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Develop Donor Polymer Using B←N Unit for Suitable LUMO/HOMO Energy Levels and Improved Photovoltaic Performance

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The LUMO/HOMO energy levels of conjugated polymers are key parameters for their applications as polymer electron donors for polymer solar cells (PSCs). The widely-used strategy to tune the LUMO/HOMO levels of polymer donors is to develop D-A type polymer based on alternating electron-donating unit (D) and electron-accepting unit (A). In this paper, we report a novel approach to tune the LUMO/HOMO levels of polymer donors via replacing a C–C unit by a B←N unit for enhanced PSC device performance. The control polymer **PCPDT** shows the LUMO/HOMO levels of –2.71 eV/–4.98 eV, which are both much higher than those required for an ideal polymer donor. By replacing a C–C unit with a B←N unit, the resulting polymer **PBNCPDT** exhibits much lower LUMO/HOMO levels of –3.23 eV/–5.20 eV. **PBNCPDT** also shows a narrower optical bandgap (E_g = 1.73 eV) than that (E_g = 1.85 eV) of **PCPDT**, which is helpful for harvesting of sunlight. Moreover, **PBNCPDT** with the B←N unit is not a typical D-A type conjugated polymer because its LUMO and HOMO are both delocalized over the whole conjugated framework. As the control PSC device based on **PCPDT** exhibits the open-circuit voltage (V_{oc}) of 0.45 V and power conversion efficiency (PCE) of 0.63%, the device of **PBNCPDT** shows much improved V_{oc} of 0.82 V and PCE of 3.74%. These results indicate that B←N unit can be used to develop polymer donors for high-performance PSC devices.

Introduction

Polymer solar cells (PSCs) have received great attention due to the advantages of low cost, flexibility and light weight.[1] Intensive efforts have been devoted to the development of polymer electron donors to improve power conversion efficiency (PCE) of PSCs.[2,3] The key requirement for polymer donor in PSC is its LUMO/HOMO energy levels. When phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) with a LUMO level of –3.9 eV is used as the acceptor, an ideal polymer donor should have a LUMO level of around –3.6 eV for efficient exciton dissociation and should have a HOMO level of around –5.1 eV for optimized high open-circuit voltage with a bandgap (LUMO/HOMO difference) of around 1.5 eV for efficient harvesting of sunlight.[4,5] As normal homopolymers, e.g. poly(3-hexylthiophene) (P3HT), always have large bandgap and cannot possess such ideal LUMO/HOMO levels, a successful strategy of alternating electron-donating unit (D) and electron-accepting unit (A) has been widely used to tune the energy levels of conjugated polymers for good PSC device performance. A large family of D-A type polymer donors with finely tuned LUMO/HOMO levels have been reported to exhibit excellent PSC device performance.[6,7] Another efficient strategy to design donor polymers with suitable LUMO/HOMO energy levels is using quinoid polymers with electron-withdrawing substitutes.[8]

B←N coordination bond and C–C covalent bond are isoelectronic and isosteric.[9] B←N unit has been widely used by Yamaguchi et al., S. Wang et al. and Y. Wang et al. to develop small molecules with low-lying LUMO levels.[10] Recently, our group has introduced B←N unit into the design of conjugated polymer acceptors. By replacing a C–C unit with a B←N unit in the D repeating unit of a D-A type conjugated polymer, the LUMO/HOMO energy levels of the conjugated polymers can be decreased by 0.5–0.6 eV and consequently the typical polymer donor is converted to a polymer acceptor.[11] In this manuscript, we report the application of B←N unit to tune the LUMO/HOMO levels of polymer donor materials for enhanced PSC device performance.

Cyclopenta-[2,1-b:3,4-b']-dithiophene unit (CPDT) is a widely used electron-donating unit.[12] The homopolymer of CPDT (**PCPDT**) exhibits the LUMO/HOMO levels of –2.71 eV/–4.98 eV, which are largely deviated from –3.60 eV/–5.10 eV of an ideal polymer donor. In this manuscript, in order to tune the LUMO/HOMO levels of **PCPDT** for good PSC device performance, we utilize B←N unit and develop an alternating polymer **PBNCPDT** with the much decreased LUMO/HOMO levels of –3.23 eV/–5.20 eV (see Scheme 1). The delocalized LUMO and HOMO over the whole conjugated framework indicate that **PBNCPDT** is not a typical D-A type polymer. As the control PSC device based on **PCPDT** exhibits the low open-circuit voltage (V_{oc}) of 0.45 V and power conversion efficiency

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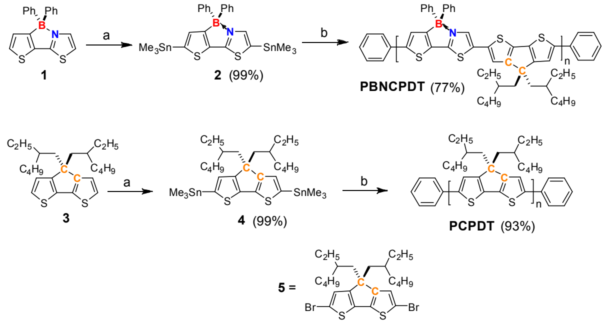
(PCE) of 0.63%, the PSC device of **PBNCPDT** shows much improved V_{oc} of 0.82 V and PCE of 3.74%. These results indicate that B←N unit is a novel approach to tune the energy levels of polymer donors for high-performance PSCs.

Results and discussion

Synthesis and Characterization

The synthetic routes of both **PBNCPDT** and **PCPDT** are shown in Scheme 1. Stille polymerization of **2** and **5** readily afforded **PBNCPDT** in 77% yield. With the unsymmetric B←N-contaning unit, **PBNCPDT** should be regiorandom because both head-to-head and head-to-tail bonding modes of the B←N-containing unit and the CPDT unit may exist. The chemical structure of **PBNCPDT** is verified by ^{1}H NMR and elemental analysis. **PCPDT** was synthesized by the Stille polymerization of the corresponding C–C unit-containing monomers **4** and **5**. The synthesis of homopolymer of **1** was also tried, and the product was insoluble in common organic solvents. Thus, the homopolymer of **1** was not discussed in this work. The number-average molecular weights (M_n) and PDI were 37100 g/mol and 2.28 for **PBNCPDT**, and 33900 g/mol and 2.75 for **PCPDT**. Their thermal stability was characterized using thermal gravimetric analyses (TGA) under a N_2 flow. **PBNCPDT** and **PCPDT** display the degrading temperature (T_d) at 5% weight loss of 331 °C and 390 °C, respectively (see the Supporting Information). Their high molecular weights and good thermal stability imply that the two polymers can be used to fabricate polymer solar cells.



Scheme 1 Synthesis of the polymers **PBNCPDT** and **PCPDT**. Reagents and conditions: a) *n*-BuLi, tetrahydronfuran, –78 °C to 25 °C, then Me_3SnCl, from –78 °C to 25 °C; b) **5**, $Pd_2(dba)_3$, P(*o*-Tolyl)$_3$, Toluene, 120 °C, then bromobenzene. Ph = Phenyl.

Theoretical Calculations

Density functional theory (DFT) calculations at the B3LYP/6-31G* level of theory were performed to theoretically investigate the effects of B←N unit on the electronic structures of **PCPDT** and **PBNCPDT**.[14] To simplifying the calculation, the model molecules with two repeating units and methyl side chains, **TCPDT** and **DBNCPDT,** were employed. As shown in Figure 1, similar to those of **TCPDT**, both the LUMO and HOMO of **DBNCPDT** with B←N unit are delocalized over the nearly entire framework. Replacing C–C unit by B←N unit in conjugated polymers does not significantly affect the distribution of electrons. D-A type conjugated polymers based on alternating electron-donating unit and electron-accepting unit always have HOMO delocalized on the entire conjugated framework and LUMO localized on the A unit.[7] The delocalized LUMO and HOMO of **DBNCPDT** indicate that **PBNCPDT** with B←N unit is not a typical D-A type polymer. Comparison of the LUMO and HOMO energy levels of **TCPDT** and **DBNCPDT** suggests that the B←N unit significantly decreases the LUMO and HOMO levels of the conjugated polymers (Figurer 1). As discussed later, the decrease of LUMO/HOMO energy levels will be beneficial for the application as polymer donor for polymer solar cells.

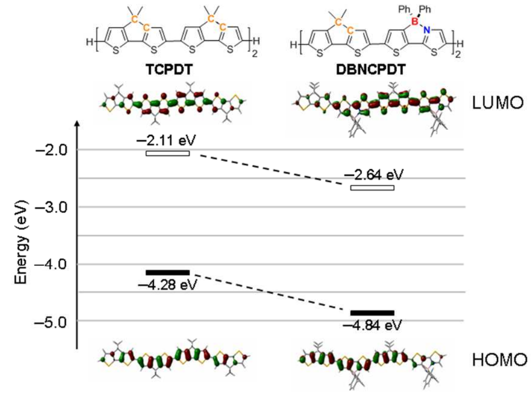


Figure 1 Electronic effects of replacing a C–C unit by a B←N unit on the model compounds, which are calculated at the B31LYP/6-31G* level.

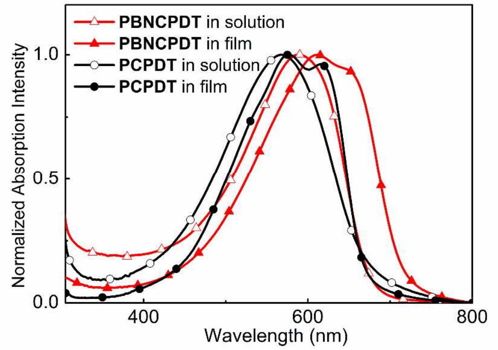


Figure 2 Normalized UV-Vis absorption spectra of **PBNCPDT** and **PCPDT** in *o*-DCB solutions and in thin films.

Optical Properties

The UV-Vis absorption spectra of the polymers in solutions (*o*-DCB) and in thin films (spin-coated onto quartz substrates) are shown in Figure 2 and the data are listed in Table 1. In solution, the absorption maximum of **PBNCPDT** (λ_{max} = 590 nm) is red-shifted by 22 nm compared to that of **PCPDT** (λ_{max} = 568 nm). In thin film, while the absorption spectrum of **PCPDT** shows a broad absorption band with two peaks at 615 nm/576 nm, the absorption spectrum of **PBNCPDT** exhibits the absorption maxima at 647 nm/612 nm. The redshifts of absorption spectra from in solution to in film for the two polymers are due to the strong intermolecular interactions and the close packing of the polymer backbones in the solid states. While **PCPDT** in thin film exhibits the optical bandgap of 1.85 eV, **PBNCPDT** shows a narrower optical bandgap of 1.73 eV due to the employment of B←N unit. As discussed above, the narrow bandgap is important for efficient harvesting of sunlight in PSC.

Table 1. Photophysical properties, electrochemical properties and energy levels of **PCPDT** and **PBNCPDT**.

polymer	λ_{abs} [b] (nm)	λ_{abs} [b] (nm)	λ_{onset} [b] (nm)	E_g opt[b] (eV)	E_{onset} ox[c] (V)	E_{onset} red[c] (V)	E_{HOMO} [d] (eV)	E_{LUMO} [d] (eV)	E_g elec[b] (eV)
PCPDT	568	576, 615	670	1.85	0.18	–2.09	–4.98	–2.71	2.27
PBNCPDT	590	612, 647	718	1.73	0.40	–1.57	–5.20	–3.23	1.97

[a] Measured in dilute *o*-DCB solution. [b] Measured in thin film. [c] Onset potential vs. Fc/Fc$^+$. [d] Calculated using the equations (E_{HOMO}= –(4.80 + E_{onset}^{ox}) eV, E_{LUMO}= –(4.80 + E_{onset}^{red}) eV).

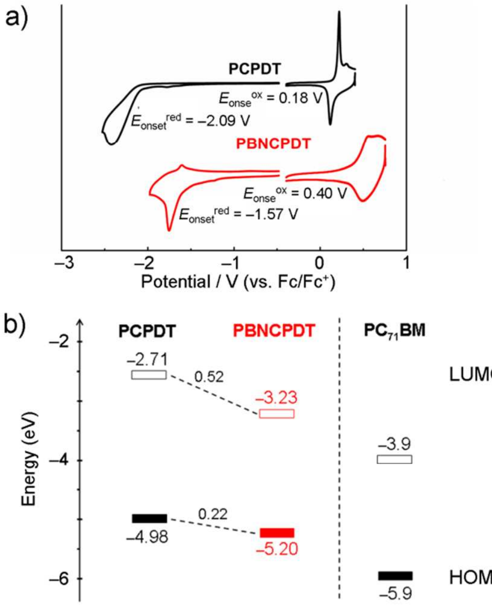


Figure 3 a) Cyclic voltammogram of **PBNCPDT** and **PCPDT** in thin films. Scan rate: 50 mV s^{-1}; working electrode: glassy carbon; reference electrode: saturated calomel; supporting electrolyte: 0.1 M *n*-Bu_4NClO_4 in CH_3CN (anodic CV) and 0.1 M *n*-Bu_4NClO_4 in DMF (cathodic CV), Fc/Fc+ = ferrocene/ferrocenium. b) The LOMO/HOMO energy levels of **PCPDT** and **PBNCPDT** and energy levels of PC$_{71}$BM are listed for comparison.

Electrochemical Properties

To investigate the effects of B←N unit on the LUMO/HOMO energy levels of the polymers, cyclic voltammetry measurements of the polymer films were performed. As shown in Figure 3a, **PCPDT** shows an irreversible reduction wave and a reversible oxidation wave with the onset reduction potential (E_{onset}^{red}) of –2.09 V and the onset oxidation potential (E_{onset}^{ox}) of +0.18 V, respectively. In comparison, **PBNCPDT** shows quasi-reversible reduction and oxidation processes with more positive onset reduction potential and onset oxidation potential (E_{onset}^{red} = –1.57 V, E_{onset}^{ox} = +0.40 V). According to these onset reduction and oxidation potentials, their LUMO/HOMO energy levels are estimated and listed in Table 1. The LUMO/HOMO levels of **PCPDT** and **PBNCPDT** are –2.71 eV/–4.98 eV and –3.23 eV/–5.20 eV, respectively. As shown in Figure 3b, the HOMO level of **PBNCPDT** with B←N unit is lowered by 0.22 eV than that of **PCPDT**, which is expected to give higher open-circuit voltage in PSCs. The LUMO level of **PBNCPDT** is decreased by 0.52 eV compared to that of **PCPDT**. Moreover, despite of the large decrease, the LUMO level of **PBNCPDT** is still higher by 0.67 eV than that of PC$_{71}$BM, providing the enough driving force for exciton dissociation in PSC devices. These results imply that the B←N unit can significantly decrease the LUMO/HOMO energy levels of conjugated polymers and make the LUMO/HOMO energy levels of **PBNCPDT** be suitable for the application as polymer donor in PSCs.

Fluorescence Spectra

Figure 4 shows the fluorescence spectra of **PBNCPDT** in organic solvents with different polarities, including chlorobenzene, tetrahydrofuran, $CHCl_3$, CH_2Cl_2 and *o*-chlorobenzene. The fluorescence peaks of **PBNCPDT** in organic solvents are all around 665 nm and no solvatochromic effects are observed. It is well-known that D-A type molecules or polymers usually exhibit redshifted fluorescence peaks in polar solvents compared to in non-polar solvents. Therefore, the absence of solvatochromic effects of **PBNCPDT** confirms that **PBNCPDT** is not a D-A type conjugated polymers. This is consistent with the theoretical calculation results of **PBNCPDT**, which shows both delocalized LUMO and delocalized HOMO.

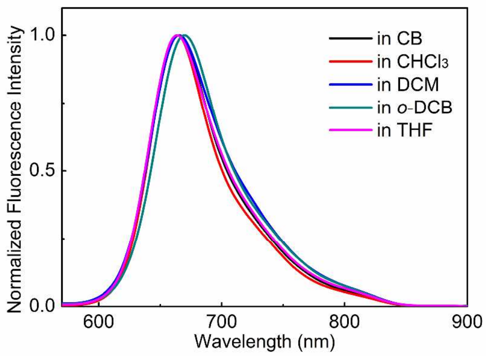


Figure 4 Normalized fluorescence spectra of **PBNCPDT** in different solvents.

Photovoltaic Properties and Active Layer Morphology

PSC devices using **PCPDT** and **PBNCPDT** as polymer donors were fabricated with a conventional configuration of ITO/PEDOT:PSS/polymer:PC$_{71}$BM/LiF/Al. The active layer was spin-coated from the solution of polymer:PC$_{71}$BM with the ratio of 1:3 (*w/w*) in *o*-DCB containing 3 vol% 1,8-diiodooctane

(DIO) as the solvent additive. Figure 5a displays the current density-voltage (*J*–*V*) curves of the devices under AM 1.5G irradiation (100 mW/cm^2) and Table 2 summarizes the device characteristics.

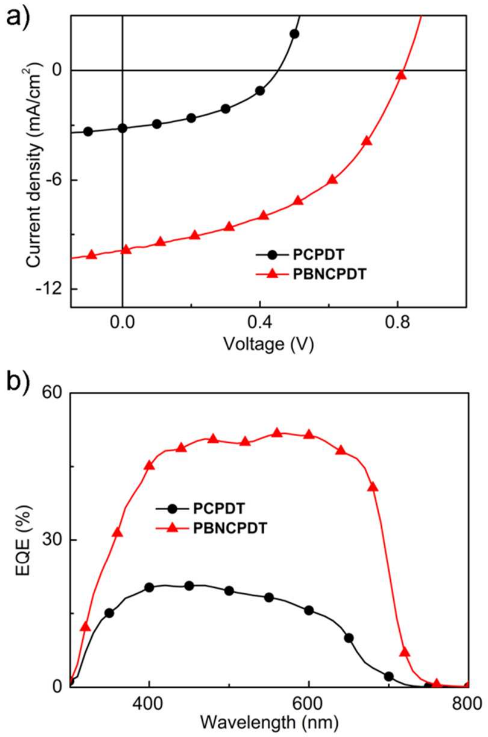


Figure 5 a) The *J*–*V* curves and b) the EQE curves of the PSC devices with **PBNCPDT** or **PCPDT** as the donor polymer.

The device based on **PCPDT** shows the power conversion efficiency (PCE) of 0.63% with the open-circuit voltage (V_{oc}) of 0.45 V, the short-circuit current (J_{sc}) of 3.16 mA/cm^2, and the fill factor (FF) of 44.3%. In comparison, the device of **PBNCPDT** shows the V_{oc} of 0.82 V, the J_{sc} of 9.89 mA/cm^2, the FF of 46.1%, corresponding to the PCE of 3.74%. V_{oc} of PSCs is related to the difference between the HOMO level of the polymer donor and the LUMO level of the PC$_{71}$BM acceptor. It is notable that the V_{oc} of the device of **PBNCPDT** with B←N unit is enhanced by 0.37 V compared to that of **PCPDT**. This is consistent with the deeper HOMO level of **PBNCPDT** compared to **PCPDT**. The much improved J_{sc} of the **PBNCPDT**-based device than that of the **PCPDT**-based device is attributed to both the improved active layer morphology and the enhanced sunlight absorption capability. Figure 5b shows the EQE curves of the two devices. The integral current density values calculated from the EQE curves and the standard AM1.5G spectrum agree well with those measured from the *J*–*V* scan. Owing to the much improved V_{oc} and J_{sc}, the PSC device of **PBNCPDT** with B←N unit exhibited much enhanced power conversion efficiency than that of **PCPDT**. The PSC device performance suggests that the LUMO/HOMO levels of **PBNCPDT** with B←N unit are more suitable for PSC polymer donor application than that of **PCPDT**.

Table 2 Characteristics of the PSC devices under AM 1.5 G illumination, and the average performance are shown in the parentheses.

Polymer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PCPDT	0.45	3.16	44.3	0.63 (0.54)
PBNCPDT	0.82	9.89	46.1	3.74 (3.62)

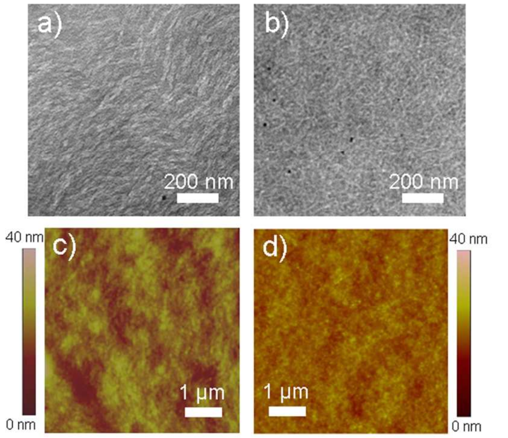


Figure 6 TEM images of a) **PCPDT**/PC$_{71}$BM and b) **PBNCPDT**/PC$_{71}$BM, and AFM images of c) **PCPDT**/PC$_{71}$BM and d) **PBNCPDT**/PC$_{71}$BM, processed with *o*-DCB containing 3 vol% DIO.

TEM and AFM were employed to study the active layer morphology of the PSC devices of the two polymers. Figure 6a and b show the TEM images of the **PCPDT**:PC$_{71}$BM blend and **PBNCPDT**:PC$_{71}$BM blend, respectively. The polymer domains appear as bright region and the PC$_{71}$BM domains appear as dark regions because of their different degrees of electron scattering. The **PCPDT**:PC$_{71}$BM blend exhibits large-scale phase separated morphology, which is not beneficial for exciton dissociation and charge transport, and thus leads to limited J_{sc} and low PCE. In comparison, the **PBNCPDT**:PC$_{71}$BM blend shows nanofibrillar network morphology and the fine fibers of the donor polymer can be clearly seen, resulting in good photovoltaic performance. Figure 6c and d display the corresponding AFM height images of the surface of the two films. Although the two films have the similar root-mean-squared (rms) roughness, much larger scale phase separation is observed in **PCPDT**:PC$_{71}$BM blend compared to that in the **PBNCPDT**:PC$_{71}$BM blend. This is in consistence with the TEM results and the device performance.

Conclusions

In summary, we demonstrate a strategy of decreasing the LUMO/HOMO energy levels of polymer electron donors via replacing a C–C unit by a B←N unit for enhanced PSC performance. The resulting polymer with the B←N unit is not a D-A type conjugated polymer because its LUMO and HOMO are both delocalized over the whole conjugated framework.

The LUMO/HOMO levels of **PBNCPDT** with B←N unit are –3.23 eV/–5.20 eV, which are lowered by 0.52 eV/0.22 eV compared to that of **PCPDT** with C–C unit (–2.71 eV/–4.98 eV). Moreover, **PBNCPDT** also shows a narrower optical bandgap than that of **PCPDT**. These improvements make **PBNCPDT** be more suitable to be used as polymer donors for PSCs. As the control PSC device based on **PCPDT** exhibits the low V_{oc} of 0.45 V and PCE of 0.63%, the PSC device of **PBNCPDT** shows much improved V_{oc} of 0.82 V and PCE of 3.74%. These results indicate that B←N unit can be used to develop polymer donors for high-performance PSC devices, and intensive studies on polymer donor materials following this strategy are in progress in our laboratory.

Experimental section

Materials.

5,5-diphenyl-5*H*-thieno[3',2':3,4][1,2] azaborolo [5,1-b]thiazol-4-ium-5-uide (**1**), 5,5-diphenyl-2,7-bis (trimethylstannyl)-5*H*-thieno[3',2':3,4][1,2]azaborolo[5,1-*b*]thiazol-4-ium-5-uide (**2**), 4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophene,4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[1, 2-*b*: 5, 4-*b*']dithiophene (**3**), (4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl) bis(trimethylstannane) (**4**), and 2,6-dibromo-4,4-bis (2-ethylhexyl)-4*H*-cyclopenta[1, 2-*b*: 5, 4-*b*']dithiophene (**5**) were prepared according to the reported literature procedures.[11,13] Commercially available solvents and reagents were used without further purification unless stated otherwise.

Measurements and Characterization.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer in $CDCl_3$ at 25 °C. Elemental analysis was performed with a VarioEL elemental analyzer. Gel permeation chromatography (GPC) was recorded at 35 °C to measure the molecule weights of the polymers with a Waters 410 instrument. Monodispersed polystyrene was used as the standard and THF was used as the eluent. Thermogravimetric analyses (TGA) of the polymers were performed under a N_2 flow under at a heating rate of 10 °C min^{-1} with a Perkin-Elmer-TGA 7. The temperature of degradation (T_d) was corresponding to a 5% weight loss. UV-Vis absorption spectra and fluorescence spectra were measured with a Shimadzu UV-3600 spectrometer and a Hitachi F-4500 spectrometer, respectively, in spectral grade solvents.

Cyclic voltammetry (CV) of the polymer films were performed with a CHI660a electrochemical workstation using *n*-Bu_4NClO_4 (0.1 M) in acetonitrile or *N*,*N*-Dimethylformamide (DMF) as electrolyte solution and ferrocene as an internal reference at a scan rate of 50 mV/S. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymers were casted on the working electrode for measurements. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of the polymers were calculated according to the equations: HOMO/LUMO = $-(4.80 + E_{ox}^{onset}/E_{red}^{onset})$ (eV). Atomic force microscopy (AFM) was recorded with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. Transmission electron microscopy (TEM) was performed with a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. The out-of plane grazing incidence X-ray diffraction (GIXD) measurement was performed using a Bruker D8 Discover reflector.

Synthesis.

Polymer PBNCPDT. The monomer of **2** (164 mg, 0.25 mmol), **5** (135 mg, 0.24 mmol), $Pd_2(dba)_3$ (4.4 mg, 0.005 mmol) and P(*o*-Tolyl) (11.7 mg, 0.039 mmol) were placed in a two-necked flask under argon, and then dried toluene (9 mL) was added. After the mixture being stirred at 120 °C for 14 h, blocking reaction was performed by adding excess of bromobenzene. The crude polymer was precipitated into methanol and the polymer was collected by filtration. Then the polymer was purified by Soxhlet extraction in acetone, hexane, and THF. The final polymer from THF phase was precipitated into methanol, which was collected and dried in vacuum overnight. A blue violet filamentary solid was obtained. Yield **PBNCPDT**: 135 mg (77%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 7.76–7.06 (m, 14H), 1.91 (br, 4H), 1.02 (m, 16H), 0.75 (br, 6H), 0.67 (m, 8H). The broad signals were due to the isomer of **PBNCPDT** with head-to-head and head-to-tail linking modes of unit **1** and **3**. In this paper, we discussed the polymer using the drawn structure of **PBNCPDT**. Anal. Calcd for $C_{44}H_{48}BNS_4$: C, 72.40; H, 6.63; B, 1.48; N, 1.92; S, 17.57. Found: C, 71.69; H, 6.62; N, 1.86; S, 17.27. GPC (THF, polystyrene standard): M_n = 37100 g/mol, PDI = 2.28.

Polymer PCPDT: The monomer of **4** (200 mg, 0.28 mmol), **5** (150 mg, 0.27 mmol), $Pd_2(dba)_3$ (4.9 mg, 0.005 mmol) and P(*o*-Tolyl) (13.1 mg, 0.043 mmol) were placed in a two-necked flask under argon, and then dried toluene (8 mL) was added. After the mixture being stirred at 120 °C for 22 h, blocking reaction was performed by adding excess of bromobenzene. The crude polymer was precipitated into methanol and the polymer was collected by filtration. Then the polymer was purified by Soxhlet extraction in acetone, hexane, and THF. The final polymer from THF phase was precipitated into methanol, which was collected and dried in vacuum overnight, and then we obtained a violet solid. Yield **PCPDT**: 200 mg (93%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) 6.99 (s, 2H), 1.90 (br, 4H), 1.05 (m, 16H), 0.75 (br, 6H), 0.67 (m, 8H). Anal. Calcd for $C_{25}H_{36}S_2$: C, 74.94; H, 9.06; S, 16.00. Found: C, 74.52; H, 9.06; S, 15.62. GPC (THF, polystyrene standard): M_n = 33900 g/mol, PDI = 2.75.

Fabrication and Characterization of Polymer Solar Cells.

$PC_{71}BM$ (American Dye Source) was purchased from the commercial resources and used as received. **PBNCPDT** and **PCPDT** were used without further treatments. ITO glass substrates were successively ultrasonicated for 10 minutes with detergent, de-ionized water, acetone, and iso-propanol, respectively. The processed ITO glass substrates were dried at 120 °C overnight and subsequently UV-ozone treatment for 25 min, and then PEDOT:PSS (Baytron P VP A1 4083) was spin-coated on these pre-cleaned ITO substrates and baked at 120 °C for 30 min. Then, all the substrates were transferred to glove box filled with nitrogen. The active layer (100 nm) based on **PBNCPDT**:$PC_{71}BM$ (1:3 *w/w*) was spin-cast with the solution in ortho-dichlorobenzene/1,8-diiodoctane (97:3 by volume). The **PCPDT**:$PC_{71}BM$ (1:3 *w/w*) active layer (100 nm) was spin-coated from the ortho-dichlorobenzene/1,8-diiodoctane (97:3 by volume) solution. Finally, LiF (1 nm) and Al (100 nm) were sequentially deposited on the top of the active layer in a vacuum chamber after the vacuum pressure being reached to 4×10^{-4} Pa. The active area of our device was 8 mm^2. Under illumination with the intensity of 100 mW/cm^2 provided by an Oriel 150W solar simulator with an AM 1.5G filter, we measured the *J–V* curves of the devices using a Keithley 2400 source meter. We measured the EQE under the short-circuit condition with a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz during illumination with a monochromatic light from a Xenon lamp.

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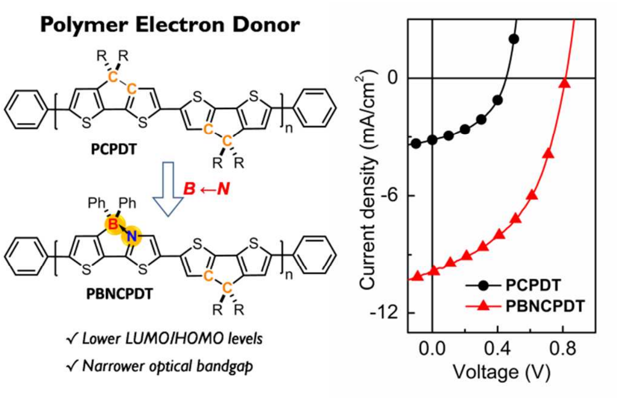
TOC



We report a novel approach to tune the LUMO/HOMO energy levels of polymer donors by replacing a C–C unit with a B←N unit. Compared to the polymer containing C–C unit, the polymer containing B←N unit exhibits lower LUMO/HOMO levels and narrower bandgap, leading to improved device performance of polymer solar cells.