

Donor–acceptor polymers based on multi-fused heptacyclic structures: synthesis, characterization and photovoltaic applications†

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Received 12th February 2010, Accepted 1st April 2010

First published as an Advance Article on the web 14th April 2010

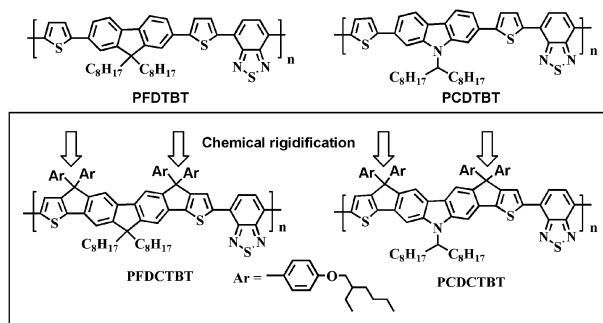
DOI: 10.1039/c003040f

We report here two novel 2,7-fluorene- and 2,7-carbazole-based conjugated polymers PFDCTBT and PCDCTBT containing ladder-type heptacyclic structures with forced planarity. PCDTBT shows excellent solubility, low band gap and high hole mobility, leading to a power conversion efficiency of 3.7%.

Over the past few years, tremendous research effort has been made on all-solution processed polymer solar cells (PSCs) in order to realize low-cost, light-weight, large-area and flexible photovoltaic devices. PSCs based on the concept of bulk heterojunction (BHJ) are the most widely adopted device architecture to ensure maximum internal donor–acceptor (D–A) interfacial area for efficient charge separation.¹ To achieve high efficiency of PSCs, the most critical challenge at the molecular level is to develop p-type conjugated polymers that simultaneously possess (1) sufficient solubility to guarantee solution processability and miscibility with an n-type material, (2) low band gap (LBG) for strong and broad absorption spectrum to capture more solar photons and (3) high hole mobility for efficient charge transport. The most effective approach to produce a LBG polymer is to incorporate electron-rich donor and electron-deficient acceptor segments along the conjugated polymer backbone.² Tricyclic 2,7-fluorene³ and 2,7-carbazole⁴ units have emerged as promising electron-rich building blocks to construct D–A polymers because their derivatives are shown to have deep-lying HOMO energy levels and good hole-transporting properties which are crucial prerequisites to achieve high open-circuit voltages (V_{oc}) and short circuit currents (J_{sc}), respectively. Besides, the electron-rich thiophene unit is the most important key element ubiquitously incorporated into D–A conjugated polymers to adjust the optical and electronic properties to optimal levels.⁵ For instance, alternating copolymers poly(2,7-fluorene-*alt*-dithienylbenzothiadiazole) (PFDTBT)⁶ and poly(2,7-carbazole-*alt*-dithienylbenzothiadiazole) (PCDTBT)⁷ have been proven to be a promising class of p-type photoactive materials for application in PSCs (Scheme 1). In addition to the D–A strategy, forced planarization by covalently fastening adjacent aromatic units in the polymer backbone strengthens the parallel p-orbital interactions to elongate effective conjugation length and facilitate π -electron delocalization, providing an

effective way to reduce the band gap.⁸ Moreover, coplanar geometries and rigid structures can suppress the rotational disorder around interannular single bonds and lower the reorganization energy, which in turn enhances the intrinsic charge mobility.⁹ However, too strong inter-chain π – π stacking interactions arising from the high degree of coplanarity tend to make the polyaromatic conjugated polymers insoluble and unprocessable. In this communication, we wish to report two novel D–A copolymers poly(fluorene-dicyclopentathiophene-*alt*-benzothiadiazole) (PFDCTBT) and poly(carbazole-dicyclopentathiophene-*alt*-benzothiadiazole) (PCDCTBT). Both polymers were designed based on the skeletons of the well-known PFDTBT and PCDTBT polymers in order to fully take advantage of their excellent properties. The structural uniqueness of PFDCTBT and PCDCTBT is that the 3-positions of two outer thiophenes are covalently tied with the 3,6-position of central fluorene or carbazole cores by a carbon bridge, forming two cyclopentadienyl (CP) rings embedded in a multi-fused heptacyclic structure (Scheme 1). Two additional substituents attached at the CP rings allow for tailoring the intermolecular interactions without causing twisting between the adjacent units, making the resulting polymers highly soluble. A preliminary test of the photovoltaic performance based on these polymers shows promise for solar cell applications.

The synthesis of the monomers **M1** and **M2** is depicted in Scheme 2. 2,7-Diboronic esters fluorene **1a** and carbazole **1b** were reacted with ethyl 2-bromothiophene-3-carboxylate **2** by Suzuki coupling to obtain compounds **3a** and **3b** respectively. Double nucleophilic addition of freshly prepared 4-(2-ethylhexyloxy)phenyl magnesium bromide **4** to the ester groups of **3** led to the formation of benzylic alcohol **5** which was subjected to intramolecular annulation through acid-mediated

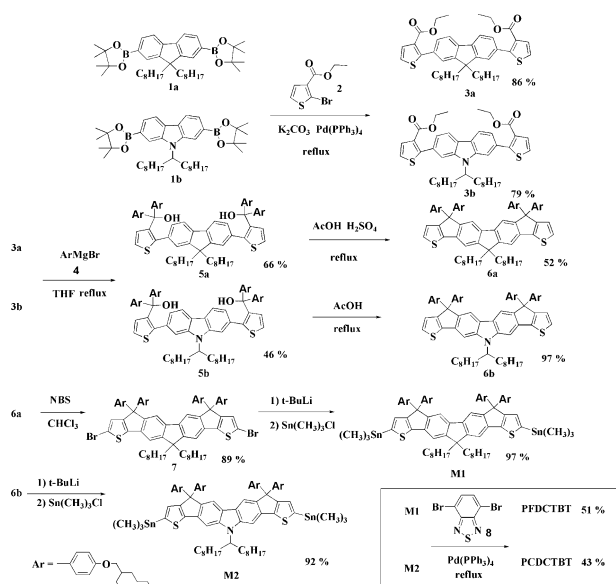


Scheme 1 Chemical structures of non-fused PFDTBT, PCDTBT polymers and fused PFDCTBT, PCDCTBT polymers.

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c003040f



Scheme 2 Synthetic route of the **M1** and **M2** monomers leading to the targeted polymers **PFDCBT** and **PCDCBT**.

Friedel–Crafts reaction to furnish the fused heptacyclic arene **6**. Because of the strong nitrogen-directing effect of the carbazole to facilitate the regioselective cyclization, **6b** was obtained in nearly quantitative yield of 97% in the presence of AcOH, whereas using stronger acids H₂SO₄/AcOH was required to generate **6a** in a moderate yield of 52%. Carbazole-based **6b** can be efficiently lithiated by *t*-butyllithium through deprotonation followed by reacting with trimethyltin chloride to afford the distannyllithium **M2**. However, fluorene-based **6a** was brominated to yield compound **7** which was then lithiated to obtain distannyllithium **M1**. **M1** and **M2** were copolymerized with the acceptor 4,7-dibromo-2,1,3-benzothiadiazole **8** by Stille coupling to give **PFDCBT** ($M_n = 8.5$ kDa, PDI = 1.89) and **PCDCBT** ($M_n = 8.2$ kDa, PDI = 1.59), respectively. Thanks to the branched 2-ethylhexyloxy side chains as the solubilizing groups, both polymers show excellent solubilities in common organic solvents, such as chloroform, toluene, dichlorobenzene, overcoming the planarity–solubility tradeoff to facilitate their processability.

The thermal stability was analyzed by thermogravimetric analysis (TGA). **PFDCBT** and **PCDCBT** exhibited sufficiently high decomposition temperatures (T_d) of 410 °C and 434 °C, respectively, indicating that carbazole-based **PCDCBT** is thermally more stable than fluorene-based **PFDCBT** (Fig. S1, ESI†).

Both **PFDCBT** and **PCDCBT** exhibited two characteristic bands in the absorption spectra (Fig. 1). The shorter wavelength absorbance comes from the π – π^* transition of the heptacyclic units, while the lower energy band is attributed to the intramolecular charge transfer (ICT) between the electron-rich and the benzothiadiazole segments. Compared to **PFDCBT** showing the absorption maxima at 411 nm and 580 nm in the thin film, **PCDCBT** exhibited a similar absorption maximum at 412 nm but a bathochromic shift of the ICT band at 607 nm. In addition, the optical band gaps (E_g^{opt}) deduced from the onset of absorption in the solid state are determined to be 1.76 eV (703 nm) for **PFDCBT**

and 1.66 eV (746 nm) for **PCDCBT**. These results suggest that the donating strength of carbazole is stronger than that of the fluorene moiety, shifting the ICT band of **PCDCBT** to lower energy. It should be emphasized that **PFDCBT** and **PCDCBT** have more red-shifted absorption spectra and smaller band gaps in comparison with their corresponding non-fused **PFDTBT** ($E_g^{\text{opt}} = 1.87$ eV) and **PCDTBT** ($E_g^{\text{opt}} = 1.88$ eV) analogues, demonstrating that the electron coupling between the rigidified donor and the acceptor units is enhanced. Because two 4-(2-ethylhexyloxy)phenyl moieties substituted at the carbon of CP rings may dilute strong intermolecular π – π interactions, the profiles of absorption spectra of **PFDCBT** and **PCDCBT** are essentially unchanged with slight broadening of the bands and red shift of the band edges from the solution state to the solid state. This result implies the amorphous nature of the polymers which can be further confirmed by no obvious thermal transition in the differential scanning calorimetry measurements (Fig. S2, ESI†). It is worth noting that the intensities of the shorter wavelength bands of both polymers in the solid state are apparently stronger than those in the solution state, which also suggests that the rigid and coplanar heptacyclic units can enhance their light absorption ability in the solid state.

Cyclic voltammetry (CV) was employed to examine the electrochemical properties (Fig. 2). Both polymers showed a stable and reversible p-doping/n-doping process in the cathodic and anodic scans. The HOMO levels being estimated to be -5.32 eV for **PFDCBT** and -5.38 eV for **PCDCBT** are in an ideal range to assure better air-stability and greater attainable V_{oc} in the final device.¹⁰ The LUMO energy levels are approximately located at -3.55 eV for **PFDCBT** and -3.61 eV for **PCDCBT**, which are positioned 0.2–0.3 eV above the LUMO level of the PC₇₁BM acceptor (3.8 eV) to ensure energetically favorable electron transfer.¹¹ This can be unambiguously evidenced by the complete photoluminescence quenching in the film of the **PFDCBT**/PC₇₁BM and **PCDCBT**/PC₇₁BM (1 : 2, w/w) blends (Fig. S3, ESI†).

Despite their amorphous nature, **PFDCBT** and **PCDCBT** show good hole transporting properties due to their rigid and coplanar structures. Based on the space-charge-limited current (SCLC) method, **PFDCBT** and **PCDCBT** exhibited high hole mobilities within the same order of magnitude (2.5×10^{-4} cm²/Vs and 1×10^{-4} cm²/Vs, respectively). On the basis of ITO/PEDOT:PSS/polymer:PC₇₁BM(1 : 2, w/w)/Ca/Al configuration, bulk heterojunction solar cells were fabricated and characterized under simulated 100 mW cm⁻² AM 1.5 G illumination. The current density–voltage characteristics of the devices are shown in Fig. 3. Without extensive

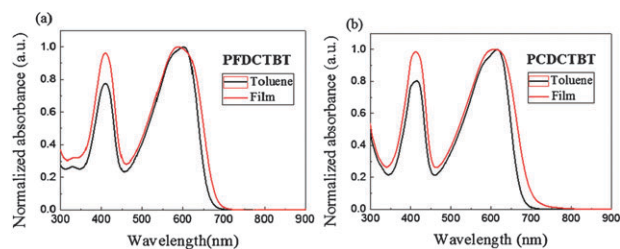


Fig. 1 Normalized absorption spectra of **PFDCBT** (a) and **PCDCBT** (b) in toluene solution and the solid state.

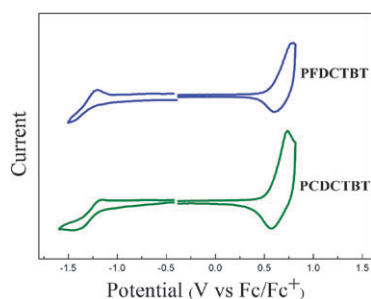


Fig. 2 Cyclic voltammograms of **PFDCTBT** and **PCDCTBT** in the thin film at a scan rate of 30 mV s^{-1} .

optimization, the preliminary photovoltaic performance based on **PFDCTBT** already showed a J_{sc} of 9.5 mA cm^{-2} , a V_{oc} of 0.77 V , a fill factor (FF) of 0.38 , leading to a decent PCE of 2.8% . More encouragingly, the device using **PCDCTBT** as the p-type material delivered superior performance with a J_{sc} of 10.7 mA cm^{-2} , a V_{oc} of 0.80 V , a FF of 0.43 , improving the PCE to 3.7% .

To further evaluate the hole mobility in the BHJ active layer, hole-only devices (ITO/PEDOT:PSS/polymer:PC₇₁BM (1:2, w/w)/Au) were fabricated. It is found that the hole mobility of the **PCDCTBT**/PC₇₁BM composite ($4 \times 10^{-4} \text{ cm}^2/\text{Vs}$) is higher than that of the **PFDCTBT**/PC₇₁BM ($5 \times 10^{-5} \text{ cm}^2/\text{Vs}$) blend under the same fabrication conditions. The enhanced hole mobility of the **PCDCTBT**/PC₇₁BM active layer might be responsible for its better photovoltaic performance over the **PFDCTBT**-based device. It is also noteworthy that the surface roughness of the **PCDCTBT**/PC₇₁BM blend observed by AFM is larger than that of the **PFDCTBT**/PC₇₁BM blend (Fig. S4, ESI†).

In summary, by utilization of facile Friedel–Crafts cyclization, we have successfully synthesized two well-designed heptacyclic monomers **M1** and **M2** in which two outer thiophene subunits are covalently fastened to the central 2,7-fluorene and 2,7-carbazole cores, respectively. Rigid, coplanar and electron-rich **M1** and **M2** were copolymerized with the electron-deficient benzothiadiazole acceptor by Stille coupling to afford two novel D–A polymers **PFDCTBT** and **PCDCTBT**, respectively. Through such a simple and straightforward engineering of molecular structures, **PFDCTBT** and **PCDCTBT** simultaneously possess excellent solubilities for solution-processability, low band gaps with suitable position of HOMO/LUMO energy levels, and high hole mobilities, leading to promising

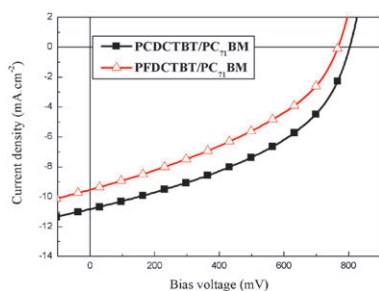


Fig. 3 Current density–voltage characteristics of ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al devices under illumination of AM 1.5 G, 100 mW cm^{-2} .

PCEs of 2.8% and 3.7% , respectively. We anticipate that further improvement of device performance is highly achievable through carefully optimizing the processing conditions which are ongoing in our laboratory.

This work is supported by the National Science Council and “Aim for the Top University Plan” of the National Chiao Tung University and Ministry of Education, Taiwan.

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