Conjugated Polymers

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An Electron-Deficient Building Block Based on the B←N Unit: An Electron Acceptor for All-Polymer Solar Cells

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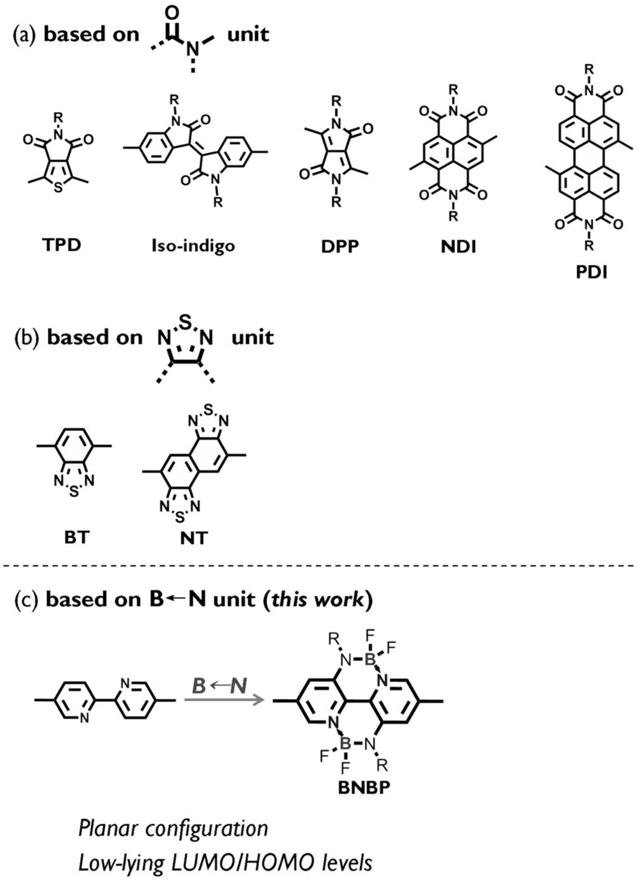
Abstract: *A double B←N bridged bipyridyl (BNBP) is a novel electron-deficient building block for polymer electron acceptors in all-polymer solar cells. The B←N bridging units endow BNBP with fixed planar configuration and low-lying LUMO/HOMO energy levels. As a result, the polymer based on BNBP units (P-BNBP-T) exhibits high electron mobility, low-lying LUMO/HOMO energy levels, and strong absorbance in the visible region, which is desirable for polymer electron acceptors. Preliminary all-polymer solar cell (all-PSC) devices with P-BNBP-T as the electron acceptor and PTB7 as the electron donor exhibit a power conversion efficiency (PCE) of 3.38 %, which is among the highest values of all-PSCs with PTB7 as the electron donor.*

Conjugated polymers based on alternating electron-rich and electron-deficient building blocks have received great attention because of their applications in high-performance polymer solar cells (PSCs) and organic field-effect transistors (OFETs).[1] While a large family of electron-rich building blocks have been reported, only a few electron-deficient building blocks have been developed, such as thieno[3,4-c]pyrrole-4,6-dione (TPD), 2,5-dihydropyrrolo[3,4,c]pyrrole-1,4-dione (DPP), isoindigo, benzo-[c][1,2,5]thiadiazole (BT), and naphtho[1,2-c:5,6-c′]bis[1,2,5]thiadiazole (NT).[2,3] As shown in Scheme 1, most of these electron-deficient building blocks are based on either amide unit or thiadiazole units. To expand the scope of conjugated polymers and advance the development of high-performance PSCs and OFETs, the new concept of designing electron-deficient building blocks needs to be developed.

All-polymer solar cells (all-PSCs), which use a polymer electron donor and a polymer electron acceptor, are of growing interest because of their great advantages over conventional polymer/fullerene PSCs.[4–7] These advantages include enhanced light absorption of the acceptor, tunability of the acceptor energy levels, and improved morphological stability of the blend. One critical issue is the development of an excellent polymer electron acceptor with low-lying LUMO/HOMO energy levels, a suitable absorption spectrum, and high electron mobility.[6] To date, only a few conjugated polymers have been reported that can work as electron acceptors for all-PSCs. Moreover, only several specific polymers based on naphthalene diimide (NDI) or perylene diimide (PDI) units can give PCE values over 3 % of all-PSCs.[5,7] It is a great challenge for chemists to develop novel polymer electron acceptors with good device performance.



Scheme 1. Examples of electron-deficient building blocks based on amide, thiadiazole, and B←N units (this work).

The B←N unit, which is isoelectronic and isosteric to the C–C unit, is a strong electron-withdrawing unit. The B←N unit has been used to develop electron-transporting materials with low-lying LUMO levels for organic light-emitting diodes (OLEDs).[8,9] We have found that the B←N unit can dramatically decrease LUMO/HOMO energy levels of conjugated polymers and consequently transform a normal

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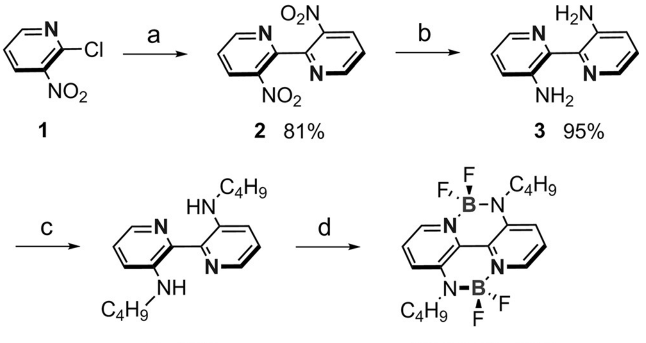
electron donor to an electron acceptor.[10] Herein we report a novel electron-deficient building block based on the B←N unit and demonstrate that the resulting conjugated polymer can be used as electron acceptor with good all-PSC device performance. Scheme 1 c shows the chemical structure of the building block, namely double B←N bridged bipyridyl (BNBP). The B←N unit is used as the bridging unit of bipyridyl framework, leading to fixed planar configuration and low LUMO/HOMO levels of BNBP. Consequently, the polymer based on the BNBP unit exhibits high electron mobility, low-lying LUMO/HOMO energy levels, and strong absorbance in the visible range, which is desirable for polymer electron acceptors. Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexy)carbonyl] thieno[3,4-b]-thiophenediyl]] (PTB7), which is a benchmark polymer donor for fullerene-based PSCs and can give a PCE value of over 9%, is selected as the electron donor in this study.[11] A preliminary all-PSC device with the resulting polymer as the electron acceptor and PTB7 as the electron donor exhibits a PCE value of 3.38%. This value is among the highest values reported for all-PSCs with the widely used PTB7 as the electron donor, thus indicating that BNBP is a promising electron-deficient building block for polymer electron acceptors with good device performance.

As illustrated in Scheme 2, the model compound of the BNBP unit (BNBP-C4) was prepared in a four-step synthesis starting from commercially available 2-chloro-3-nitropyridine.[12] The dimerization of **1** and subsequent reduction of **2** with $SnCl_2$ afforded **3**, which was alkylated with nBuLi/nC_4H_9Br to give **4**. Treatment of **4** with $BF_3{\cdot}Et_2O/Et_3N$ readily produced BNBP-C4 as a yellow solid in a high yield of 86%. Compound BNBP-C4 is highly stable in air, dilute acidic, or basic aqueous solution, and can be purified by column chromatography on silica gel. The chemical structure of BNBP-C4 was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy and elemental analysis (see the Supporting Information).

Single crystals of BNBP-C4 were obtained by recrystallization from $CHCl_3/CH_3OH$ solutions. The X-ray crystallographic analysis (Figure 1 a) shows an almost planar geometry of the framework.[13] The B–N covalent bond length is 1.489(2) Å. The B←N coordination distance is 1.580(2) Å, which is around 0.1 Å longer than the average B–N covalent bond length. Moreover, the C–C bond between the two pyridine units (1.437(3) Å) in BNBP-C4 is much shorter than that in bipyridine (1.490(13) Å) (see the Supporting Information),[14] thus suggesting that the C–C bond has more double-bond character and that the two pyridine units are more effectively conjugated in BNBP-C4 than in bipyridine. In the crystal packing, (Figure 1 b), a slipped face-to-face π-stacked column is observed with the mean plane distance of 3.57 Å. The intermolecular F···H interactions concomitantly appear between the neighboring molecular columns (see the Supporting Information). Both the close π-stacking and F···H interactions should be favorable for high electron mobility of conjugated polymers based on the BNBP unit.



Scheme 2. Synthetic route to BNBP-C4. Reagents and conditions: a) Cu powder, DMF, 150 °C; b) $SnCl_2{\cdot}2H_2O$, HCl, 100 °C; c) nBuLi, THF, −78 °C, then nC_4H_9Br, −78 °C→35 °C; d) $BF_3{\cdot}Et_2O$, Et_3N, CH_2Cl_2, 50 °C.

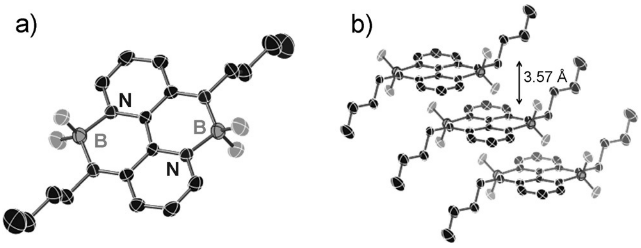


Figure 1. a) Single-crystal structure of BNBP-C4 (50% probability for thermal ellipsoids) and b) its slipped π-stacked structure.

Figure 2 a shows the UV/Vis absorption spectra and fluorescence spectra of BNBP-C4 and **4** in $CHCl_3$ solution. The low-energy absorption band of BNBP-C4 with B←N bridging units is red-shifted by around 80 nm compared to that of **4** without the bridging units, thus suggesting that the B←N bridging units lead to more delocalized π electrons over the framework. This observation is consistent with the short C–C bond between the two pyridine units in BNBP-C4. In comparison to **4** with the fluorescence peak at 450 nm and low fluorescence quantum yield (Φ_{PL}) of 0.08, BNBP-C4 has a red-shifted fluorescence spectrum with a peak at 528 nm and a much higher Φ_{PL} value of 0.98 (see the Supporting Information). These differences are attributed to the more effective π conjugation and the more rigid skeleton with the B←N bridging units in BNBP-C4.

Figure 2 b shows the cyclic voltammograms of BNBP-C4 and **4**. According to the onset potentials of reduction and oxidation, the LUMO/HOMO energy levels of BNBP-C4 are estimated to be −3.19 eV/−5.63 eV (see the Supporting Information). Its electrochemical HOMO–LUMO gap (2.44 eV) is consistent with the optical band gap (2.34 eV) calculated from the onset wavelength of the absorption spectrum. Compound **4** exhibits only irreversible oxidation processes and the reduction wave cannot be detected. Thus, based on the onset oxidation potential and the optical band gap, the LUMO/HOMO energy levels of **4** are estimated to be −2.24 eV/−5.03 eV. Comparison of the LUMO/HOMO energy levels of the two compounds suggests that the B←N bridging units result in the low LUMO/HOMO levels of BNBP-C4.

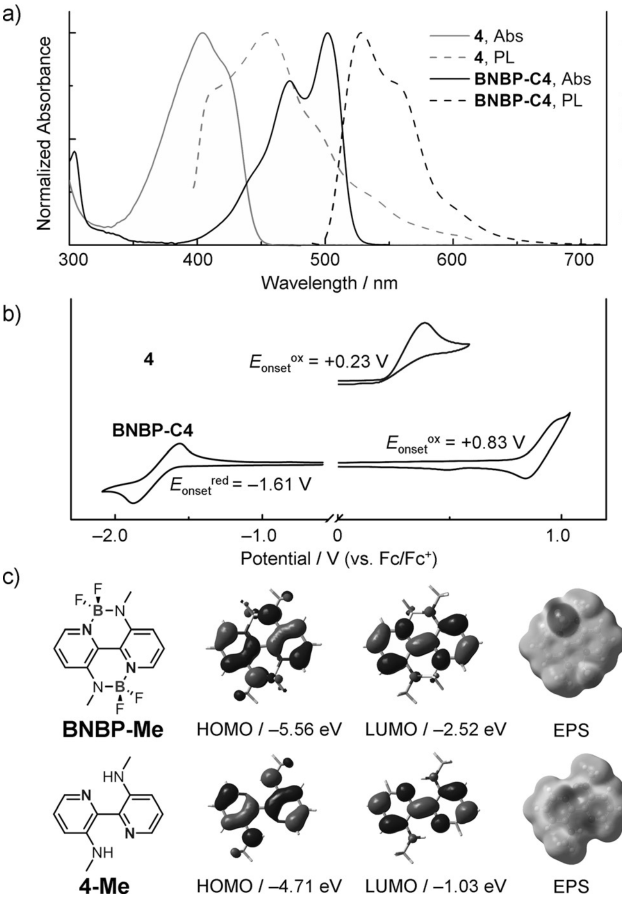
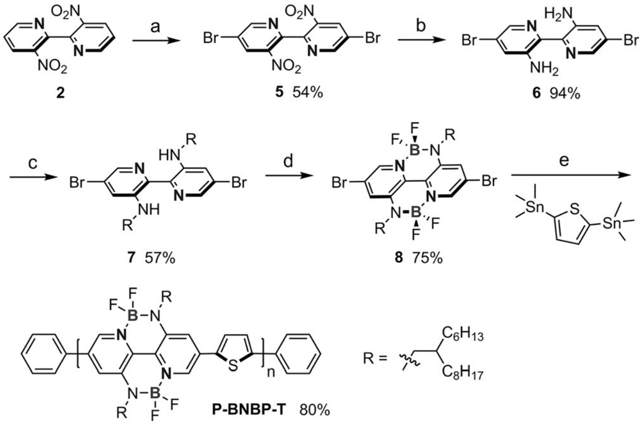


Figure 2. a) UV/Vis absorption spectra and fluorescence spectra of BNBP-C4 and **4** in $CHCl_3$ solutions; b) Cyclic voltammograms of BNBP-C4 and **4**, Fc = ferrocene; c) LUMO/HOMO and energy levels, as well as electrostatic potential surface (EPS) maps at the 0.0004 electron density of the model compounds BNBP-Me and **4-Me**.



Scheme 3. Synthesis of P-BNBP-T. Reagents and conditions: a) HBr, CH_2Cl_2 and then Br_2, 150 °C; b) $SnCl_2 \cdot 2H_2O$, HCl, 100 °C; c) *n*BuLi, THF, −78 °C, then 1-iodo-2-hexyldecane, from −78 °C to 65 °C; d) $BF_3 \cdot Et_2O$, Et_3N, CH_2Cl_2, 50 °C; e) [$Pd_2(dba)_3$], P(*o*-Tolyl)$_3$, toluene, 120 °C, then bromobenzene.

To gain insight into the electronic structure of BNBP-C4, density functional theory (DFT) calculations of BNBP-Me and **4-Me** were performed at the B3LYP/6-31G* level of theory (Figure 2c).[15] The DFT calculation shows that the LUMO/HOMO of both BNBP-Me and **4-Me** are similarly delocalized over the entire π-conjugated frameworks and that the LUMO/HOMO levels of BNBP-Me are much lower than that of **4-Me**. These results are consistent with the aforementioned experimental results. In the calculated electrostatic potential surface (EPS) maps, the colors red and blue represent negative and positive charges, respectively.[16] While the conjugated bipyridyl unit in **4-Me** is electronically negative, the bipyridyl unit in BNBP-Me is electronically positive, thus demonstrating that the B←N coordination bond enhances the electron-deficient nature of the central framework of BNBP-Me.

For the application of BNBP as building block in conjugated polymers, the key issue is to introduce reactive groups on BNBP unit. We successfully synthesized dibromo-substituted derivative **8** starting from **2** (Scheme 3). Moreover, the Stille coupling of **8a** with organotin compounds afforded a single product with no detectable byproduct in the reaction mixture (see the Supporting Information), thus suggesting that **8a** with B←N units is stable enough for the Stille coupling reaction. Thus, we carried out Stille polymerization of **8** and ditrimethylstannnyl thiophene in the presence of [$Pd_2(dba)_3$] as the catalyst to synthesize the polymer P-BNBP-T (Scheme 3). Its chemical structure was confirmed by ^{1}H NMR and elemental analysis. According to gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene as the eluent at 150 °C, the number-average molecular weight (M_n) of P-BNBP-T is 24600 and the polydispersity (PDI) is 2.01. P-BNBP-T shows high thermal stability with thermal degradation temperature (T_d) of 357 °C and good solubility in common organic solvents, such as $CHCl_3$, toluene, and chlorobenzene.

The absorption spectrum of P-BNBP-T in $CHCl_3$ solution shows a strong absorption band with the peak at $\lambda = 589$ nm and absorption coefficient as high as $1.53 \times 10^5\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ (Figure 3a and the Supporting Information). The intermolecular interactions in thin films result in the absorption spectrum being red-shifted by around 33 nm. According to the onset absorption wavelength of thin film, the optical band gap of P-BNBP-T is estimated to be 1.92 eV. As shown in Figure 3b, the cyclic voltammogram of P-BNBP-T exhibits irreversible reduction and oxidation waves with the onset potentials of $E_{onset}^{red} = -1.30$ V and $E_{onset}^{ox} = +0.97$ V, respectively. Accordingly, its LUMO/HOMO energy levels are estimated to be −3.50 eV/−5.77 eV. The low-lying LUMO/HOMO levels indicate that P-BNBP-T can be used as electron acceptors for PSCs. The electron mobility (μ_e) of P-BNBP-T was estimated to be $6.9 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ by using the space-charge-limited current (SCLC) method with the current density/voltage curve of the electron-only device (device structure: ITO/ZnO/P-BNBP-T/LiF/Al). The μ_e value of P-BNBP-T is roughly comparable to those of many high-performance nonfullerene electron acceptors.[4–7,17]

The low-lying LUMO/HOMO levels, high electron mobility, and strong absorption in the visible range of P-BNBP-T prompted us to fabricate all-PSC devices with this polymer as the electron acceptor. As shown in the inset of Figure 3b, the

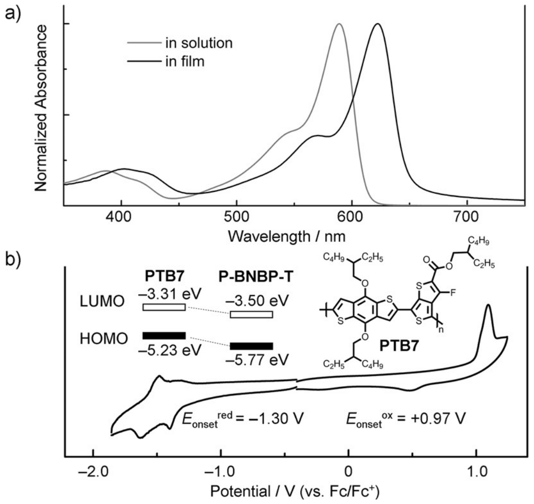


Figure 3. a) UV/Vis absorption spectra of P-BNBP-T in $CHCl_3$ solution and in film; b) Cyclic voltammogram of P-BNBP-T in film. Fc = ferrocene. Insets: Schematic of the energy level alignments of P-BNBP-T and PTB7, and chemical structure of PTB7.

differences between the LUMO and HOMO of PTB7 and P-BNBP-T enable the photoinduced electron transfer from PTB7 to P-BNBP-T and the photoinduced hole transfer from P-BNBP-T to PTB7. The all-PSC device configuration is ITO/PEDOT:PSS/PTB7:P-BNBP-T (2:1 w/w)/LiF/Al. The active layer is spin-coated from the $CHCl_3$ solution of the two polymers (see the Supporting Information). Figure 4 shows the current density-voltage (J–V) curve and external quantum efficiency (EQE) spectrum of the device under AM 1.5 G illumination with an intensity of 100 mW cm^{-2}. The device shows the short-circuit current density (J_{sc}) of 7.09 mA cm^{-2}, the open-circuit voltage (V_{oc}) of 1.09 V, fill factor (FF) of 0.44, corresponding to the PCE value of 3.38 %. The device shows an EQE response from 300 nm to 800 nm with the maximum value of 43 %. The J_{sc} value calculated from integration of the EQE and the AM 1.5G reference spectrum is 7.21 mA cm^{-2}, which is in good agreement with the J_{sc} value obtained from the J–V curve. The V_{oc} of the all-PSC device is around 0.35 V higher than that of typical PTB7/fullerene device, which is attributed to the relatively higher LUMO level of P-BNBP-T than that of fullerene derivatives. It is noteworthy that the highly efficient all-PSCs always use two-dimensional donor polymers with conjugated side chains and that PTB7 always exhibits moderate photovoltaic performance in all-PSC devices.[4b,c] The PCE value of the PTB7:P-BNBP-T system is among the highest values reported for all-PSCs with the widely-used PTB7 as the electron donor, thus indicating that P-BNBP-T is a promising polymer electron acceptor. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) of the active layer of the all-PSC device indicate that PTB7 and P-BNBP-T are intimately mixed when processed with chloroform as the solvent (see the Supporting Information). This morphology may be not optimal for charge carrier transporting and may produce the low FF of the all-PSC device. Optimization of the active layer morphology is in progress and is expected to give improved device performance.

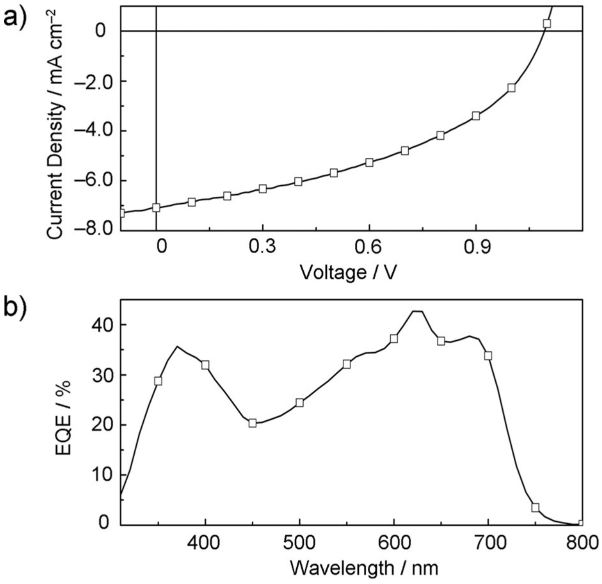


Figure 4. a) J–V curve and b) EQE spectrum of the all-PSC device based on PTB7:P-BNBP-T blend.

In summary, we have developed BNBP as a new class of electron-deficient building block for polymer electron acceptors and demonstrated its good all-PSC device performance. The B←N bridging unit endows BNBP with fixed planar configuration and low LUMO/HOMO energy levels. As a result, the polymer based on BNBP exhibits high electron mobility, low LUMO/HOMO energy levels, and strong absorbance in the visible range, which is desirable for polymer electron acceptors. The preliminary all-PSC device based on PTB7:P-BNBP-T blend exhibits an impressive PCE value of 3.38 %. This work not only comprises a promising polymer electron acceptor material for all-PSCs, but also provides a novel strategy for the design of building blocks with B←N units for functional conjugated polymers.

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