

Synthesis of pyridine-capped diketopyrrolopyrrole and its use as a building block of low band-gap polymers for efficient polymer solar cells†

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A new building block for low band-gap polymers, diketopyrrolopyrrole (DPP) flanked by pyridine (PyDPP), has been synthesized via a simple synthetic route. PyDPP was polymerized with bithiophene (BT) to afford a low band-gap copolymer (PBTPyDPP) which was used as an electron donor of the active layer in polymer solar cells. The solar cell device based on PBTPyDPP exhibited a promising PCE of 4.9% with a high V_{OC} over 0.9 V, which is one of the highest values among DPP-based polymer solar cells.

Over the last decade, semiconducting conjugated polymers (SCPs) consisting of various building blocks have been developed for use in the next generation optoelectronic devices.¹ Among various types of SCPs, low band-gap copolymers based on donor–acceptor (D–A) structure have intensively been investigated for applications in organic electronics including polymer solar cells (PSCs) due to their light-weight, high flexibility and easy processing as well as the potential to tune the optical, mechanical, and electrical properties.²

Several building blocks for SCPs which meet the basic criteria for high performance organic semiconductors have been developed.³ Among the most successful building blocks, 2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione flanked by thiophene (TDPP) has widely been utilized for constructing D–A type SCPs, and has emerged as a promising building block for photoactive materials in organic electronics.⁴ Various SCPs based on TDPP have intensively been used as an electron donor material for PSCs.⁵

Although TDPP has shown great potential as a building block for high performance SCPs, a number of studies have reported that charge transport properties were further improved when the sulfur atom in thiophene was replaced by oxygen or selenium.⁶ Differences in the electron donating nature of furan, thiophene and selenophene can affect not only optical and electrochemical

characteristics of SCPs but also photovoltaic properties such as short circuit current density (J_{SC}), open circuit voltage (V_{OC}), and thus the power conversion efficiency (PCE). Therefore, the change of the flanking group of the DPP core could be an effective method to tune optoelectronic properties of SCPs and thus to achieve highly efficient PSCs.

When the SCPs based on benzene-flanked DPP (BzDPP) were used as electron donors for PSCs, BzDPP-based PSCs exhibited unsatisfactory performance mainly due to the high-lying highest occupied molecular orbital (HOMO) energy level and poor coplanarity of the polymer backbone.⁷ The high-lying HOMO energy level causes low V_{OC} and the poor coplanarity prevents self-assembly of SCPs and thus impedes charge transport.^{8a} Hence, both lowering the HOMO level of DPP-based SCPs and enhancement of the coplanarity of the polymer backbone have been important issues.^{5d} Pyridine, in this regard, can be a novel candidate as a flanking group of DPP, because the nitrogen in pyridine does not have a hydrogen, and therefore the repulsive interaction between DPP and pyridine units can be significantly reduced to make the polymer backbone more planar. Since the imine (C=N) group in pyridine pulls electrons because of the strong electronegativity of nitrogen,⁸ pyridine-flanked DPP (PyDPP) becomes a stronger electron-accepting group and thus lowers the frontier molecular orbital energy levels such as the HOMO level of SCPs.^{8e,f}

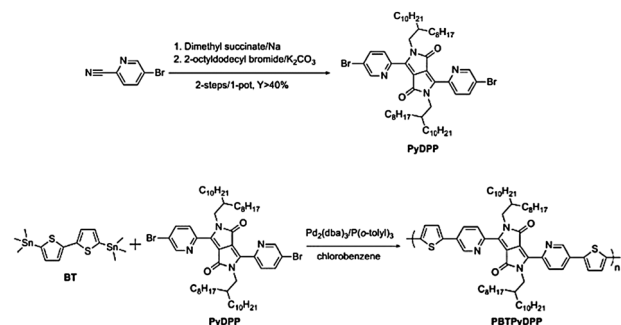
In this work, we introduced pyridine as a flanking group of DPP, and utilized PyDPP as an electron-accepting unit for synthesizing a D–A type low band-gap copolymer (PBTPyDPP) by reacting PyDPP with 2,2'-bithiophene (BT). Since PyDPP acts as a strong electron-withdrawing unit, PBTPyDPP had a very low HOMO energy level of -5.8 eV which is much lower than that of TDPP-based copolymers, and thus the PSCs fabricated from PBTPyDPP exhibited a high V_{OC} over 0.9 V, which is one of the highest reported values among DPP-based PSCs to the best of our knowledge, leading to a promising PCE of 4.9%.

The synthetic routes of PyDPP and PBTPyDPP are demonstrated in Scheme 1. PyDPP was synthesized via a 1-pot and 2-step simple reaction from 5-bromo-2-pyridinecarbonitrile. PBTPyDPP was synthesized via the Stille-coupling reaction between BT and PyDPP using $Pd_2(dba)_3$ and $P(o-tol)_3$ as catalysts in chlorobenzene. PBTPyDPP is

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Scheme 1 Synthetic schemes of PyDPP and PBTPyDPP.

very soluble in common solvents such as chloroform, THF, and chlorobenzene owing to the long and bulky side group on PyDPP.

The number-average molecular weight (M_n) of PBTPyDPP was 18 kDa with a polydispersity index (PDI) of 1.22, as determined using size-exclusion chromatography.

The absorption spectra of PBTPyDPP in dilute solution and thin film states are shown in Fig. 1. PBTPyDPP absorbs photons in the range of 500–750 nm with two distinct absorption maxima (λ_{max}) at 620 and 664 nm and exhibits an absorption onset (λ_{onset}) at 725 nm. The λ_{max} of the film state was red-shifted by 20 nm showing stronger intensity as compared to that of solution. The HOMO and the lowest occupied molecular orbital (LUMO) energy levels of PBTPyDPP were -5.77 and -3.86 eV in the film and -5.90 eV and -3.92 eV in solution, as estimated from the oxidation and reduction potentials of cyclic voltammograms, respectively (see Fig. S1, ESI†). The HOMO energy level of -5.90 eV of PBTPyDPP is among the lowest values of DPP-based polymers. This low-lying HOMO level is expected to afford a high V_{OC} . When the HOMO and LUMO energy levels of PBTPyDPP were calculated using the density functional theory at the B3LYP/6-31G* level, the electron density at HOMO was mainly located in the DPP core, while the electrons at LUMO were delocalized and extended to the pyridine unit (Fig. S2, ESI†). This indicates that pyridine acts as an electron-withdrawing group and therefore PyDPP exhibits a strong electron-withdrawing nature leading to a low-lying HOMO level, like fluorine substituted SCs.⁸

Photovoltaic properties of PBTPyDPP were measured using the conventional device structure of ITO/PEDOT:PSS/PBTPyDPP:PC₇₁BM/Ca/Al. When the blend ratio of PBTPyDPP to PC₇₁BM was varied from 1:1 to 1:3 to optimize the photovoltaic properties, the blend ratio of 1:2 afforded the best PCE of 3.68% with a high V_{OC} of 0.91 V (Fig. S3 and Table S1, ESI†). The V_{OC} over 0.9 V is one of the highest values of the PSCs fabricated from DPP-based SCs.⁹ To further optimize the photovoltaic performance, a small amount of a processing additive was added to the solution of the PBTPyDPP:PC₇₁BM (1:2 w/w) blend.

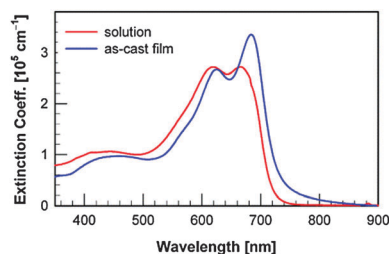


Fig. 1 UV-Vis absorption spectra of PBTPyDPP in solution and thin film states.

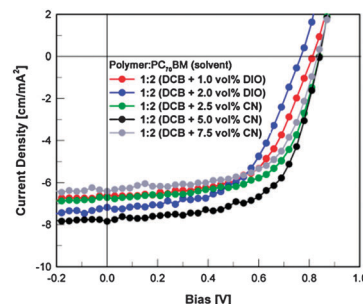


Fig. 2 Current density–voltage curves of the PSC devices fabricated from PBTPyDPP:PC₇₁BM solution with different amounts of DIO (or CN) under the illumination of AM 1.5G, 100 mW cm^{−2}.

When 1,8-diiodooctane (DIO) was added as an additive, a positive effect on PCE was not observed, although J_{SC} was slightly increased (see Fig. 2 and Table 1). However, when 1-chloronaphthalene (CN) was used as an additive, the PCE was significantly increased: the addition of 5.0 vol% CN afforded a promising PCE of 4.9% with a V_{OC} of 0.92 V, a J_{SC} of 9.6 mA cm^{−2} and a FF of 65.8%. The influence of the additive type on the morphology of the active layer of the PBTPyDPP-PC₇₁BM blend was studied using transmission electron microscopy (TEM). The active layer film cast from *o*-dichlorobenzene (DCB) alone does not show a phase-separated structure (Fig. S5, ESI†). When 2.0 vol% of DIO was added, fibril-like microstructures were dimly developed, but the phase separation was not clear. However, the active layer fabricated from 5.0 vol% CN solution exhibits more discernible fibril-like nanostructures with the formation of a continuous network. Therefore, the improved morphology upon addition of CN contributes to the enhancement of J_{SC} and FF leading to a higher PCE. The charge carrier mobilities in PBTPyDPP-PC₇₁BM blends were measured by the space-charge-limited current (SCLC) method with a hole only device structure of ITO/PEDOT:PSS/PBTPyDPP:PC₇₁BM/Au, and estimated from the slope of the linear region of the curve ($J^{1/2}$ vs. V) using the Mott–Gurney relation (Fig. S6, ESI†). The hole mobility of the active layer cast from DCB solution was 1.26×10^{-4} cm² V^{−1} s^{−1}, and addition of DIO and CN increased the hole mobility to 3.87×10^{-4} cm² V^{−1} s^{−1} and 6.28×10^{-4} cm² V^{−1} s^{−1}, respectively. This enhancement of hole mobility upon addition of the additive is mainly attributed to development of fibril-like morphology, as evidenced by the TEM images of the active layer.

When the crystal structure and its orientation of PBTPyDPP were investigated using the grazing-incidence wide angle X-ray scattering (GIWAXS), as shown in Fig. 3, the pristine PBTPyDPP film was found to have a highly crystalline nature revealing four pronounced reflection peaks [(100), (200), (300) and (400)] and a relatively weak (010) peak in the q_z direction. The (h 00) reflections of PBTPyDPP in the q_{xy} direction were also clearly observed, indicating that polymer chains

Table 1 Photovoltaic properties of PBTPyDPP and PC₇₁BM

Ratio (PBTPyDPP:PC ₇₁ BM)	Solvent	V_{OC} (V)	J_{SC} (mA cm ^{−2})	FF (%)	PCE (%)
1:2	DCB + 1.0 vol% DIO	0.86	6.61	58.8	3.34
1:2	DCB + 2.0 vol% DIO	0.82	7.18	56.1	3.31
1:2	DCB + 2.5 vol% CN	0.89	6.61	59.1	3.48
1:2	DCB + 5.0 vol% CN	0.92	7.96	65.8	4.88
1:2	DCB + 7.5 vol% CN	0.90	7.63	57.8	3.97

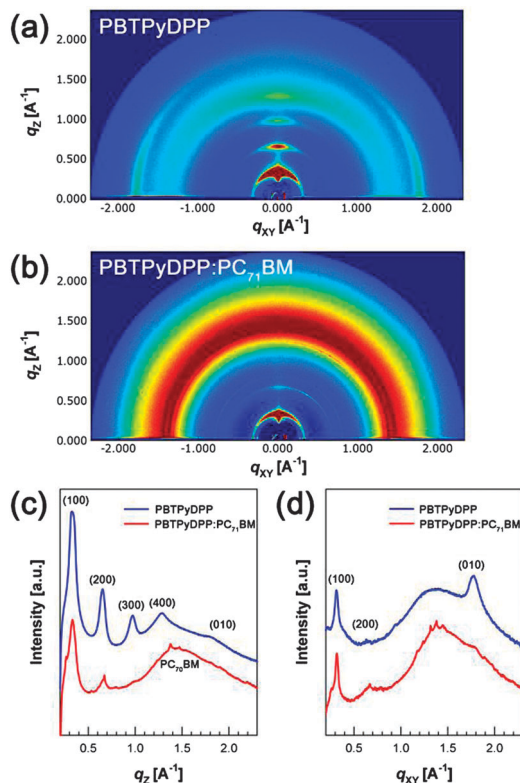


Fig. 3 2D-GIWAXS images of (a) pristine PBTPyDPP and (b) PBTPyDPP:PC₇₁BM blend films; (c) out-of-plane and (d) in-plane line cuts of GIWAXS patterns.

are packed in lamella stacks with both face-on and edge-on orientations. The PBTPyDPP:PC₇₁BM blend film cast from DCB with 5.0 vol% CN shows weaker (*h*00) reflection peaks in the q_z direction while the (100) and (200) peaks in the q_{xy} direction were more pronounced as compared to the pristine PBTPyDPP film, indicating that the orientation of polymer crystallites was changed from edge-on to face-on, as PBTPyDPP was blended with PC₇₁BM. The highly crystalline nature with predominant face-on orientation of PBTPyDPP is another reason for enhanced hole mobility upon addition of an additive. When the mean size of PBTPyDPP crystallites at the (100) reflection (L_{100}) was estimated using the Scherrer formula, the L_{100} values of pristine PBTPyDPP in q_z and q_{xy} directions were 12.2 and 14.6 nm, indicating that the thickness of face-on crystallites is larger than that of edge-on crystallites. More importantly, the L_{100} of edge-on crystallites and face-on crystallites in the blend was 12.2 nm and 22.5 nm, respectively, indicating that the size of face-on crystallites is much larger than that of edge-on crystallites in the blend. It should be also noted that the (010) reflection corresponding to the π - π stacking direction is more pronounced in the out-of-plane direction than the in-plane direction in the blend, which would be beneficial for efficient charge transport to electrodes.

In conclusion, we have synthesized a promising building block, PyDPP, for constructing semiconducting conjugated polymers *via* a simple route, and demonstrated the possibility of using the PyDPP-based polymer as the active layer material of PSCs. The end-capping of DPP by pyridine led to a low HOMO level to afford a high V_{OC} of PSCs. The PSCs fabricated from PBTPyDPP exhibited a promising PCE of 4.9% with a high V_{OC} of 0.92 V, suggesting that PyDPP can be used as a novel building block for the design of high-performance SCPS.

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