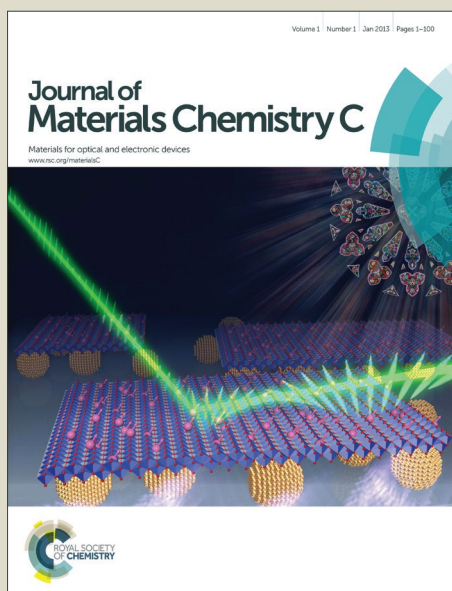


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A perylene bisimide derivative with LUMO level of -4.56 eV for non-fullerene solar cells

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Conjugated polymers with LUMO levels of -4.00 eV and a perylene bisimide derivative with LUMO level of -4.56 eV were used in non-fullerene solar cells in which power conversion efficiencies up to 1.4% were achieved.

Non-fullerene solar cells that use conjugated materials as electron acceptor to replace fullerene derivatives have attracted much attention in recent years,¹⁻⁵ resulting in high power conversion efficiencies (PCEs) > 9%.⁶⁻⁸ This achievement is partially attributed to the vast material diversity of conjugated molecules, which can be built from many electron-deficient building blocks, such as benzothiadiazole (BT),⁹ cyanoacetate,^{7,8} naphthalene diimide,¹¹ perylene bisimide (PBI)^{12-14,15} and diketopyrrolopyrrole (DPP).^{16,17} Because of this, the absorption spectra, energy levels and charge transport properties of electron acceptors can be optimized to achieve high performance solar cells. For instance, most electron acceptors were designed to have high-lying lowest unoccupied molecular orbital (LUMO) levels compared to the fullerene derivatives, such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), which could help to reduce the LUMO offset between the electron donor and acceptor and meanwhile enhance the open circuit voltage (V_{oc}) in solar cells.^{18,19} Interestingly, conjugated molecules with LUMO levels below that of PCBM are rarely reported as electron acceptor for application in solar cells.

Conjugated molecules with deep LUMO levels below -4.0 eV have been successfully applied in high performance field-effect transistors (FETs) with air-stable electron mobilities,²⁰⁻²³ indicating their potential application as electron acceptor. However, when using electron acceptors with very deep LUMO levels in bulk-heterojunction solar cells, high LUMO offsets between the donor and acceptor can easily be generated,

which will enhance the energy loss²⁴ and are detrimental for photovoltaic performance. In order to reduce the energy loss, conjugated polymers with LUMO levels close or equal to PCBM will be the candidates as electron donor. Although these polymers with low-lying LUMO levels have good air-stability, the LUMO offset between the polymers and PCBM is insufficient for exciton separation into free charges. Therefore, it will be interesting to study organic solar cells by incorporating electron donors and acceptors with deep LUMO levels.

In this work, a PBI derivative with a low lying LUMO level was designed and used as electron acceptor for non-fullerene solar cells. The idea starts from a bis-PBI compound, SdiPBI as shown in Fig. 1a, which has a similar LUMO level as PCBM and showed high performance solar cells.²⁵ In order to further lower the LUMO level, two cyano groups were introduced. It has been widely reported that by introducing strong electron-withdrawing cyano units, conjugated molecules can get deep LUMO levels, which was beneficial for air-stable electron mobilities.^{20-22,26} The cyano substituted PBI compound, SdiCNPBI (Fig. 1a), is found to provide a LUMO level of -4.56 eV. The new molecule as electron acceptor and two conjugated polymers based on DPP units²⁴ (Fig. 1b) with LUMO levels around -4.00 eV as electron donor were applied in solar cells. The photovoltaic results show that PCEs up to 1.4% can be achieved, indicating the efficient charge transfer, which was further confirmed by highly quenching photoluminescence (PL) spectra. This is the first time that organic solar cells based on donors and acceptors with LUMO levels both below -4.0 eV are reported.

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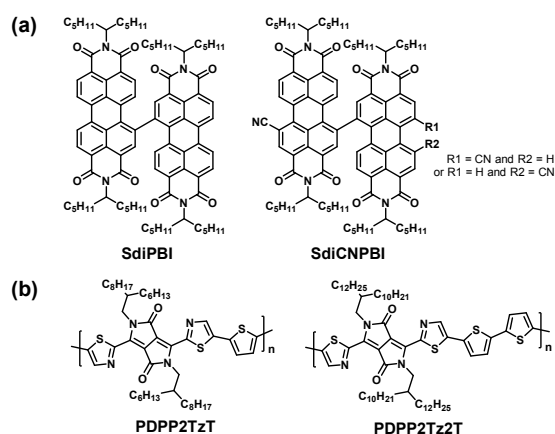
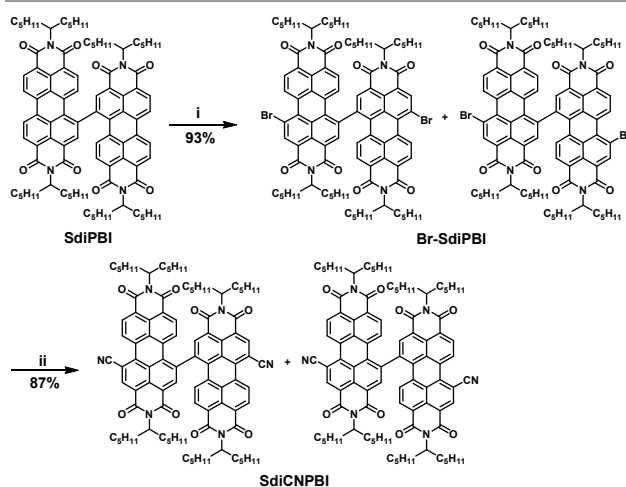


Fig. 1 The chemical structures investigated in this work. (a) The electron acceptors SdiPBI and SdiCNPBI; (b) The conjugated polymers PDPP2TzT and PDPP2Tz2T.

The synthetic procedure is presented in scheme 1. The bay-linked perylene bisimide acceptor, SdiPBI,²⁷ was selected as the starting material. Bis-PBI structures are able to prevent the aggregation of the PBI core, which is helpful for controlling the micro-phase separation in bulk-heterojunction systems.^{12,13} SdiPBI was converted into dibromo-derivative Br-SdiPBI with a yield of 93%, followed by cyanation with Zn(CN)₂ to afford the final compound SdiCNPBI with a yield of 87%. For both the brominated and cyanated PBI materials, a mixture of isomers is present, as indicated by NMR spectroscopy (Fig. S1, supporting information, ESI†).



Scheme 1 Synthetic route of SdiCNPBI. (i) Br₂ in CH₃COOH, 60 °C, 24 h. (ii) Zn(CN)₂, Pd₂(dba)₃, dppf, 1,4-dioxane, 100 °C, 12h.

Absorption spectra of SdiCNPBI in CHCl₃ solution and thin film are shown in Fig. S2 (ESI†), and the data is summarized in Table 1. The molecule SdiCNPBI shows similar absorption spectra in solution and thin film, indicating that the twisted bis-PBI units prevent the aggregation in thin film. This material exhibits similar absorption spectra as SdiPBI, with an optical band gap (E_g) of 2.03 eV in thin films. The DPP polymers PDPP2TzT and PDPP2Tz2T investigated in this work have an E_g

of 1.44 eV and 1.47 eV (Table 1). The complementary absorption between donor and acceptor is helpful for harvesting sunlight.

The highest occupied molecular orbital (HOMO) and LUMO levels of SdiCNPBI were determined by cyclic voltammetry (CV) measurements and referenced to a work function of ferrocene of -5.23 eV (Fig. S3, ESI†). The energy levels of the donors and acceptors are also summarized in Table 1. SdiCNPBI shows HOMO and LUMO levels of -6.59 eV and -4.56 eV, while SdiPBI without the two cyano-groups has HOMO and LUMO levels of -6.35 eV and -4.28 eV. To compare, the LUMO level of PCBM was determined to -4.16 eV (Fig. S3, ESI†). Since the LUMO levels of PDPP2TzT and PDPP2Tz2T are at -4.07 eV and -3.95 eV, the LUMO offset between the polymers and SdiPBI is close to or below 0.3 eV, while the LUMO offset of the DPP polymers to SdiCNPBI is increased to 0.49 eV and 0.61 eV. The increased LUMO offset will enhance the driving force for exciton dissociation into free charges, which is beneficial for improving device performance.

Table 1 Optical and electrochemical properties of the DPP polymers.

Material	E_g^{film} (eV)	LUMO ^a (eV)	HOMO ^b (eV)
SdiPBI	2.07	-4.28	-6.35
SdiCNPBI	2.03	-4.56	-6.59
PDPP2TzT ^c	1.44	-4.07	-5.44
PDPP2Tz2T ^c	1.47	-3.95	-5.42

^a Determined using a work function value of -5.23 eV for Fc/Fc⁺. ^b Determined as $E_{\text{LUMO}} - E_g^{\text{film}}$. ^c Ref 24.

We also measured the hole and electron mobilities of the donor polymers PDPP2TzT and PDPP2Tz2T by FETs with a bottom gate – bottom contact configuration. The results are summarized in part 6, ESI†. These two polymers perform ambipolar charge mobilities, with a hole mobility of 0.14 cm² V⁻¹ s⁻¹ for PDPP2TzT and 0.54 cm² V⁻¹ s⁻¹ for PDPP2Tz2T (Table S1, ESI†). The results demonstrate that these two polymers can have good hole transport properties for application in organic solar cells.

The DPP polymers and PBI derivatives with deep energy levels were applied in solar cells using an inverted configuration, where ITO/ZnO and MoO₃/Ag were used as electrodes. For the photo-active layers, the ratio of donor to acceptor is 1:1. Other processing conditions, such as solvent, with or without additive, and thickness, were carefully optimized to achieve the best performance (Table S2 and Table S3, ESI†). The optimized performance of the solar cells is shown in Fig. 2 and the photovoltaic parameters are summarized in Table 2.

When using SdiPBI as electron acceptor, PDPP2TzT or PDPP2Tz2T based cells provided PCEs below 0.10% due to very low short circuit current densities (J_{sc}) (Table 2). The solar cells performance was dramatically improved by using SdiCNPBI as acceptor. PDPP2TzT:SdiCNPBI cells showed the best PCE of 0.72%, with a J_{sc} of 2.7 mA cm⁻², V_{oc} of 0.81 V and fill factor (FF) of 0.33. PDPP2Tz2T:SdiCNPBI had a better PCE of 1.4% with a

high J_{sc} of 5.5 mA cm^{-2} . The improved J_{sc} s were also reflected by the external quantum spectra (EQE). Both cells with SdiCNPBI showed a broad photoresponse between 300 nm and 850 nm with a maximum EQE of 0.25 (Fig. 2b).

Table 2 Solar cell parameters of optimized solar cells.

Blend ^a	J_{sc} ^b [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
PDPP2TzT:SdiPBI ^c	0.05	0.89	0.28	0.01
PDPP2TzT:SdiCNPBI ^c	2.70	0.81	0.33	0.72
PDPP2TzT:SdiPBI ^d	0.31	0.93	0.35	0.10
PDPP2TzT:SdiCNPBI ^d	5.50	0.77	0.34	1.40

^a Ratio of donor to acceptor is 1:1. ^b J_{sc} as calculated by integrating the EQE spectrum with the AM1.5G spectrum. ^c The thickness of active layer is 60 nm and the fabrication solution is CHCl_3 with 5% *o*-DCB. ^d The thickness of active layer is 100 nm and the fabrication solution is CHCl_3 with 0.2% DIO.

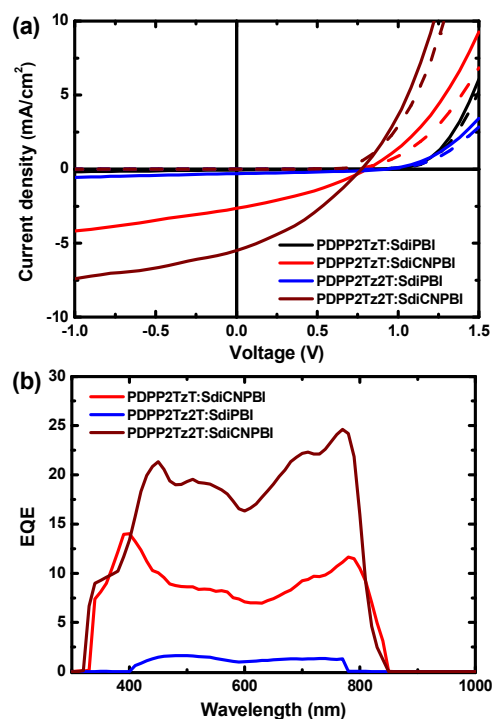


Fig. 2 (a) *J-V* characteristics in dark (dashed lines) and under simulated AM1.5G illumination (solid lines) of optimized solar cells of the DPP polymers with PBI-based acceptors. (b) EQE of the same devices. The EQE spectrum of PDPP2TzT:SdiPBI is too low to be detected.

We further used PL measurement to study the charge transfer in these photo-active layers, as shown in Fig. 3. All the thin films were excited at 770 nm and the intensity was calibrated according to their absorption spectra (Fig. S5, ESI†). Both DPP polymers exhibit PL emission between 800 nm and 1100 nm with a peak around 950 nm. When the polymers were blended with SdiPBI, similar or even higher PL intensities compared to those of the pure thin films were observed, indicating that there is no charge transfer from the polymer donors to SdiPBI. It is interesting to note that PDPP2TzT:SdiPBI

thin films gave a higher PL signal, which may originate from less aggregation of PDPP2TzT in blended films. When using SdiCNPBI as electron acceptor, the PL signal was strongly quenched, which illustrates that efficient charge transfer occurred in these systems. The PL quenching result is consistent with the photovoltaic performance.

The DPP polymer:SdiCNPBI cells have reasonable PCEs, but are less efficient compared to other non-fullerene solar cells, which is mainly due to low J_{sc} and FF. We examined the morphology of the photo-active layers by atom force microscopy (AFM), which showed smooth surfaces with roughnesses of 0.89 – 1.80 nm (Fig. S6, ESI†). It has been reported that the phase separation in bulk-heterojunction systems can be reflected by the surface characterization from AFM images, in which the coarse surface with high roughness means the large phase separation.²⁸ Therefore, in our study, the smooth surfaces may be indicative of a very fine phase separation between donor and acceptor. In addition, DPP polymers have been reported to have high hole mobilities,²⁹ while twisted PBI units showed low electron mobilities due to reduced crystallinity. The unbalanced hole and electron mobility could enhance the charge recombination during charge transport. Therefore, designing new PBI units with twisted backbone but meanwhile maintaining high electron mobility could be a potential strategy to improve the PCE of these kinds of solar cells.

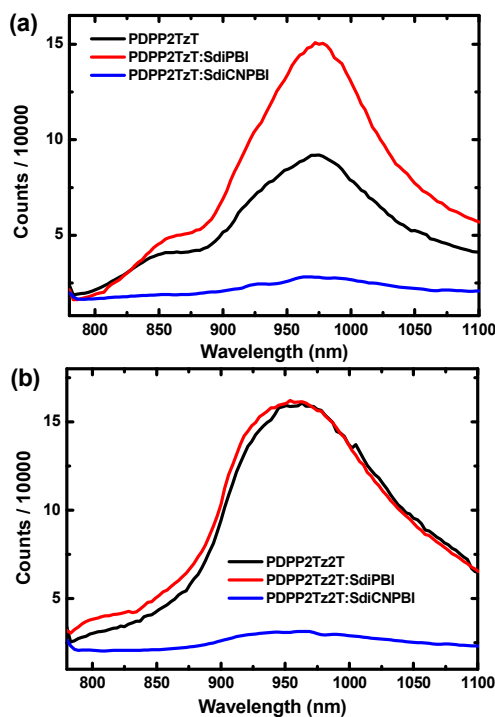


Fig. 3 Photoluminescence spectra of the DPP polymer:PBI derivative thin films. Both of PDPP2TzT and its blend thin films were fabricated from CHCl_3 with 5% *o*-DCB. Both of PDPP2TzT and its blend thin films were fabricated from CHCl_3 with 0.2% DIO. The PL intensity has been calibrated with absorption spectra of the thin films (Fig. S5, ESI†). The excitation wavelength is 770 nm.

Conclusions

A PBI derivative with a deep LUMO level of -4.56 eV was designed and synthesized by introducing two cyano groups into the molecule. The molecule was applied as an electron acceptor in non-fullerene solar cells, where two conjugated polymers with LUMO levels around -4.00 eV were used as electron donors. A PCE of 1.4% was achieved, which was further explained by efficient charge separation observed in PL experiments. This is the first study about the photovoltaic properties of conjugated donors and acceptors with LUMO levels both below -4.0 eV.

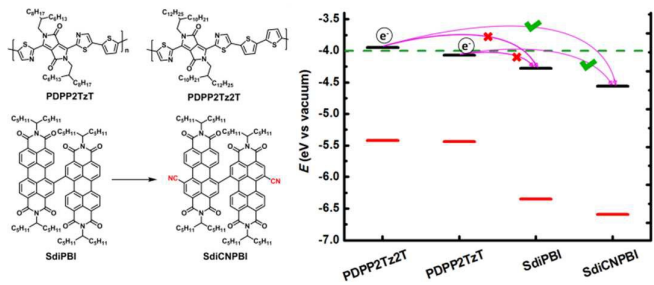
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Graphic:



Text:

Conjugated polymers with LUMO levels of -4.00 eV combined with a newly designed perylene bisimide compound with LUMO level of -4.56 eV were found to have efficient charge transfer and provide power conversion efficiencies up to 1.4% in solar cells.