Crystalline low band-gap alternating indolocarbazole and benzothiadiazole-cored oligothiophene copolymer for organic solar cell applications†‡

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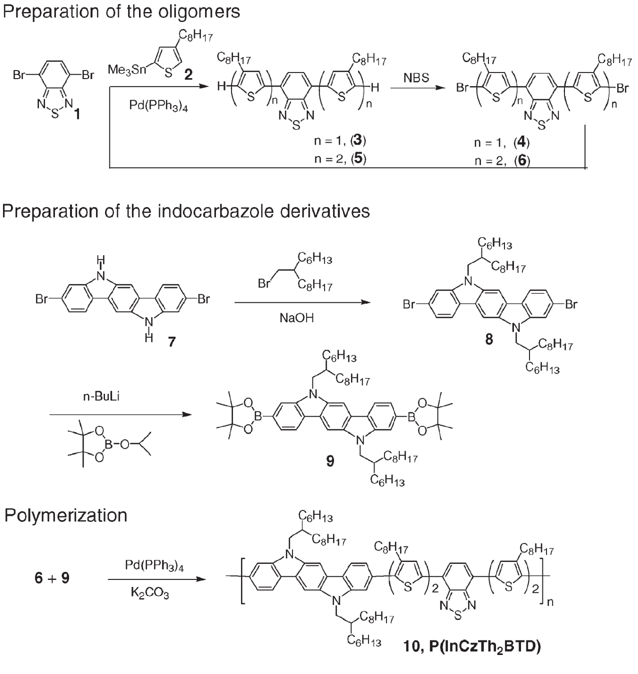
A low band-gap alternating copolymer of indolocarbazole and benzothiadiazole-cored oligothiophene demonstrated balanced crystallinity and solubility; a solar cell combining this polymer with $PC_{61}BM$ in a preliminary test demonstrated power conversion efficiencies of 3.6%.

Low cost, high efficiency and long term stability are the key factors for commercializing photovoltaic (PV) technology. Organic PV is one of the most promising candidates due to the low material cost and compatibility with the high throughput wet processes.[1] Although significant progresses have been made in organic solar cells based on heterojunction networks of p- and n-type materials in the past 10 years, the cell power conversion efficiency (PCE) of 5–6% on laboratory scale is still too low.[2] To further enhance the PCE, it is of paramount importance to develop new p-type organic/polymer semiconductors with high charge mobility and narrow energy band gaps.[1i]

The concept of internal electron donor–acceptor (D–A) interaction has been extensively exploited to prepare low band-gap organic semiconductors.[3] Using this strategy, new low band-gap materials have been developed to better cover the solar spectrum, especially in the 1.4–1.9 eV region.[4] In addition, it is generally accepted that the formation of strong intermolecular π–π stacking is necessary to achieve high charge mobility in organic semi-conductors. Rigid coplanar fused aromatic rings efficiently enhance this interaction and hence improve charge mobilities.[5,6] Therefore, copolymers consisting of an electron-accepting benzothiadiazole-cored oligothiophene and an electron-donating indolo[3,2-*b*]carbazole unit has been designed. We expect this polymer would have narrow band-gaps and high charge mobility owing to the large fused heterocyclic aromatic ring of indolocarbazole and the D–A structure in the polymer backbone.

Meanwhile, a sufficient amount of flexible substituent has to be introduced to the polymer as side chains to improve the solubility for solution processing. As a side effect, these side chains may dilute the content of electroactive components and lower the polymer crystallinity, resulting in lower charge mobility. We report herein an innovative way to balance the solubility and crystallinity of conjugated polymers by rationally designing the structures and patterns of the substitutent, so that high charge mobility of the polymers can be maintained.

The synthesis of the benzothiadiazole-cored oligothiophenes involved a repetitive bromination and Stille coupling procedure starting from commercially available 2,1,3-benzothiadiazole (Scheme 1). Each cycle extended the resulting oligomers by adding one more thiophene unit on each side of the benzothiadiazole core. It is worth pointing out that the bromination condition was different for each cycle in order to get high bromination yield at the desired position. For example, 4,7-dibromo-2,1,3-benzothiadiazole (**1**) was synthesized using liquid Br_2 as the brominating agent in a refluxing



Scheme 1 Synthetic route to **P(InCzTh$_2$BTD)**.

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47% HBr solution,[7] while 4,7-bis(4-octyl-2-thienyl)-2,1,3-benzothiadiazole (**3**) was brominated with *N*-bromosuccinimide (NBS) at room temperature in the presence of silica gel as a catalyst. The bromination of 4,7-bis(3,4′-dioctyl-2,2’-bithiophen-5-yl)-2,1,3-benzothiadiazole (**5**) should be done under even milder condition, at −10 °C to avoid the bromination at the other positions. 3,9-Dibromoindolo[3,2-*b*]carbazole was synthesized based on literature procedures,[8] and then alkylated with 2-ethylhexyl bromide, 2-butyloctyl bromide or 2-hexyldecyl bromide. The resulting alkylated dibromoindolocarbazoles were converted to the corresponding diboronates *via* lithiation with *n*-butyllithium at −78 °C, followed by the treatment with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Low band-gap conjugated polymers were synthesized by Suzuki coupling reaction between indolocarbazole diboronates and benzothiadiazole-cored oligothiophene dibromides in refluxing toluene using $Pd(PPh_3)_4$ as a catalyst under Ar. It was found that when the alkyl group attached at the N atoms of indolocarbazole was 2-ethylhexyl, the solubility of the resulting polymer in organic solvents was very poor. The solubility was improved when the size of alkyl chain was increased from C_8 (2-ethylhexyl) to C_{12} (2-butyloctyl), leading to an enhanced solubility in hot dichlorobenzene. However, being soluble only in hot solvents is not convenient for device fabrication. With the aim of further enhancing the solubility, a branched C_{16} chain (2-hexyldecyl) was selected and the obtained polymers, **P(InCzTh$_2$BTD)** were easily soluble in chlorinated hydrocarbons such as chlorobenzene, dichlorobenzene and chloroform even at room temperature. The polymer is also well soluble in the polymerization solution, possesses a high molecular weight (M_n = 19.5 kDa) with a narrow distribution (PDI = 2.08), and was obtained in high yield (above 80%). The purity was confirmed by elemental analysis.

The absorption spectra of **P(InCzTh$_2$BTD)** measured in chloroform are characterized with a strong, broad and structureless absorption peak at 538 nm ($\lambda^{abs}{}_{max}$), corresponding to the intramolecular charge-transfer (ICT) transition, together with a strong absorption band at shorter wavelength (~395 nm) owing to higher energy transitions such as a π–π* transition. Fig. 1 shows that the polymer emits deep red fluorescence in $CHCl_3$ solution with an emission peak at 691 nm, regardless of excitation at 400 or 535 nm. This suggests that there is a very efficient energy transfer from the indolocarbazole unit to the benzothiadiazole-cored oligothiophene unit. Compared with the solution absorption, the film sample prepared by spin-coating a dichlorobenzene solution using a slow solvent evaporation process,[2c] showed pronounced peak broadening and a significant red shift of ~100 nm of the absorption edge. More importantly, this feature remained in the polymer/$PC_{61}BM$ blending film used in the PV device (see ESI‡). This phenomenon is attributed to the planarization of aryl rings and the presence of interchain interactions in the solid state.[9] More interestingly, in contrast to the strong solution fluorescence, the thin films only exhibited very weak fluorescence (not shown). This suggests the formation of strong interchain interaction in the solid state, leading to fluorescence self-quenching.[10]

The thermal properties of **P(InCzTh$_2$BTD)** were analyzed by DSC and TGA, showing high thermal stability with onset decomposition temperatures >410 °C under nitrogen. Fig. 2 shows that the polymer has a strong tendency to crystallize, as evidenced by the appearance of a very sharp crystallization peak at 209 °C, and the lack of an apparent glass transition. The heats of melting and crystallization are both about 17 J g^{-1}, similar to regioregular P3HT.[11] The physical properties of the polymer are summarized in Table 1.

Cyclic voltammetry (CV) measurements of this polymer were carried out under argon in a three-electrode cell using 0.1 M Bu_4NPF_6 in anhydrous CH_3CN as the supporting electrolyte. The polymers were coated on the platinum-working electrode. The CV curves were recorded referenced to an Ag quasi-reference electrode, which was calibrated using a ferrocene–ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level) as an external standard. The $E_{1/2}$ of the Fc/Fc^+ redox couple was found to be 0.40 V *vs.* the Ag quasi-reference electrode. The CV scans of the polymer film resulted in highly reproducible cathodic reduction and anodic oxidation processes (see ESI‡), indicating a potentially high stability of the material for both hole and electron injection. As shown in Fig. 3, an additional reduction peak was observed for **P(InCzTh$_2$BTD)**, probably owing to the electron-withdrawing benzothiadiazole units in the polymer backbone. The formation of this peak narrowed the energy gap, in comparison with P3HT.[2] Meanwhile, its HOMO energy level remains low at ~5.17 eV, which is important for maintaining the large open-circuit voltage (V_{oc}) and high air stability.

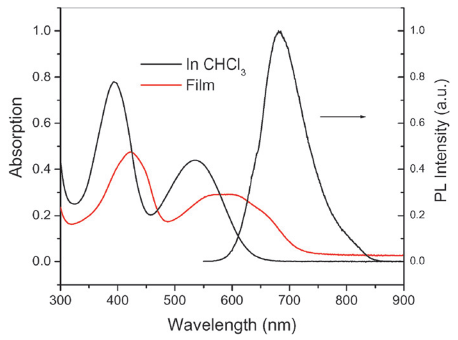

Fig. 1 Absorption spectra of **P(InCzTh$_2$BTD)** in chloroform and in a thin film of 100 nm in thickness; its fluorescence spectrum in chloroform is also included.

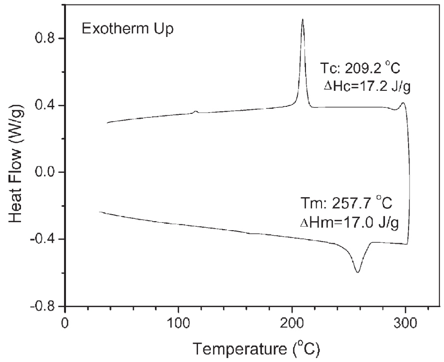

Fig. 2 DSC curves of **P(InCzTh$_2$BTD)** at a heating–cooling rate of 10 °C min^{-1} under nitrogen.

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Table 1 Physical properties of **P(InCzTh$_2$BTD)**

$\lambda^{abs}{}_{max}$/nm ($10^{-4}\varepsilon_{max}$/M^{-1} cm^{-1})[a]	538 (4.39)
$E^{ox}{}_{1/2}$; $E^{red}{}_{1/2}$/V[b]	1.13; −1.29, −1.75
HOMO, LUMO/eV[c]	−5.17, −3.15
$E_g{}^{O}$,[d] $E_g{}^{E}$[e]/eV	1.89, 2.02
T_m[f], T_{decomp}[g]/°C	258, 424

[a] Measured in $CHCl_3$. [b] Half wave potential referred to Ag quasi-reference electrode. [c] Calculated from onset potentials. [d] Optical energy gap estimated from the absorption edge of polymer solutions in $CHCl_3$. [e] Energy gap = HOMO − LUMO. [f] Determined by DSC from 2nd heating after cooling with a rate of 10 °C min^{-1} under N_2. [g] 1 wt% Loss temperature, determined by TGA with a heating rate of 10 °C min^{-1} under N_2.

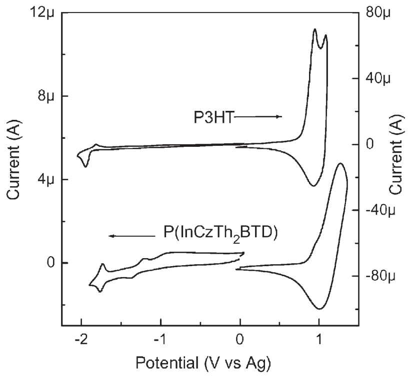

Fig. 3 Cyclic voltammograms of **P(InCzTh$_2$BTD)** and **P3HT** thin films on Pt electrode in 0.1 M Bu_4NPF_6 acetonitrile solution at 50 mV min^{-1}.

The potential of this polymer to be used as a hole-transporting light-absorbing component in photovoltaic cells were explored. Bulk heterojunction PV cells with a device structure of ITO|PEDOT-PSS|**P(InCzTh$_2$BTD)** : $PC_{61}BM$ (1 : 2 w/w)|LiF (1 nm)|Al (100 nm) were fabricated using a slow solvent evaporation process.[2c] Fig. 4 shows the current–voltage characteristics of the fabricated PV cells in the dark and under the AM 1.5 simulated solar illumination at irradiation intensity of 100 mW cm^{-2}. These PV cells gave relatively larger V_{oc} than P3HT based devices (0.60 V), which are attributed to the high oxidation potential of **P(InCzTh$_2$BTD)**. These devices also exhibited low series resistance (~10.3 Ω cm^2), implying higher charge mobility, being related to the higher crystallization tendency of the polymer as shown in Fig. 2. As a result, PCE = 3.6%, V_{oc} = 0.69 V, short circuit current (J_{sc}) = 9.17 mA cm^{-2}, and fill factor (FF) = 0.57 have been obtained in some preliminary devices. This result confirms our previous finding that high crystallinity of the photoactive material is important to achieve high device performance.[12] In future work, we will focus on device optimization to further improve device efficiency and stability.

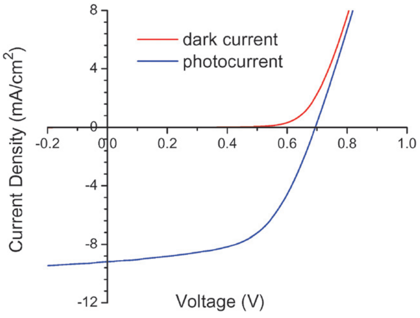

Fig. 4 Current density–voltage characteristics of the **P(InCzTh$_2$BTD)** based devices under AM 1.5 simulated solar illumination of 100 mW cm^{-2}.

Notes and references

1 (*a*) N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474; (*b*) G. Yu, J. Gao, C. J. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789; (*c*) C. J. Brabec, N. S. Sariciftci and C. J. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 15; (*d*) K. M. Coakley and M. D. McGehee, *Chem. Mater.*, 2004, **16**, 4533; (*e*) H. Spanggaard and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 125; (*f*) H. Hoppe and N. S. Sariciftci, *J. Mater. Chem.*, 2006, **16**, 45; (*g*) R. A. J. Janssen, J. C. Hummelen and N. S. Sariciftci, *MRS Bull.*, 2005, **30**, 33; (*h*) S. E. Shaheen, D. S. Ginley and G. E. Jabour, *MRS Bull.*, 2005, **30**, 1; (*i*) S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324; (*j*) M. T. Lloyd, J. E. Anthony and G. G. Malliaras, *Mater. Today*, 2007, **10**(11), 34; (*k*) M. Jørgensen, K. Norrman and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2008, **92**, 686.

2 (*a*) Y. Kim, S. A. Choulis, J. Nelson, D. D. C. Bradley, S. Cook and J. R. Durrant, *Appl. Phys. Lett.*, 2005, **86**, 63502; (*b*) W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, *Adv. Funct. Mater.*, 2005, **15**, 1617; (*c*) G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 826; (*d*) Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. Mcculloch, C. S. Ha and M. Ree, *Nat. Mater.*, 2006, **5**, 197; (*e*) J. Peet, J. Y. kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497; (*f*) J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222.

3 Review articles for low band gap polymers: (*a*) C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, 2004, **14**, 1077; (*b*) E. Bundgaard and F. C. Krebs, *Sol. Mater. Energy Sol. Cells*, 2007, **91**, 954.

4 (*a*) D. Mülbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Mater.*, 2006, **18**, 2884; (*b*) K. Schulze, C. Uhrich, R. Schüppel, K. Leo, M. Pfeiffer, E. Brier, E. Reinold and P. Bäuerle, *Adv. Mater.*, 2006, **18**, 2872; (*c*) S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *J. Am. Chem. Soc.*, 2006, **128**, 3459; (*d*) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2008, **130**, 732.

5 (*a*) M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986; (*b*) S. T. Bromley, M. Mas-Torrent, P. Hadley and C. Rovira, *J. Am. Chem. Soc.*, 2004, **126**, 6544; (*c*) I. Mcculloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. Chabinyc, R. Kline, M. McGehee and M. Toney, *Nat. Mater.*, 2006, **5**, 328.

6 (*a*) Y. Li, Y. Wu, S. Gardner and B. S. Ong, *Adv. Mater.*, 2005, **17**, 849; (*b*) P.-L. T. Boudreault, S. Wakim, N. Blouin, M. Simard, C. Tessier, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2007, **129**, 9125; (*c*) S. Wakim, J. Bouchard, M. Simard, N. Drolet, Y. Tao and M. Leclerc, *Chem. Mater.*, 2004, **16**, 4386.

7 Q. Hou, Q. Zhou, Y. Zhang, W. Yang, R. Yang and Y. Cao, *Macromolecules*, 2004, **37**, 6299.

8 (*a*) L. N. Yudina and J. Bergman, *Tetrahedron*, 2003, **59**, 1265; (*b*) N. Blouin, M. Leclerc, B. Vercelli, S. Zecchin and G. Zotti, *Macromol. Chem. Phys.*, 2006, **207**, 175.

9 P. J. Brown, D. S. Thomas, A. Köhler, J. S. Wilson, J. S. Kim, C. M. Ramsdale, H. Sirringhaus and R. H. Friend, *Phys. Rev. B: Condens. Matter. Mater. Phys.*, 2003, **67**, 642031.

10 T. Swager, *Nat. Mater.*, 2002, **1**, 151.

11 (*a*) S. Malik and A. K. Nandi, *J. Polym. Sci. Part B: Polym. Phys.*, 2002, **40**, 2073; (*b*) H. Yang, T. J. Shin, L. Yang, K. Cho, C. Y. Ryu and Z. Bao, *Adv. Funct. Mater.*, 2005, **15**, 671.

12 J. Lu, P. Xia, P. Lo, Y. Tao and M. Wong, *Chem. Mater.*, 2006, **18**, 6194.