

Isoindigo fluorination to enhance photovoltaic performance of donor–acceptor conjugated copolymers†

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Yuchong Yang, Renming Wu, Xin Wang,* Xiaopeng Xu, Zuoja Li, Kai Li and Qiang Peng*

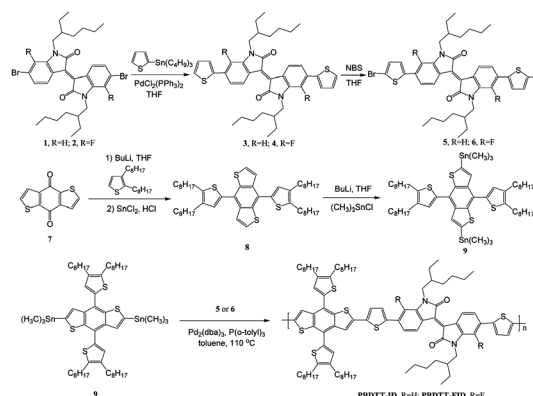
Conjugated copolymers based on isoindigo/fluorinated isoindigo and bis(dialkylthienyl)benzodithiophene, PBDTT-ID and PBDTT-FID, were designed and synthesized for organic photovoltaic applications. The isoindigo fluorination made PBDTT-FID show high PCE of 5.52% and 7.04% in its conventional and inverted PSCs, respectively.

Recently, tremendous efforts on low band gap (LBG) copolymers and their polymer solar cells (PSCs) have been devoted to improve the power conversion efficiencies (PCEs) from 1% to over 10%.¹ Isoindigo (ID) was newly developed as an efficient acceptor block due to the strong electron-withdrawing character and large optical transition dipole of two lactam rings. Reynolds *et al.* reported the first ID-based photovoltaic oligomer, exhibiting a PCE of 1.76%.² Andersson *et al.* synthesized a new ID-based copolymer, PTI-1, using thiophene as a donor block with designed side chains. PSCs fabricated from PTI-1 and PC₇₁BM as the photoactive layer showed a PCE of 6.3%.³ Other ID-based copolymers containing different donor blocks, such as dithienosilole, benzodithiophene, naphthalene, anthracene and cyclopentadithiophene, were also synthesized and investigated later.⁴ The ID-based polymers reported so far exhibit broad absorption and the low-lying HOMO (−5.50 to −5.90 V) and LUMO (−3.70 to −4.00 V) with low band gaps ranging from 1.3 to 1.8 eV. In addition, they possess high carrier mobilities. Pei *et al.* reported ID-based conjugated polymers with hole mobility up to 1.06 cm² V^{−1} s^{−1}.⁵ Bao *et al.* introduced siloxane-terminated solubilizing groups on the isoindigo skeleton for shortening the π – π stacking distance, which improved the hole mobility to 2.48 cm² V^{−1} s^{−1}.⁶ After this, Pei *et al.* reported another fluorinated ID-based polymer PFI2T with good ambient stability. The electron mobility increased from 10^{−2} to 0.43 cm² V^{−1} s^{−1} with high hole mobility up to 1.85 cm² V^{−1} s^{−1}.⁷

In this communication, we firstly reported the design and synthesis of the D–A photovoltaic copolymers of isoindigo (ID)/fluorinated

isoindigo (FID) and bis(dialkylthienyl) benzodithiophene (BDTT), PBDTT-ID and PBDTT-FID, along with their detailed characterization. The BDTT unit is selected as a donor block because the thienyl-substitution is helpful to broaden the absorption band, lower the HOMO level and improve hole mobility of the related copolymers.^{1c} Conventional PSCs fabricated from PBDTT-ID/PBDTT-FID and PC₇₁BM as the photoactive layer showed PCEs of 4.76% and 5.52% with high V_{oc} up to 0.94 V. Using an inverted device structure with a thin conjugated polyelectrolyte layer, PSCs based on PBDTT-FID achieved an impressively high PCE of up to 7.04%.

The synthesis of monomers and copolymers is depicted in Scheme 1. Detailed procedures for synthesis of copolymers are described in ESI.† PBDTT-ID and PBDTT-FID showed good solubility in common organic solvents, such as toluene, chloroform, chlorobenzene, dichlorobenzene, which could be attributed to the alkyl side chains attached on the BDTT and ID skeletons. As determined by GPC using THF as the eluent and monodisperse polystyrene as the standard, PBDTT-ID has a number-average molecular weight (M_n) of 36.8 kDa and a polydispersity index (PDI) of 2.41, while PBDTT-FID has a comparable M_n of 37.2 kDa and a larger PDI of 2.65. PBDTT-ID and PBDTT-FID showed good thermal stabilities with decomposition temperatures over 350 °C (5% weight loss)



Scheme 1 Synthetic route to PBDTT-ID and PBDTT-FID.

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, China.

E-mail: qiangpengjohnny@yahoo.com; Fax: +86-28-86510868; Tel: +86-28-86510868

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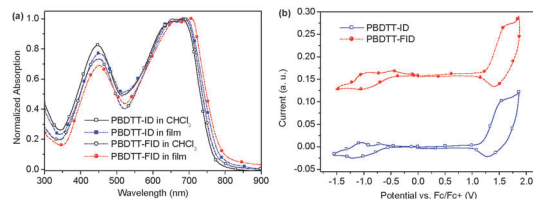


Fig. 1 (a) Normalized absorption spectra of PBDTT-ID and PBDTT-FID in chloroform solutions and as thin solid films. (b) Cyclic voltammograms of PBDTT-ID and PBDTT-FID films measured at a scan rate of 50 mV s⁻¹.

investigated by thermal gravimetric analysis (TGA), which are adequately suitable for PSC fabrications and evaluations. No phase transition was observed for both copolymers by differential scanning calorimetry (DSC) from room temperature to 300 °C.

The UV-vis absorption spectra of PBDTT-ID and PBDTT-FID in chloroform solution and in thin films are shown in Fig. 1a. Both copolymers exhibit a high energy absorption band due to π - π^* transition and a low-energy band due to intramolecular charge transfer. The vibrational shoulders in the longer wavelength region are attributed to aggregation resulting from strong polymer chain packing even in solutions.^{1a,8} In chloroform solution, PBDTT-ID showed broad absorptions with main peaks at 447, 649 and 679 nm. After introducing fluorine atoms, PBDTT-FID exhibited a red-shifted absorption. A similar behavior was observed in the absorption spectra of the polymer films. The slightly broader peaks in the wavelength range of 500–800 nm showed different red-shifts of 5, 13 nm and 10, 23 nm for PBDTT-ID and PBDTT-FID, respectively. The reason can be explained by the somewhat formation of π -stacked structures in the solid state. It is known that the fluorination can afford F-H, F- π_F and F-S interactions and efficiently enhance this aggregation of polymer backbones.^{1a,8} This phenomenon was also identified here by the broader absorption shape and pronounced shoulders of a low-energy absorption band of PBDTT-FID. The onset absorption edges of the thin films were at 777 nm and 783 nm for PBDTT-ID and PBDTT-FID, which determined the corresponding optical bandgaps to be 1.60 and 1.58 eV, respectively. Both copolymers show low bandgaps with broad absorption bands, which is very important to harvest more solar photons in their PSCs.

The HOMO and LUMO levels of the copolymers were measured by cyclic voltammetry. As shown in Fig. 1b, the onset oxidation potentials of PBDTT-ID and PBDTT-FID are located at 1.12 V and 1.24 V, leading to the corresponding HOMO levels to be -5.52 eV and -5.64 eV, respectively. The deep HOMO levels indicate that both copolymers are air stable and have desired high V_{oc} for PSCs.⁹ Isoindigo fluorination can effectively lower the HOMO level, and PBDTT-FID exhibits a 0.12 eV deeper HOMO level than that of PBDTT-ID, which is in agreement with our previous fluorinated copolymers.^{1c} On the other hand, the onset reduction potentials of PBDTT-ID and PBDTT-FID are positioned at -0.55 eV and -0.42 eV, resulting in the corresponding LUMO levels to be -3.85 eV and -3.98 eV, respectively. PBDTT-FID shows a deeper LUMO level than that of PBDTT-ID, indicating the positive effect of fluorine atoms due to their strong electron-withdrawing properties. The LUMO energy levels of both copolymers are aligned with fullerene derivatives (Fig. S1†), thus effective charge separation and transfer can be obtained.⁹ The electrochemical bandgaps (E_g) of

PBDTT-ID and PBDTT-FID were calculated to be about 1.67 and 1.66 eV. In order to explore the electronic properties of PBDTT-ID and PBDTT-FID, molecular simulations (BDTT-ID and BDTT-FID) were performed on their trimers.¹⁰ As shown in Fig. S2,† the localization of HOMO distributed in the middle part of the conjugated molecular system, but mainly focused on the donor skeletons. From a HOMO \rightarrow LUMO transition, the electron clouds of LUMO localized on the part of the ID fragment, which indicated that there was significant charge-transfer character. This is consistent with the observed strong low-energy absorption band in Fig. 1a. The electronic features of the corresponding donor and acceptor have an important effect on the HOMOs and LUMOs of the copolymers. However, the introduced fluorine atoms had a very little influence on the HOMO and LUMO distributions. Compared with HOMO, HOMO - 1 orbitals are mainly on the donor units, which implies that the internal charge transfer is possible. This transfer trend becomes more evident in BDTT-FID with FID, which was also observed in LUMO + 1. The strong electron-withdrawing properties of fluorine atoms enhanced the electron deficient power of isoindigo, which would promote the charge transfer and result in a lower bandgap.

The hole mobilities of PBDTT-ID and PBDTT-FID were measured by a space charge limited current (SCLC) method (Fig. S3a†),¹¹ and calculated to be 6.5×10^{-4} cm² V⁻¹ s⁻¹ and 3.2×10^{-3} cm² V⁻¹ s⁻¹, respectively. PBDTT-FID exhibits one order higher hole mobility than PBDTT-ID, which can be attributed to the fluorine substitution on isoindigo skeletons. This fluorination would reduce charge recombination and boost the long-lived charge separation, resulting in improved carrier transporting properties.¹² As shown in Fig. S3b,† the distance between F and H (BDTT-FID, 2.26 Å) is shorter than that between H and H (BDTT-ID, 2.28 Å). The dihedral angle between isoindigo and thiophene for BDTT-FID is calculated to be 16.64°, which is smaller than 19.62° determined for BDTT-ID. The results indicated that PBDTT-FID favoured a more planar conformation and better polymer packing, which enabled the electrons to be delocalized across the whole conjugated molecular system for higher carrier mobility.¹³

The photovoltaic properties were firstly investigated in conventional PSCs with a structure of ITO/PEDOT:PSS/copolymer:PC₇₁BM/Ca/Al. The device performances were optimized by varying the weight ratios of blend, changing the thickness of the active layer, choosing the different solvent and additives. The optimized weight ratio between the copolymer and PC₇₁BM is 1:2 (w/w). 1,8-Diiodooctane (DIO) was used as a processing additive to optimize the morphology of the active blends. All the active layers were processed with 3% (v/v) DIO in *o*-dichlorobenzene. The current density-voltage (J - V) curves are presented in Fig. 2a. The PBDTT-ID device exhibited a PCE of 4.76% with a V_{oc} of 0.88 V, a J_{sc} of 8.95 mA cm⁻², and an FF of 0.60. The PCE is comparable to those values obtained for other reported ID-containing copolymers.⁴ When using PBDTT-FID:PC₇₁BM (1:2, w/w) as the active layer, the best performance was obtained with a V_{oc} of 0.94 V, a J_{sc} of 9.62 mA cm⁻², and an FF of 0.61, giving rise to a PCE of 5.52%. Since the V_{oc} is proportional to the difference between the HOMO level of the polymer and the LUMO level of the PCBM,¹⁴ as expected, both PSCs showed relatively high V_{oc} values due to the low-lying HOMO levels. The PBDTT-FID device exhibited higher V_{oc} , which

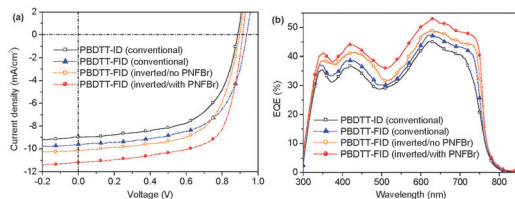


Fig. 2 (a) J - V curves of copolymer/ PC_{71}BM (1 : 1.5) based polymer solar cells under AM 1.5 G illumination, 100 mW cm^{-2} . (b) EQE curves of copolymer/ PC_{71}BM (1 : 1.5) based polymer solar cells.

can be attributed to the deeper HOMO energy level of PBDTT-FID arising from the introduction of fluorine atoms on isoindigo skeletons. Although the FFs were almost the same for both PSCs, the PBDTT-FID device also showed higher J_{sc} than the PBDTT-ID device. The reasons for PBDTT-FID possessing smaller bandgap and enhanced hole mobility have been discussed above. This was further verified by external quantum efficiency (EQE) (Fig. 2b) and surface morphology investigations by AFM (Fig. S4†). In Fig. 2b, the PBDTT-FID device displays wider curve shape and higher photo-conversion efficiency with a peak EQE value of over 47%. This result matched well with the improved J_{sc} of the PBDTT-FID device obtained from J - V measurements. The surface roughness measured from the AFM topographic image was 2.3 and 1.9 for the PBDTT-ID blend and the PBDTT-FID blend, respectively. The results indicated that the domain of the PC_{71}BM rich phase of the PBDTT-FID blend was more continuous and the domain size was smaller than that of the PBDTT-ID blend. This morphological information can explain the relatively high J_{sc} and FF of the PBDTT-FID device, which is in accordance with the EQE measurements.

To optimize the photovoltaic performance of PBDTT-FID, inverted devices with structures $\text{ITO}/\text{ZnO}/\text{PBDTT-FID}:\text{PC}_{71}\text{BM}$ (1 : 2)/ MoO_3/Ag and $\text{ITO}/\text{ZnO}/\text{PNFBr}/\text{PBDTT-FID}:\text{PC}_{71}\text{BM}$ (1 : 2)/ MoO_3/Ag were fabricated. As shown in Fig. 2a, inverted PSCs without the PNFBr layer showed a V_{oc} of 0.90 V, a J_{sc} of 10.16 mA cm^{-2} , an FF of 0.62 and the corresponding PCE of 5.70%. After introducing a thin PNFBr layer, inverted PSCs showed a V_{oc} of 0.92 V, a J_{sc} of 11.30 mA cm^{-2} , a FF of 0.68 and a related PCE of 7.04%. To our knowledge, this is the highest PCE reported to date for a PSC fabricated using an ID-based polymer. Compared to the conventional device, the V_{oc} of the inverted device is not changed so much, suggesting the presence of an ohmic contact between the active layer and the collecting electrode.¹⁵ However, the J_{sc} and FF have been increased to a relatively large extent, especially for the PSCs with the PNFBr layer, resulting in a higher PCE. The enhanced J_{sc} can be verified by the improved EQE response as shown in Fig. 2b, with increased maximum peak value up to about 53% (with PNFBr layer) for more efficient light harvest. The J_{sc} calculated here by integration of the EQE curve also agrees well with the J_{sc} obtained from the J - V measurement of the inverted device. The deposited PNFBr layer also played an important role in PCEs because it could suppress bimolecular recombination and reduce the barrier height between the hole collecting electrode and the active layer, which led to improved J_{sc} and FF values.¹⁶

In summary, we synthesized two D-A copolymers based on isoindigo (ID)/fluorinated isoindigo (FID) and bis(dialkylthienyl)-benzodithiophene (BDTT), PBDTT-ID and PBDTT-FID, for organic photovoltaic applications. The fluorinated substitution made this

type of copolymer prefer a more planar configuration arising from introduced F-H, F-S and F- π_{F} interactions. As expected, PBDTT-FID has a smaller bandgap, lower energy levels and a better carrier mobility compared to PBDTT-ID. Conventional PSCs fabricated from PBDTT-ID and PBDTT-FID blends with PC_{71}BM (1 : 2) showed PCEs of 4.76% and 5.52% with high V_{oc} up to 0.94 V. Using an inverted device structure, the PBDTT-FID device with a thin conjugated polyelectrolyte layer achieved an impressively high PCE of 7.04%. The molecular engineering strategies toward both BDTT and ID blocks demonstrated in this work have been proved to be effective approaches to develop high performance LBG copolymers for future organic solar cell applications.

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