Electron Transport **Hot Paper**

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Developing Conjugated Polymers with High Electron Affinity by Replacing a C–C Unit with a B←N Unit**

Chuandong Dou, Zicheng Ding, Zijian Zhang, Zhiyuan Xie, Jun Liu, and Lixiang Wang*

Abstract: *The key parameters of conjugated polymers are lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels. Few approaches can simultaneously lower LUMO and HOMO energy levels of conjugated polymers to a large extent (> 0.5 eV). Disclosed herein is a novel strategy to decrease both LUMO and HOMO energy levels of conjugated polymers by about 0.6 eV through replacement of a C–C unit by a B←N unit. The replacement makes the resulting polymer transform from an electron donor into an electron acceptor, and is proven by fluorescence quenching experiments and the photovoltaic response. This work not only provides an effective approach to tune the LUMO/HOMO energy levels of conjugated polymers, but also uses organic boron chemistry as a new toolbox to develop conjugated polymers with high electron affinity for polymer optoelectronic devices.*

Conjugated polymers with π-electrons delocalized over the backbones are an important class of semiconducting materials and have been used in various devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), polymer solar cells (PSCs), etc.[1] The key parameters of conjugated polymers are lowest unoccupied molecular orbital (LUMO)/highest occupied molecular orbital (HOMO) energy levels. Accordingly, there are many *p*-type conjugated polymers with high LUMO/HOMO energies and many ambipolar conjugated polymers with low LUMO and high HOMO energies.[2] In comparison, n-type conjugated polymers with low-lying LUMO/HOMO levels and high electron affinity are scare, irrespective of their applications as electron transport materials in OLEDs, n-type materials in OFETs, or electron acceptor materials in PSCs, etc.[3] Several strategies have been reported to tune the LUMO/HOMO levels of conjugated polymers. To decrease LUMO and increase HOMO energy levels for narrow band gaps of conjugated polymers, one may enforce coplanarity of the polymer backbone, increase quinoidal character of the polymer backbone, or use alternating electron-poor and electron-rich units.[4] To slightly increase (or decrease) both the LUMO and HOMO energies of conjugated polymers, one may introduce electron-rich (or electron-poor) substituents to the polymer backbone.[5] However, few approaches can simultaneously lower both the LUMO and HOMO energy levels of conjugated polymers to a large extent (> 0.5 eV).[6] Thus, novel molecular design strategies to greatly decrease both the LUMO and HOMO energies of conjugated polymers for high electron affinity are important and challenging.

Thanks to the recent progress in organic boron chemistry,[7] conjugated polymers containing boron elements have received great attention.[8] Jäkle, Chujo, and Wagner et al. have reported several families of boron-containing conjugated polymers which exhibit either unusual properties or excellent performance.[8] Bazan et al. have performed reversible intermolecular B–N coordination reactions to tune the emission color of conjugated polymers.[9] The B←N unit and C–C unit are isoelectronic and isosteric.[10] In a C–C unit, each carbon atom has four valence electrons. In a B←N unit, the boron atom has three valence electrons and the nitrogen atom has five valence electrons. Therefore, in contrast to C–C being a covalent bond with a dipole of zero and bond dissociation energy of 90.1 kcal mol^{-1}, B←N is a coordination bond with a dipole of 5.2 D and bond dissociation energy of 27.2 kcal mol^{-1}.[11] The B←N unit has been used by Yamaguchi et al., S. Wang et al., and Y. Wang et al. to develop conjugated small molecules with high electron affinity.[12] These molecules have been applied as electron transport materials or emitters in OLEDs and n-type semiconductors in OFETs. Herein, we report that replacing a C–C unit by a B←N unit in conjugated polymers can lower both the LUMO and HOMO energies by about 0.6 eV (Figure 1). As a result, the replacement changes the resulting conjugated polymer from an electron donor to an electron acceptor. Our results indicate that organic boron chemistry provides a new toolbox for developing conjugated polymers with high electron affinity, which is required for OLEDs, OFETs, and OPVs.

Figure 1 shows the chemical structures of the model polymer with the C–C unit, poly[(4,4-bis(2-ethylhexyl)cyclopenta-[2,1-b:3,4-b′]-dithiophene-2,6-diyl)-alt-(5-(2-octyldodecyl)thieno[3,4-c]pyrrole-4, 6-dione-1,3-diyl)] (**P**-CC), and the corresponding polymer with a B←N unit, poly[((3-diphenylboryl-2-thienyl)-2-thiazole-2,6-diyl)-alt-(5-(2-octyldodecyl)thieno[3,4-c]pyrrole-4,6-dione-1,3-diyl)] (**P**-BN).

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[*] Dr. C. Dou, Dr. Z. Ding, Z. Zhang, Prof. Z. Xie, Prof. J. Liu, Prof. L. Wang
State Key Laboratory of Polymer Physics and Chemistry Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun 130022 (P. R. China)
E-mail: liujun@ciac.ac.cn

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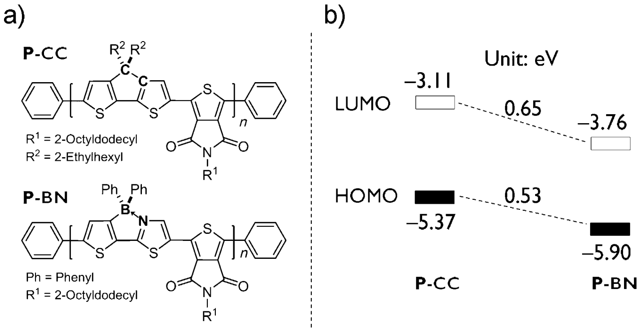
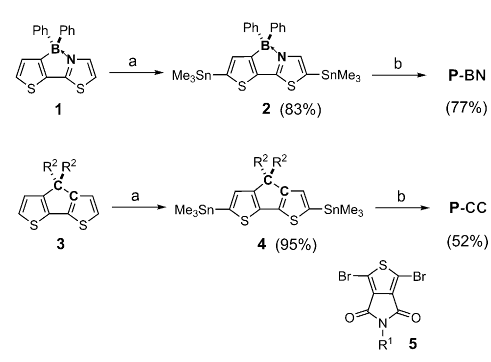


Figure 1. a) Chemical structures of the model polymer **P**-CC containing a C–C unit and the designed polymer **P**-BN containing a B←N unit. Note that the chemical structure of **P**-BN should be regiorandom as a result of the unsymmetric B←N-containing unit. b) LUMO/HOMO energy levels of the two polymers.

The thieno[3,4-c]pyrrole-4,6-dione-1,3-diyl (TPD) unit is used for the two alternating copolymers because of its weak electron-accepting feature. Thus, **P**-CC is a typical conjugated polymer with alternating electron-rich cyclopenta-[2,1-b:3,4-b′]-dithiophene units (CPDT) and electron-poor TPD units.[13] **P**-BN can be used to investigate the effects of replacing a C–C with B←N in a conjugated polymer.

Scheme 1 illustrates the synthetic routes to **P**-BN and **P**-CC. The diphenylboryl-substituted thienylthiazole **1** was prepared according to the previous report of the dimesitylboryl analogue from the group of Yamaguchi.[12d] Lithiation with 2.2 equivalents of *n*BuLi on **1**, and subsequent treatment with Me_3SnCl produced the key monomer **2**. Stille polymerization of **2** and **5** readily afforded **P**-BN in 77% yield. With the unsymmetric BN-containing unit, **P**-BN should be regiorandom because both head-to-head and head-to-tail bonding modes of the BN-containing unit and the TPD unit may exist. The chemical structure of **P**-BN was verified by ^1H NMR and ^{11}B NMR spectroscopy, as well as elemental analysis. The sharp signal at $\delta = 0.6$ ppm in the ^{11}B NMR spectrum suggests a tetracoordinated boron center (see the Supporting Information). **P**-CC was synthesized by the Stille polymerization of the corresponding C–C-containing monomer **4** and **5**. Both **P**-CC and **P**-BN are stable enough to be purified in air, and they have good thermal stability and photostability (see the Supporting Information). Our attempts to synthesize the diethylboryl analogue of **P**-BN failed because its corresponding B←N-containing monomer was sensitive to air and moisture, and unsuitable for polymerization.



Scheme 1. Synthesis of **P**-BN and **P**-CC. Reagents and conditions: a) *n*BuLi, tetrahydrofuran, −78 °C, then Me_3SnCl, from −78 °C to 25 °C; b) **5**, $[Pd_2(dba)_3]$, P(*o*-Tolyl)$_3$, toluene, 120 °C, then phenylboronic acid and bromobenzene. Ph = Phenyl, R^1 = 2-octyldodecyl, R^2 = 2-ethylhexyl.

To elucidate the effects of the B←N unit, we performed density-functional theory (DFT) calculations at the B3LYP/6-31G* level of theory on the model compounds of **P**-CC and **P**-BN (M-CC-Me and M-BN-Ph; Figure 2).[14] Both M-CC-Me and M-BN-Ph contain two repeat units with the long alkyl chains replaced by the methyl groups. Their optimized structures show fully planar skeletons owing to the fusion with the C–C or B←N unit (see the Supporting Information). This effect is in stark contrast to the distorted backbone of conjugated polymers with an intermolecular B–N Lewis acid–base effect reported by Bazan et al., and is due to the steric hindrance of the boron-containing moieties.[9] The calculation indicates that the HOMO of M-CC-Me is mainly localized on the electron-rich CPDT unit, and the LUMO is mainly localized on the electron-poor TPD unit, thus suggesting an electron-donor–acceptor feature with the intramolecular charge transfer of **P**-CC. In contrast, the HOMO and LUMO of M-BN-Ph were both well delocalized over the entire framework. Thus, replacing the C–C unit by a B←N unit in conjugated polymers obviously affects the distribution of electron densities and decreases the electron-donor–acceptor character. To clarify the effects of the B←N unit on LUMO/HOMO energy levels, the DFT calculations on the dimethylboryl analogue M-BN-Me was also conducted. Replacing a C–C unit in M-CC-Me by a B←N unit in M-BN-Me decreases the LUMO/HOMO energy levels by 0.39/0.59 eV. The substituents on the boron atom can further lower the LUMO/HOMO energy levels. The LUMO/HOMO energy levels of M-BN-Ph are lowered by 0.50 eV/0.69 eV compared to those of M-CC-Me. Thus, DFT calculations suggest that the B←N unit can endow conjugated polymers with high electron affinity.

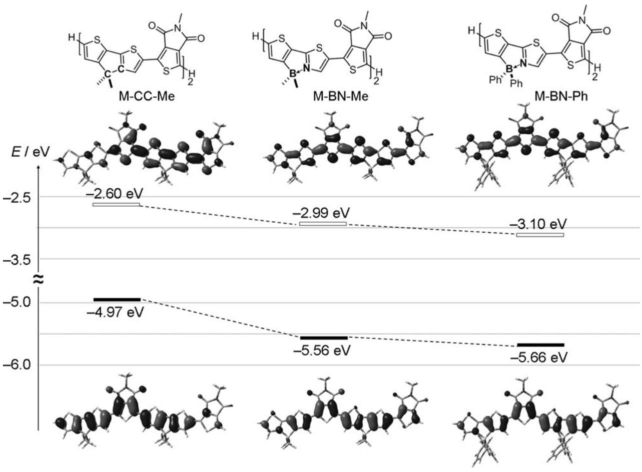


Figure 2. Electronic effects of replacing a C–C unit by a B←N unit on the model compounds, which is calculated at the B31 LYP/6-31G* level.

To verify the effects of the B←N unit substitution on the LUMO/HOMO energy levels of the polymers, we measured cyclic voltammetry of the polymer films (Figure 3). **P**-CC

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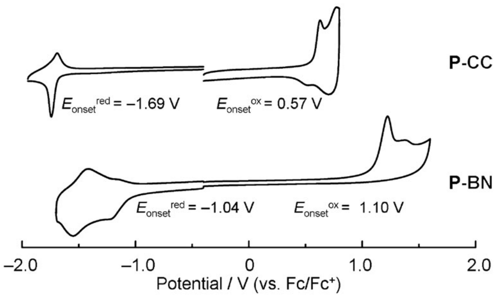

Figure 3. Cyclic voltammogram of the films of **P**-BN and **P**-CC.

shows a reversible reduction wave and two quasireversible oxidation waves with the onset reduction potential ($E_{\text{onset}}^{\text{red}}$ vs. Fc/Fc$^+$) of −1.69 V and onset oxidation potential ($E_{\text{onset}}^{\text{ox}}$) of 0.57 V. In comparison, **P**-BN shows multiple irreversible reduction and oxidation processes with more-positive onset reduction and oxidation potentials ($E_{\text{onset}}^{\text{red}} = -1.04$ V, $E_{\text{onset}}^{\text{ox}} = 1.10$ V). According to these onset reduction and oxidation potentials, the LUMO/HOMO energy levels of the two polymers are estimated and listed in Table 1. Compared with those of **P**-CC, the LUMO and HOMO of **P**-BN are lowered by 0.53 eV and 0.65 eV, respectively. This lowering is consistent with the DFT calculation results and manifests the effects of B←N unit. The low-lying LUMO/HOMO energies of **P**-BN ($E_{\text{LUMO}} = -3.76$ eV, $E_{\text{HOMO}} = -5.90$ eV) imply that **P**-BN has a high electron affinity. Indeed, its LUMO/HOMO energy levels are fairly comparable to those of Phenyl-C61-butyric acid methyl ester ($PC_{61}BM$; $E_{\text{LUMO}} = -3.88$ eV, $E_{\text{HOMO}} = -6.10$ eV), a widely used electron-acceptor material in PSCs (see the Supporting Information).

The replacement of a C–C unit by a B←N unit in the conjugated polymers leads to a blueshift of the absorption spectra and fluorescence spectra, as well as increase of the optical band gap. As shown in Figure 4, the absorption spectrum of **P**-CC in solution shows a broad band with peaks at $\lambda = 646/598$ nm, while the absorption spectrum of **P**-BN in solution exhibits an absorption maxima at $\lambda = 574$ nm with a shoulder at $\lambda = 610$ nm. This difference is evidenced by the different color of the solutions of the two polymers as shown in the insets of Figure 4. In the thin film, **P**-BN exhibits an onset absorption at $\lambda = 660$ nm, thus corresponding to the optical band gap of 1.88 eV. In comparison, **P**-CC shows an onset absorption at $\lambda = 730$ nm, thus indicating the optical band gap of 1.69 eV. Both **P**-BN and **P**-CC show an obvious redshift in absorption spectra in going from solution to film because the planar configurations of the polymer backbones facilitate the interactions of polymer backbones in the solid state. While both **P**-BN and **P**-CC show high fluorescence quantum efficiencies of 0.21 and 0.16, respectively, the peak of the fluorescence spectrum of **P**-BN is blue-shifted by 43 nm compared to that of **P**-CC.

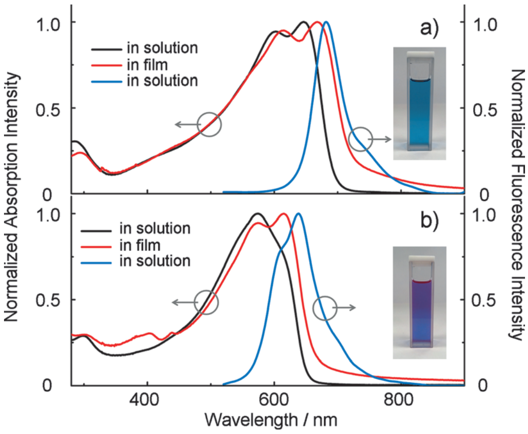

Figure 4. UV/Vis absorption spectra and fluorescence spectra of a) **P**-CC and b) **P**-BN in $CHCl_3$ solution and in film. Insets: photographs of **P**-CC and **P**-BN in $CHCl_3$ solution.

For a blend of two organic/polymeric materials, if the ΔLUMO (or ΔHOMO) of the two materials is larger than 0.3–0.4 eV, electron transfer (or hole transfer) between them can occur and leads to exciton dissociation and fluorescence quenching, thus photovoltaic performance may be expected.[15] The fluorescence quenching experiments of **P**-CC and **P**-BN were performed on thin films. As shown in Figure 5, the **P**-CC film shows no detectable fluorescence and the **P**-BN film exhibits fluorescence with the peaks at $\lambda = 650/710$ nm. The fluorescence of the film of a **P**-CC/**P**-BN (1:1) blend is undetectable, thus indicating that the fluorescence of **P**-BN is fully quenched by **P**-CC. This fluorescence quenching is assigned to the electron/hole transfer between the two polymers and confirms the low-lying LUMO/HOMO energy

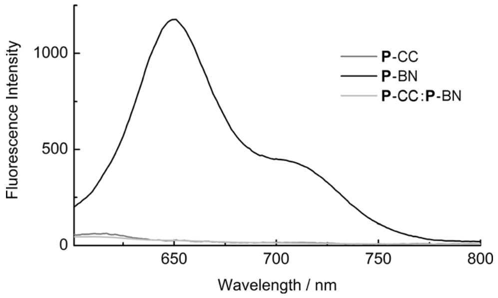

Figure 5. Fluorescence spectra of the films of **P**-CC, **P**-BN, and **P**-CC/**P**-BN (1:1), excited at $\lambda = 570$ nm.

Table 1: Photophysical properties, electrochemical properties, and energy levels of **P**-BN and **P**-CC.

Polymer	λ_{abs}[a] [nm]	ε_{max}[a] [$\text{M}^{-1}\,\text{cm}^{-1}$]	λ_{em}[a] [nm]	ϕ_F[a]	λ_{abs}[b] [nm]	E [eV]	$E_{\text{onset}}^{\text{ox}}$[c] [V]	$E_{\text{onset}}^{\text{red}}$[c] [V]	E_{HOMO}[d] [eV]	E_{LUMO}[d] [eV]
P-CC	598, 646	78 900	681	0.16	667, 612	1.69	0.57	−1.69	−5.37	−3.11
P-BN	574, 610	89 600	638	0.21	614, 574	1.88	1.10	−1.04	−5.90	−3.76

[a] Measured in $CHCl_3$ solution. [b] Measured in thin film. [c] Onset potential vs. Fc/Fc$^+$. [d] Calculated using the equation ($E_{\text{HOMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}})$ eV, $E_{\text{LUMO}} = -(4.80 + E_{\text{onset}}^{\text{red}})$ eV).

levels of **P**-BN. Encouraged by this result, we fabricated PSC devices with a **P**-CC/**P**-BN blend as the active layer. The device exhibits a photovoltaic response with an open-circuit voltage of 1.08 V, a short-circuit current density of 0.35 $\mathrm{mA\,cm^{-2}}$, a fill factor of 0.23, and a power conversion efficiency of 0.085 % (see the Supporting Information). The device performance is not so satisfactory, probably because of the large phase separation size of the blend film (see the Supporting Information). Both the fluorescence quenching experiment and the photovoltaic response suggest that the replacement of a C–C unit in **P**-CC by a B←N unit in **P**-BN changes the polymer from an electron donor to an electron acceptor.

To clearly verify the capability of **P**-BN as an electron-acceptor/hole donor when blended with normal conjugated polymers, we selected a typical electron donor, poly(3-hexylthiophene) (P3HT), and conducted the fluorescence quenching experiments in solution.[16] As shown in Figure 6 a, P3HT exhibits a strong orange fluorescence peak around $\lambda = 573$ nm in $CHCl_3$ solution (10 $\mu g\,mL^{-1}$). When **P**-BN was added to the P3HT solution, the intensity of P3HT fluorescence gradually decreased. Considering the energy level alignments of P3HT and **P**-BN (see the inset of Figure 6 a), we attribute the fluorescence quenching of P3HT by **P**-BN to the electron transfer from P3HT to **P**-BN with the LUMO difference of 0.56 eV (see the Supporting Information). Similarly, as shown in Figure 6 b, the red fluorescence of **P**-BN can also be quenched by P3HT because of the hole transfer from **P**-BN to P3HT with the HOMO difference of 0.70 eV.[17] The fluorescence quenching of **P**-BN and P3HT is further confirmed by the smaller fluorescence intensities of the blend of **P**-BN and P3HT in solution compared with the individual solutions of the two polymers at the same concentration (see the Supporting Information). The PSC device with a P3HT/**P**-BN blend as the active layer also exhibits photovoltaic performance with a power conversion efficiency of 0.14 % (see the Supporting Information). The fluorescence quenching results and the photovoltaic response of **P**-BN and P3HT confirm the effects of the low-lying LUMO/HOMO energy levels of **P**-BN.

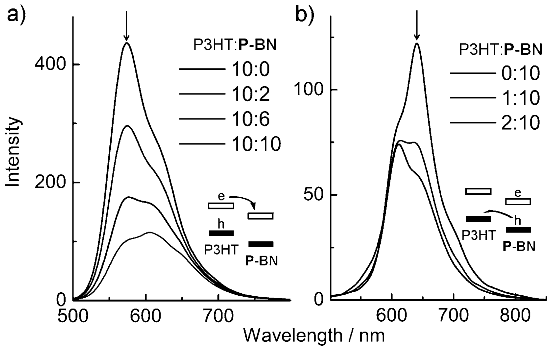

Figure 6. Fluorescence quenching spectra of P3HT/**P**-BN in $CHCl_3$ ($\mu g\,mL^{-1}$) with varying a) **P**-BN and b) P3HT concentrations ($\lambda_{ex} = 453$ nm). Insets: schematic of the energy level alignments and electron/hole transfer of P3HT and **P**-BN.

In summary, we demonstrate a strategy to greatly lower both the LUMO and HOMO energy levels of conjugated polymers for high electron affinity by replacing a C–C unit by a B←N unit. With the replacement, the LUMO and HOMO energy levels are lowered by 0.65 eV and 0.53 eV, respectively, thus making the conjugated polymer transform from an electron donor to an electron acceptor. This transformation is confirmed by fluorescence quenching experiments and the photovoltaic response. Following this strategy, further studies on conjugated polymers containing a B←N unit as an electron acceptor material in PSCs are in progress in our laboratory.

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