferrocene reference value of −4.8 eV below the vacuum level.[23] The LUMO levels of PCDTBT and PCDTTz were calculated to be −3.57 and −3.24 eV, as estimated from the optical band gaps and HOMO energy levels (Fig. 1b).

The hole mobilities of the polymers were calculated from the transfer characteristics of field effect transistors (FETs) fabricated with bottom-contact geometry using Au electrodes, and the results are plotted in Fig. 2. A field-effect hole mobility of 3.8×10^{-3} cm^2 V^{-1} s^{-1} and an on/off ratio of 10^5 were observed in PCDTTz FETs. The mobility of PCDTBT was about 1.7×10^{-4} cm^2 V^{-1} s^{-1} and the on/off ratio was found to be 10^5 under the same experimental conditions (Fig. S5, ESI†). The hole mobility in pure PCDTTz was an order of magnitude higher than that obtained in PCDTBT. The hole mobility fell within a desirable range for PSC materials (higher than or close to 10^{-3} cm^2 V^{-1} s^{-1})[24] allowing for efficient charge extraction and a good fill factor.

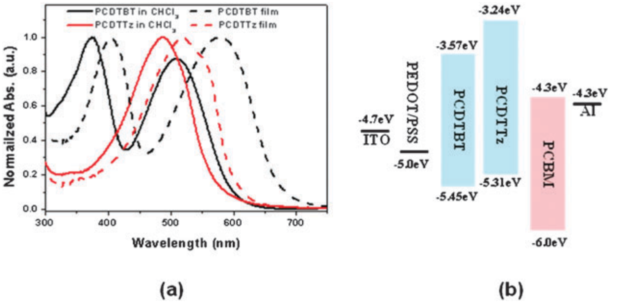

Fig. 1 (a) UV-Vis absorption spectra of PCDTBT (black line) and PCDTTz (red line) in chloroform (solid line) and in the solid state (dashed line). (b) Energy levels for the copolymers.

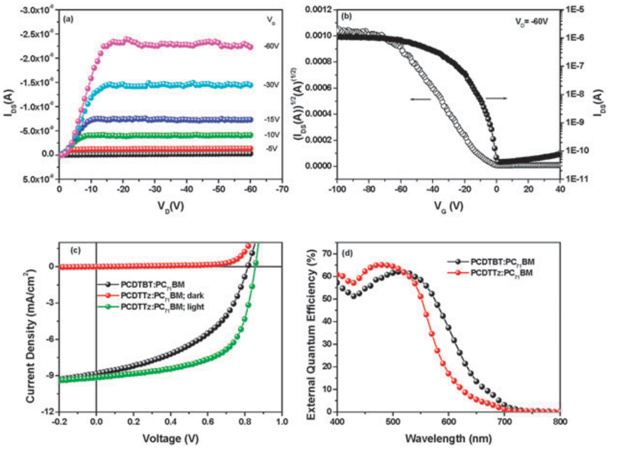

Fig. 2 (a) Output characteristics at different gate voltages for PCDTTz. (b) Transfer characteristics in the saturated regime for PCDTTz. (c) Current–voltage characteristics of polymer solar cells under AM 1.5 G conditions (100 mW cm^{-2}). (d) External quantum efficiency of PCDTBT:PC$_{71}$BM and PCDTTz:PC$_{71}$BM.

Polymeric bulk heterojunction solar cells were fabricated with the structure of ITO/PEDOT:PSS/polymer:PC$_{71}$BM/LiF/Al. The detailed device fabrication process is described in the ESI.† The performance of PSCs is strongly affected by processing parameters, such as the choice of solvent, blend ratio of polymer to PC$_{71}$BM, solution concentration, and thermal annealing.[25] We investigated the performance of the PSC materials under variety of conditions (see the ESI†). Optimal fabrication conditions were obtained from a 14 mg mL^{-1} *o*-dichlorobenzene solution, spin-coated at 600 rpm, and a polymer/PC$_{71}$BM ratio of 1 : 3 (w/w). The thicknesses of the layers were PEDOT:PSS (50 nm), the active layer (60 nm), LiF (0.7 nm) and Al (100 nm). Fig. 2(c) shows the current–voltage characteristics of PSC devices based on the polymer and PC$_{71}$BM blends. The optimized cells provided a V_{OC} of 0.86 V, a J_{SC} of 9.15 mA cm^{-2}, and a FF of 0.62 under simulated AM 1.5 G (100 mW cm^{-2}) conditions, resulting in an estimated power conversion efficiency (η) of 4.88%. For the purpose of direct comparison, a PCDTBT:PC$_{71}$BM device was also fabricated, and an efficiency of 3.34% was achieved (Table 1). Fig. 2(d) compares the external quantum efficiency (EQE) spectra of devices fabricated using PCDTBT:PC$_{71}$BM

Table 1 FET and PSC performances of PCDTTz and PCDTBT

Polymer	μ^a/ cm^2 V^{-1} s^{-1}	$I_{on}/I_{off}{}^a$	$V_{OC}{}^b$/V	$J_{SC}{}^b$/ mA cm^{-2}	FF^b	η^b (%)
PCDTTz	3.8×10^{-3}	10^5	0.86	9.15	0.62	4.88
PCDTBT	1.7×10^{-4}	10^5	0.82	8.84	0.46	3.34

[a] The field-effect carrier mobilities and on/off current ratios of the polymers were investigated by fabricating FETs with bottom-contact geometry using Au electrodes. [b] The device was fabricated with the structure of ITO/PEDOT:PSS/polymer:PC$_{71}$BM/LiF/Al.

and PCDTTz:PC$_{71}$BM materials. Convolution of the spectral response with the photon flux of the AM 1.5 G spectrum (100 mW cm^{-2}) provided an estimate for the J_{SC} under irradiation. The calculated J_{SC} for PCDTTz devices was 8.11 mA cm^{-2}. Due to the mismatch between the EQE and the photon flux under AM 1.5 G illumination, an approximate mismatch of 11% was present between the convolution and solar simulator data.

To the best of our knowledge, a PCE as high as 4.88% has not been reported for polymer solar cells based on polymers with a band gap above 2.0 eV.

In summary, a highly processable, new semiconducting polymer, PCDTTz, based on alternating carbazole and thiazolothiazole units was synthesized. Polymer solar cells prepared from blends of this polymer with fullerene derivatives exhibited high solar energy conversion efficiencies of 4.88% without special treatments. Considering the field-effect carrier mobility and photovoltaic properties of PCDTTz, this polymer exhibits promising potential as a candidate for next generation solar cell materials. Moreover, this polymer constitutes a requisite large band gap material for tandem construction of PSCs that absorb well over a broad visible spectrum when combined with narrow band gap polymers with a band gap of less than 1.74 eV. Considering that the PCE of PSCs based on PCDTBT increased from 3.6% to 6.1% when titanium oxide was used as the optical spacer and hole blocking layer,[3] ongoing investigations into PCDTTz are predicted to deliver even better performance enhancements.

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Notes and references

1 H.-Y. Chen, J. H. Hou, S. Q. Zhang, Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649.

2 J.-H. Park, D. S. Chung, D. H. Lee, H. Kong, I. H. Jung, M.-J. Park, N. S. Cho, C. E. Park and H.-K. Shim, *Chem. Commun.*, 2010, **46**, 1863.

3 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.

4 F. C. Krebs, J. Fyenbo and M. Jorgensen, *J. Mater. Chem.*, 2010, **20**, 8994.

5 H. Kim, W.-W. So and S.-J. Moon, *Sol. Energy Mater. Sol. Cells*, 2007, **91**, 581.

6 F. C. Krebs, T. Tromholt and M. Jorgensen, *Nanoscale*, 2010, **2**, 873.

7 F. C. Krebs, T. D. Nielsen, J. Fyenbo, M. Wadstrom and M. S. Pedersen, *Energy Environ. Sci.*, 2010, **3**, 512.

8 J.-Y. Jung, Z. Guo, S. -W. Jee, H.-D. Um, K.-T. Park and J.-H. Lee, *Opt. Express*, 2010, **18**, A286.

9 G. Zhang, Y. Fu, Q. Zhang and Z. Xie, *Chem. Commun.*, 2010, **46**, 4997.

10 G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf and C. J. Brabec, *Adv. Mater.*, 2008, **20**, 579.

11 J. F. Morin and M. Leclerc, *Macromolecules*, 2002, **35**, 8413.

12 S. K. Lee, N. S. Cho, J. H. Kwak, S. K. Lim, H.-K. Shim, D.-H. Hwang and C. J. Brabec, *Thin Solid Films*, 2006, **511**, 157.

13 Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, G. Li and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 56.

14 I. H. Jung, Y. K. Jung, J. Lee, J.-H. Park, H. Y. Woo, J.-I. Lee, H. Y. Chu and H.-K. Shim, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7148.

15 I. Osaka, R. Zhang, G. Sauve, D. Smilgies, T. Kowalewski and R. D. McCullough, *J. Am. Chem. Soc.*, 2009, **131**, 2521.

16 I. Osaka, G. Sauve, R. Zhang, T. Kowalewski and R. D. McCullough, *Adv. Mater.*, 2007, **19**, 4160.

17 H.-Y. Chen, J. Hou, A. E. Hayden, H. Yang, K. N. Houk and Y. Yang, *Adv. Mater.*, 2010, **22**, 371.

18 M. M. Wienk, M. Turbiez, J. Gilot and R. A. J. Janssen, *Adv. Mater.*, 2008, **20**, 2556.

19 J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222.

20 S. Sista, M.-H. Park, Z. Hong, Y. Wu, J. Hou, W. L. Kwan, G. Li and Y. Yang, *Adv. Mater.*, 2010, **22**, 380.

21 N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, **19**, 2295.

22 A. Gadisa, W. Mammo, L. M. Andersson, S. Admassie, F. Zhang, M. R. Andersson and O. Inganäs, *Adv. Funct. Mater.*, 2007, **17**, 3836.

23 S. K. Lee, D.-H. Hwang, B.-J. Jung, N. S. Cho, J. Lee, J.-D. Lee and H.-K. Shim, *Adv. Funct. Mater.*, 2005, **15**, 1647.

24 S. K. Lee, N. S. Cho, S. Cho, S.-J. Moon, J. K. Lee and G. C. Bazan, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6873.

25 L.-M. Chen, Z. Hong, G. Li and Y. Yang, *Adv. Mater.*, 2009, **21**, 1434.