# Fine-Tuning LUMO Energy Levels of Conjugated Polymers Containing a B←N Unit

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S *Supporting Information*

ABSTRACT: The LUMO and HOMO energy levels (E_{LUMO}/E_{HOMO}) are key parameters for conjugated polymers, which can greatly affect their applications in organic optoelectronic devices. In this manuscript, with donor−acceptor (D−A) type conjugated polymers based on double B←N bridged bipyridine (BNBP) unit, we report fine-tuning of E_{LUMO} of conjugated polymers in a wide range via substitutions on both D unit and A unit. We synthesize eight D−A type conjugated polymers with alternating electron-deficient BNBP unit and electron-rich bithiophene (BT) unit in the main chain. By changing the substitutes on BNBP or BT, the E_{LUMO} of these polymers can be finely tuned in a wide range from −3.3 eV to −3.7 eV. We comprehensively investigate the electronic structures, photophysical properties, charge-transporting properties and polymer solar cell (PSC) device applications of these polymers. In PSC devices, these BNBP-based polymers can be used either as electron donors (with high-lying E_{LUMO}/E_{HOMO}) or as electron acceptors (with low-lying E_{LUMO}/E_{HOMO}). The PSC device with the BNBP-based polymer donor exhibits a PCE of 2.92% and the PSC device with the BNBP-based polymer acceptor exhibits a PCE of 5.16%. These results indicate a new approach to modulate the LUMO energy levels of D−A type conjugated polymers by modifications on both D unit and A unit.
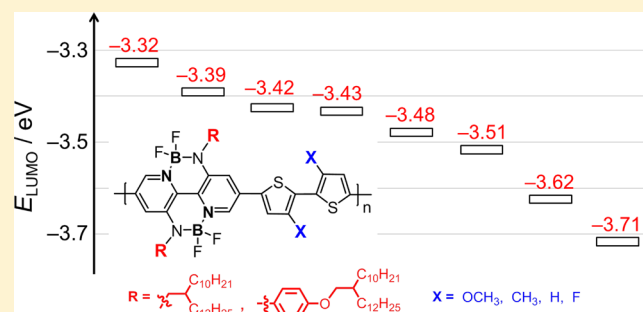
INTRODUCTION

Conjugated polymers are an important class of semiconducting materials for organic electronic devices, such as organic thin film transistors (OTFTs), polymer light-emitting diodes (PLEDs), and polymer solar cells (PSCs), etc.[1−6] The key parameters of conjugated polymers are lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels (E_{LUMO}/E_{HOMO}). Tuning their E_{LUMO}/E_{HOMO} is very important for improving opto-electronic device performance.[7−10] For example, in PSCs, polymers with high-lying E_{LUMO} can be used as electron donors and polymers with low-lying E_{LUMO} can be used as electron acceptors.[11−20] Moreover, the E_{LUMO} of these polymers are closely correlated with the PSC device characteristics. The E_{LUMO} offset between electron donor and electron acceptor is considered to be the energetic driving force for charge separation. The difference between the E_{LUMO} of electron acceptor and the E_{HOMO} of electron donor is associated with open-circuit voltage (V_{oc}) of PSCs. In order to ensure adequate driving force for charge separation and to maximize V_{oc}, the E_{LUMO} of polymer electron donors/acceptors have to be carefully optimized.[21−27]

High-performance polymer materials for PSCs and OTFTs are always D−A type conjugated polymers, in which electron-rich units (D) and electron-deficient units (A) are alternatively linked in the polymer backbone.[28−36] In these polymers, the E_{LUMO} are predominantly determined by the A units. Therefore, tuning of E_{LUMO} is always carried out by selecting appropriate A units, such as benzo[c][1,2,5]thiadiazole (BTz), naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz), isoindigo (IID), benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD), dithienyldiketopyrrolopyrrole (DPP), thieno[3,4-c]pyrrole-4,6-dione-1,3-diyl (TPD), naphthalene diimide (NDI), and perylene diimide (PDI), etc.[37−42] In addition, E_{LUMO} can be further finely tuned by introducing various electron donating or withdrawing side groups onto the A units of conjugated polymers.[43−48] However, despite these approaches, there are few reports on tuning E_{LUMO} of conjugated polymers in a wide range, e.g., changing the polymer from an electron donor to an electron acceptor.[49,50] Moreover, it still remains challenging for polymer chemists to precisely tune E_{LUMO} of conjugated polymers.[51,52]
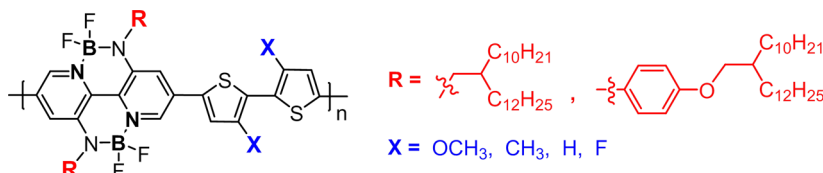
Recently, we have reported a new kind of electron-deficient unit based on boron-nitrogen coordination bond (B←N), double B←N bridged bipyridine (BNBP).[53] BNBP has been successfully used to develop D−A type conjugated polymers for applications as polymer electron acceptors for PSCs and as
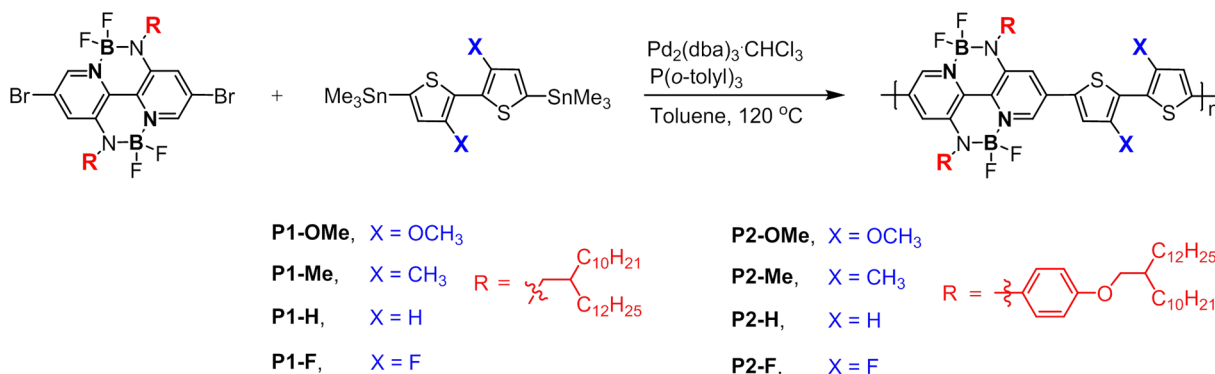
Scheme 1. Chemical Structures of the BNBP-Based Polymers

Scheme 2. Synthesis of the BNBP-Based Polymers

P1-OMe, X = OCH₃
P1-Me, X = CH₃
P1-H, X = H
P1-F, X = F

P2-OMe, X = OCH₃
P2-Me, X = CH₃
P2-H, X = H
P2-F, X = F

electron-transporting polymer semiconductors for OTFTs.[54−59] We find that the LUMOs of D−A type conjugated polymers containing BNBP are delocalized over both A unit and D unit. This indicates that their E_{LUMO} values can be tuned through modifications on both D unit and A unit.

In this manuscript, based on the BNBP-based D−A type conjugated polymers, we report fine-tuning of E_{LUMO} of conjugated polymers in a wide range via substitutions on both D unit and A unit. We synthesize eight D−A type conjugated polymers with the same backbone but different substitutes on the A unit (BNBP unit) or the D unit (bithiophene unit). Their E_{LUMO} are finely tuned within a wide range from −3.3 eV to −3.7 eV. In PSCs, the polymers with high-lying E_{LUMO} can be used as electron donor and the polymers with low-lying E_{LUMO} can be used as electron acceptor. We comprehensively investigate the electronic structures, photophysical properties, charge-transporting properties and PSC device applications of these polymers.

RESULTS AND DISCUSSION

Synthesis and Characterization. Scheme 1 shows the chemical structures of these eight polymers with the same polymer backbone of alternating electron-deficient BNBP unit and electron-rich BT unit. The BNBP unit is bonded with the alkyl and alkoxyphenyl side chains. The BT unit is equipped with the electron-donating methyloxy, methyl, and hydrogen substitutes or electron-withdrawing fluoro substitutes. Scheme 2 shows the synthetic routes of these polymers. All the monomers were prepared according to the reported methods (see Supporting Information).[57,60] The polymers were synthesized by Stille-polymerization of the corresponding monomers using the catalyst/ligand of Pd₂(dba)₃·CHCl₃/P(o-Tolyl)₃. The chemical structures of the monomers and the polymers were verified by ¹H NMR, ¹³C NMR, and elemental analysis. According to gel permeation chromatography (GPC) at 150 °C with 1,2,4-trichlorobenzene as the eluent, the number-average molecular weights (M_n) of these polymers are estimated to be in the range of 39−91 kDa and the polydispersity indexes (PDI) are in the range of 1.70−3.17

(Table 1). According to thermogravimetric analysis (TGA) (Figure S1), these polymers show good thermal stability with

Table 1. Molecular Weights and Thermal Decomposition Temperatures (T_d) of the BNBP-Based Polymers

polymer	$M_n{}^a$ (kDa)	PDI^a	$T_d{}^b$ (°C)
P1-OMe	43.0	2.01	359
P1-Me	39.2	2.03	403
P1-H	50.3	1.72	394
P1-F	66.2	3.17	391
P2-OMe	67.4	1.70	348
P2-Me	55.9	2.20	372
P2-H	64.5	1.84	378
P2-F	91.2	2.77	387

^{a}Determined by GPC at 150 °C in 1,2,4-trichlorobenzene. ^{b}Estimated by TGA under N₂ atmosphere.

thermal decomposition temperatures (T_d) at 5% weight loss of over 340 °C.

Theoretical Calculation. Density functional theory (DFT) calculations at the B3LYP/6-31G* level of theory were performed to elucidate the backbone configurations and molecular orbitals of these polymers. We use the model compounds containing four repeating units with long alkyl chains replaced by methyl groups. In the optimized structures (Figure S2), the polymers containing −OCH₃, −H, and −F groups (**P1-OMe, P2-OMe, P1-H, P2-H, P1-F, and P2-F**) exhibit nearly planar backbone configurations, while **P1-Me** and **P2-Me** show twisted backbone structures due to the steric hindrance of −CH₃ group.

As shown in Figure 1 and Figure S3, all the calculated LUMOs of the model compounds are delocalized over the conjugated backbones. The polymers containing −OCH₃, −H, and −F groups display similar LUMOs, indicating that the −OCH₃, −H and −F groups, as well as the methyl and methoxyphenyl side chains have negligible effects on the distributions of electron densities. For **P1-Me** and **P2-Me**, the −CH₃ group results in more electron densities of LUMOs on
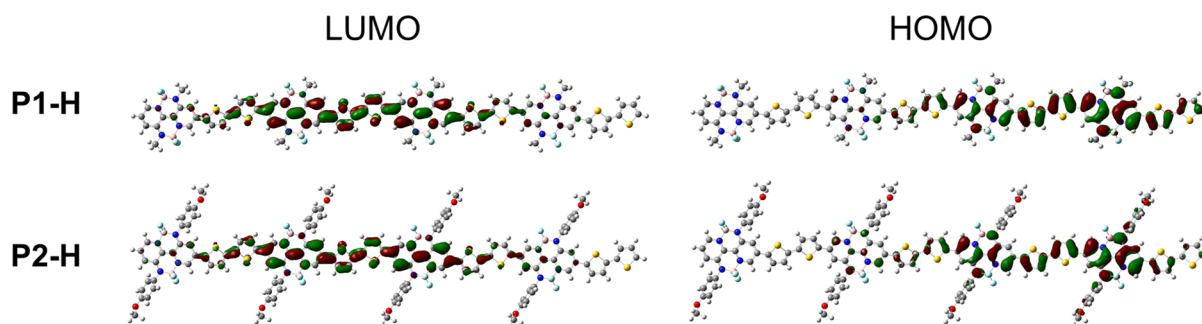
Figure 1. Kohn−Sham LUMOs and HOMOs of the model compounds of **P1-H** and **P2-H**, based on the calculations at the B3LYP/6-31G* level.

electron-deficient BNBP unit. It is due to their less backbone conjugations, which are the results of the twisted configurations induced by the steric hindrance of the −CH₃ group. Moreover, the HOMOs of these polymers are delocalized on the BNBP and BT units with various distributions of electron densities (Figure S3).

Electrochemical Property and Energy Level. Cyclic voltammentry (CV) was employed to investigate the electrochemical properties and estimate the LUMO/HOMO energy levels of these polymers. The CV measurements were carried out with their thin films (see Supporting Information). As shown in Figure 2, these polymers show the reversible
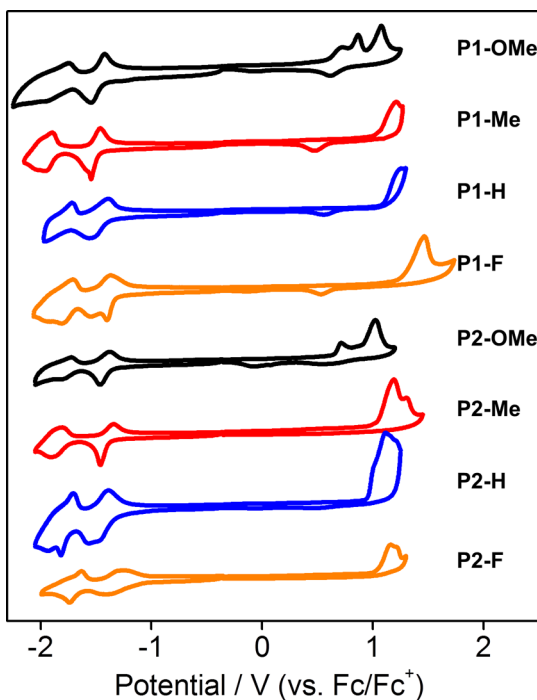
Figure 2. Cyclic voltammograms of the BNBP-based polymers in thin films, using a Ag/AgCl reference electrode, Fc = ferrocene.

reduction processes with the onset reduction potentials (E_{red}) versus Fc/Fc⁺ in the range from −1.48 to −1.09 V and the irreversible oxidation processes with the onset oxidation potentials (E_{ox}) between +0.57 and +1.24 V.

The E_{LUMO}/E_{HOMO} of these polymers are calculated with the onset reduction/oxidation potentials using the equations of $E_{LUMO}/E_{HOMO} = −(4.80 + E_{red}/E_{ox})$ eV. The results are shown in Figure 3 and listed in Table 2. Their E_{LUMO} gradually decrease from −3.3 to −3.7 eV, e.g. −3.32 eV for **P1-Me**, −3.39
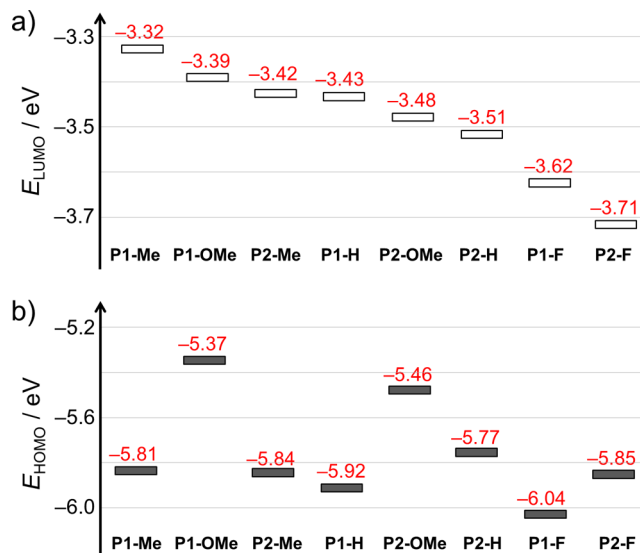
Figure 3. (a) LUMO and (b) HOMO energy level alignments of the BNBP-based polymers.

eV for **P1-OMe**, −3.42 eV for **P2-Me**, −3.43 eV for **P1-H**, −3.48 eV for **P2-OMe**, −3.51 eV for **P2-H**, −3.62 eV for **P1-F**, and −3.71 eV for **P2-F**, respectively. The E_{HOMO} of these polymers are in the range between −5.37 eV and −6.04 eV. In comparison to −H, the −OMe group slightly increases the E_{LUMO} and largely increases the E_{HOMO} of the BNBP-based polymers, thus resulting in significantly reduced bandgaps. This is because of the strong electron-donating capability of −OMe. The −OMe group can obviously enhance the E_{LUMO} of the polymers while maintain their E_{HOMO}, which may be related to the twisted backbone configurations as discussed above. For the −F group, it can simultaneously decrease the E_{LUMO} and E_{HOMO} of the polymers owing to its high electron-withdrawing character. In addition, the alkoxyphenyl side chain on BNBP can lower the E_{LUMO} of the polymers compared with the alkyl side chain, which is probably ascribed to the conjugation between the extra phenyl group and the nitrogen atom in BNBP unit.[61]

As shown in Figure 3, **P1-F** and **P2-F** exhibit the low-lying E_{LUMO}/E_{HOMO}, which are very desirable for applications as electron acceptors in PSCs. **P1-OMe** and **P2-OMe** possess the high-lying E_{LUMO}/E_{HOMO}, indicating that they may be used as electron donors in PSCs.

Photophysical Property. UV/vis absorption spectra of these polymers in hot o-DCB solutions (100 °C) and in thin films were measured (Figure 4). In solutions, their maximum absorption peaks (λ_{max}) are between 556−682 nm (Table 2). In

Table 2. Photophysical and Electrochemical Properties of the BNBP-Based Polymers

polymer	$\lambda_{max}{}^{a}$ (nm)	$\varepsilon_{max}{}^{a}$ (M^{-1} cm^{-1})	$\lambda_{max}{}^{b}$ (nm)	$E_g{}^{b}$ (eV)	$E_{ox}{}^{c}$ (V)	$E_{red}{}^{c}$ (V)	$E_{HOMO}{}^{d}$ (eV)	$E_{LUMO}{}^{d}$ (eV)
P1-OMe	682	9.11×10^4	683	1.72	+0.57	−1.41	−5.37	−3.39
P1-Me	563	7.07×10^4	570	1.83	+1.01	−1.48	−5.81	−3.32
P1-H	589	9.28×10^4	638	1.91	+1.12	−1.37	−5.92	−3.43
P1-F	593	8.25×10^4	623	1.90	+1.24	−1.24	−6.04	−3.62
P2-OMe	646	8.42×10^4	682	1.66	+0.66	−1.32	−5.46	−3.48
P2-Me	556	6.36×10^4	562	1.81	+1.04	−1.38	−5.84	−3.42
P2-H	585	7.79×10^4	634	1.85	+0.97	−1.29	−5.77	−3.51
P2-F	586	8.56×10^4	630	1.84	+1.05	−1.09	−5.85	−3.71

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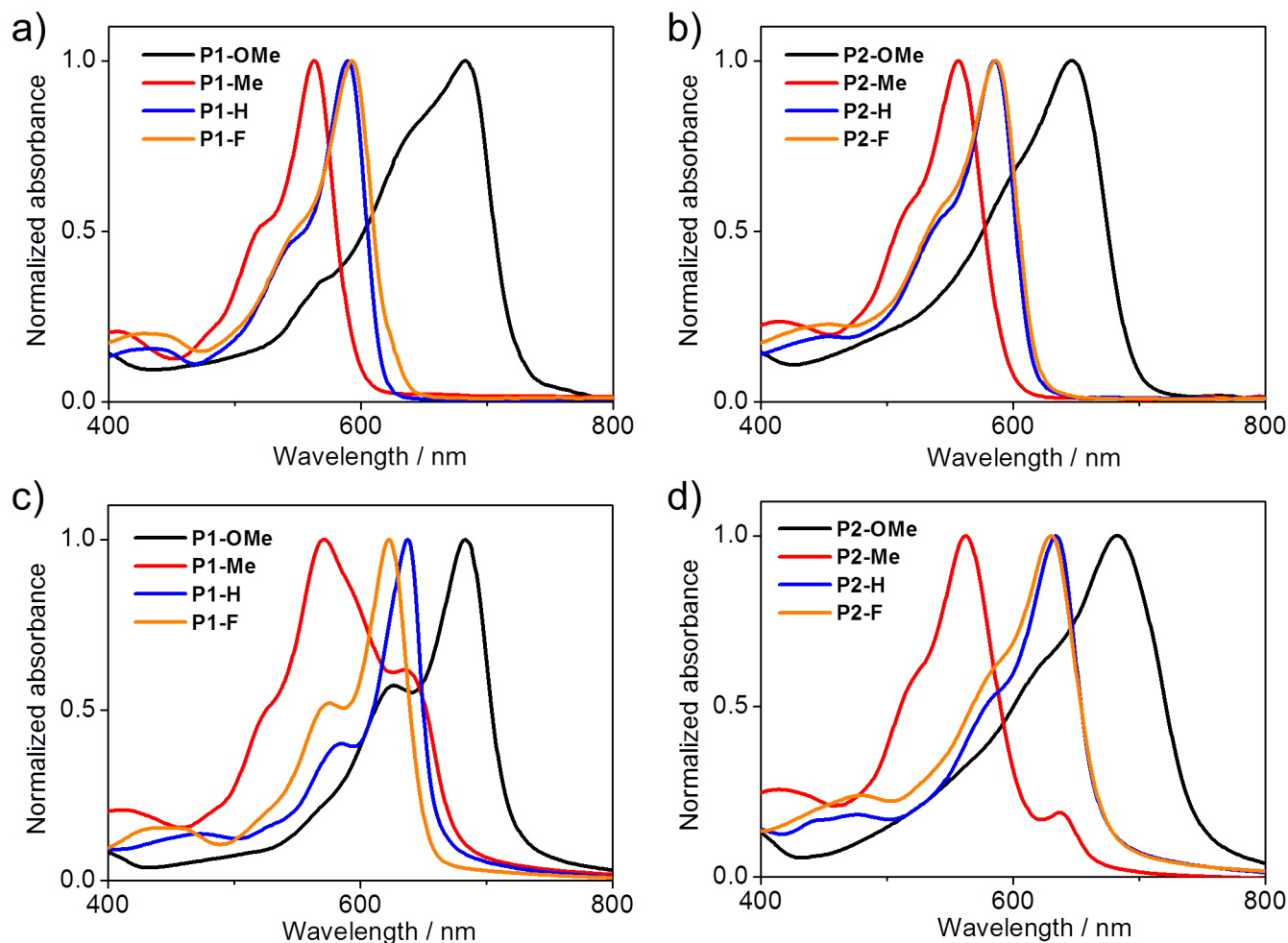

Figure 4. UV/vis absorption spectra of the BNBP-based polymers (a, b) in hot *o*-DCB solutions and (c, d) in thin films.

comparison to **P1-H** and **P2-H**, the corresponding polymers containing −OMe exhibit red-shifted absorption spectra, while the polymers containing −Me show blue-shifted absorption bands. These changes are in accordance with the variations of their E_{LUMO}/E_{HOMO} and bandgaps. The polymers with alkoxyphenyl side chain exhibit slightly blue-shifted absorption spectra compared to the corresponding polymers with alkyl side chain. These polymers all show the high absorption coefficients (ε) of over 6×10^4 M^{-1} cm^{-1}, suggesting their intense light absorptions in the visible region. In thin films, the main absorption peaks are red-shifted to the range of 562−683 nm because of intermolecular interactions of conjugated polymer chains in solid states. According to the onset

absorption wavelength in thin films, the optical band gaps (E_g) of the polymers are estimated to be from 1.66 to 1.91 eV.

Molecular Stacking and Charge Carrier Mobility. The molecular stackings of these polymers were studied by grazing incident X-ray diffraction (GI-XRD) with the drop-cast films on SiO_2 substrates from their *o*-DCB solutions. The XRD patterns are shown in Figure 5 and the data are listed in Table 3. The polymers show the (010) diffraction peaks in the range of 2θ = 24.6 °−19.3 °, indicating the $\pi-\pi$ stacking distances of 3.62 Å− 4.60 Å. While **P1-OMe**, **P1-Me**, **P1-H**, and **P1-F** show the $d_{\pi-\pi}$ of 4.25 Å, 4.39 Å, 3.62 and 3.95 Å, **P2-OMe**, **P2-Me**, **P2-H**, and **P2-F** exhibit the $d_{\pi-\pi}$ of 4.27 Å, 4.60 Å, 3.65 and 3.97 Å, respectively. Obviously, the substituents on BT unit affect the
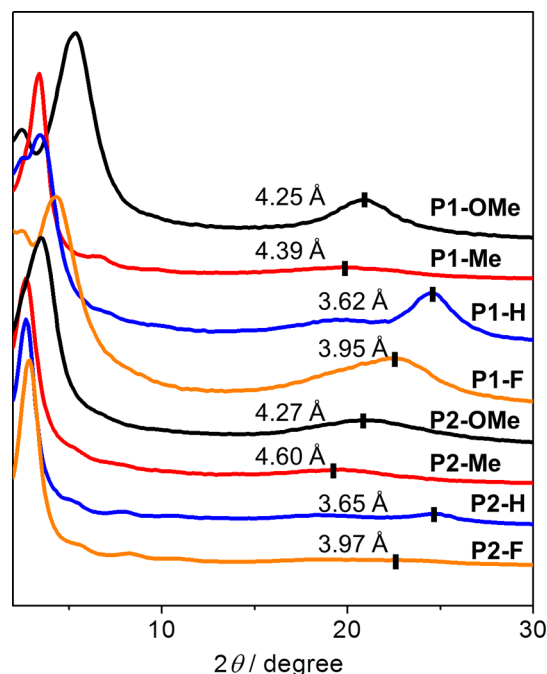
Figure 5. Grazing incident X-ray diffraction patterns of the BNBP-based polymers. The $\pi-\pi$ stacking distances of these polymers are shown.

**Table 3. $\pi-\pi$ Stacking Distances and Charge Carrier Mobilities of the BNBP-Based Polymers**

polymer	$d_{\pi-\pi}$ (Å)	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})
P1-OMe	4.25	1.40×10^{-4}	8.98×10^{-8}
P1-Me	4.39	0.78×10^{-4}	2.44×10^{-9}
P1-H	3.62	2.44×10^{-4}	1.15×10^{-6}
P1-F	3.95	1.49×10^{-4}	4.17×10^{-7}
P2-OMe	4.27	0.54×10^{-4}	4.51×10^{-7}
P2-Me	4.60	0.55×10^{-4}	9.09×10^{-11}
P2-H	3.65	0.95×10^{-4}	5.21×10^{-6}
P2-F	3.97	0.68×10^{-4}	4.89×10^{-9}

$\pi-\pi$ stacking distances of the polymers. The −Me and −OMe groups with large steric hindrance lead to increased $\pi-\pi$ stacking distances of the polymers. In addition, the alkyl and alkoxyphenyl side chains on BNBP unit have minimal effects on the $\pi-\pi$ stacking distances of the polymers.

The electron/hole mobilities (μ_e/μ_h) of the BNBP based-polymers were estimated using space-charge-limited current (SCLC) method with the current density−voltage ($J-V$) curves of the electron/hole-only devices.[62] The device configurations and the method to estimate μ_e/μ_h are provided in the Supporting Information (Figures S5 and S6). As listed in Table 3, these polymers show the electron mobilities from 0.54 $\times 10^{-4}$ to 2.44 $\times 10^{-4}$ cm^2 V^{-1} s^{-1} and the hole mobilities from 5.21 $\times 10^{-6}$ to 9.09 $\times 10^{-11}$ cm^2 V^{-1} s^{-1}. Their electron mobilities are much higher than the corresponding hole mobilities. This is consistent with our previous results that BNBP-based polymers show much higher electron mobilities than hole mobilities.[57] The electron mobilities of these polymers are fairly comparable to those of high-performance polymer electron acceptors for PSCs.[16−18,63] Moreover, the electron mobilities of these polymers are well correlated with their $d_{\pi-\pi}$ values in thin films. For example, **P1-H** and **P2-H**

with the smallest $\pi-\pi$ stacking distances exhibit the highest electron mobilities.

Fabrication and Characterization of Polymer Solar Cells. PSC devices were fabricated to investigate the applications of these polymers with tunable E_{LUMO}/E_{HOMO} in organic opto-electronic devices. Among these polymers, **P1-OMe** and **P2-OMe** show the high-lying E_{LUMO}/E_{HOMO}, which match well with the E_{LUMO}/E_{HOMO} of a widely used electron acceptor, Phenyl-C71-butyric acid methyl ester (PC$_{71}$BM). The E_{LUMO} offset and the E_{HOMO} offset between **P1-OMe/P2-OMe** and PC$_{71}$BM enable efficient photoinduced intermolecular electron transfer and hole transfer, respectively. Thus, we use **P1-OMe** and **P2-OMe** as the electron donors and PC$_{71}$BM as electron acceptor to fabricate PSCs (see Supporting Information). The device configuration is ITO/PEDOT:PSS/**P1-OMe** or **P2-OMe**:PC$_{71}$BM/Ca/Al. Figure 6 shows the $J-V$ curve
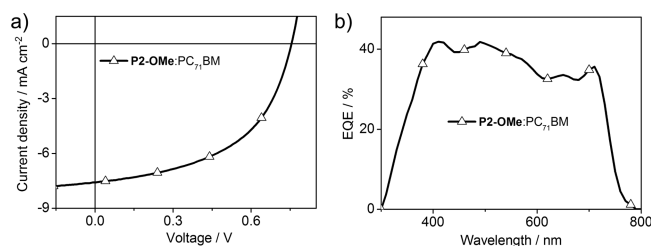
Figure 6. (a) $J-V$ curves and (b) EQE spectra of the PSCs device based on the **P2-OMe**:PC$_{71}$BM blend.

under AM 1.5G illumination (100 mW cm^{-2}) and external quantum efficiency (EQE) spectrum of the device with the **P2-OMe**:PC$_{71}$BM (w:w, 1:2) blend in CHCl$_3$ solution with 2% 1,8-diiodooctane (DIO) additive. The PSC device based on the **P2-OMe**:PC$_{71}$BM blend exhibits a V_{oc} of 0.76 V, a short-circuit current (J_{sc}) of 7.59 mA cm^{-2} and a fill factor (FF) of 50.6%, corresponding to a PCE of 2.92%. This device shows a broad EQE response from 300 to 780 nm. BNBP-based conjugated polymers are always used as electron acceptors in PSCs with excellent photovoltaic performance. To our best knowledge, this is the first report of polymer electron donors based on BNBP unit. The **P1-OMe**:PC$_{71}$BM device shows a moderate PCE of 0.59% (Figure S13). This is probably due to the limited solubility of **P1-OMe**, which leads to large-size phase separation in the **P1-OMe**:PC$_{71}$BM active layer (Figure S15).

On the other hand, among these polymers, **P1-F** and **P2-F** show the low-lying E_{LUMO}/E_{HOMO} and high electron mobilities, indicating that these two polymers can be used as efficient polymer electron acceptors for PSCs. We select a widely used polymer electron donor, poly[(ethylhexylthiophenyl)-benzodithiophene−(ethylhexyl)thienothiophene] (PTB7-Th), to blend with **P1-F/P2-F** to fabricate all-PSC devices (see Supporting Information). The device configuration is ITO/PEDOT:PSS/PTB7-Th:**P1-F** or **P2-F**/Ca/Al. As shown in Figure 7, the all-PSC device based on the PTB7-Th:**P1-F** (w:w, 1:1) blend from their CB solution with 0.5% chloronaphthalene (CN) additive exhibits a PCE of 5.16% with a V_{oc} of 1.09 V, a J_{sc} of 10.13 mA cm^{-2}, and a FF of 46.7%, while the optimal PTB7-Th:**P2-F** all-PSC device exhibits a PCE of 3.70% with a V_{oc} of 1.12 V, a J_{sc} of 7.33 mA cm^{-2}, and a FF of 45.1%. In these devices, the calculated J_{sc} values from the integrations of EQE spectra and the AM 1.5G spectrum agree well with the J_{sc} values obtained from the $J-V$ curves within 5% error. These results demonstrate that the BNBP-based polymers with tunable
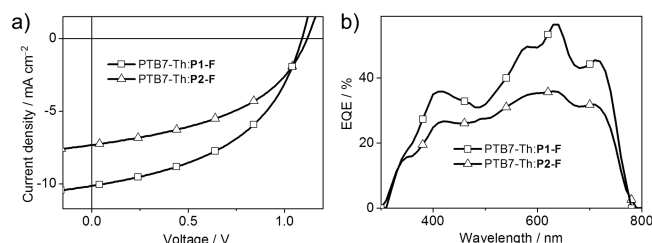
Figure 7. (a) *J*−*V* curves and (b) EQE spectra of the all-PSC devices based on the PTB7-Th:**P1-F** and PTB7-Th:**P2-F** blends.

E_{LUMO}/E_{HOMO} can be used either as electron donors or as electron acceptors in PSCs (Table 4).

Table 4. Summary of PSC Device Performance

active layer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
P2-OMe:PC$_{71}$BM	0.76	7.59	50.6	2.92
PTB7-Th:**P1-F**	1.09	10.13	46.7	5.16
PTB7-Th:**P2-F**	1.12	7.33	45.1	3.70

CONCLUSIONS

We have synthesized a series of D−A type conjugated polymers with alternating electron-deficient BNBP unit and electron-rich BT unit in the main chain. By changing the substitutes on BNBP or on BT, the E_{LUMO} of these polymers can be finely tuned in a wide range from −3.3 eV to −3.7 eV owing to the delocalized LUMOs. As the result, these BNBP-based polymers can be used either as electron donors (with high-lying E_{LUMO}/E_{HOMO}) or as electron acceptors (with low-lying E_{LUMO}/E_{HOMO}) in PSC devices. The PSC device with the BNBP-based polymer electron donor exhibit a PCE of 2.92% and the all-PSC device with the BNBP-based polymer electron acceptor exhibit a PCE of 5.16%. These results indicate a new approach to modulate the LUMO energy levels of D−A type conjugated polymers by modifications on both D unit and A unit.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01986.

Synthesis and ^{1}H and ^{13}C NMR characterizations, TGA measurements, photophysical properties, and theoretical calculations of BNBP-based conjugated polymers, as well as PSC device fabrications and characterizations (PDF)

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Notes
The authors declare no competing financial interest.

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