

An Alternating Polymer of Two Building Blocks Based on B←N Unit: Non-fullerene Acceptor for Organic Photovoltaics*

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Abstract B←N coordination bond can be used to develop polymer electron acceptors for efficient all-polymer solar cells (all-PSCs). Here, we report a new alternating conjugated polymer containing two building blocks based on B←N unit. The polymer exhibits strong light absorption in the visible range, low-lying LUMO/HOMO energy levels and moderate electron mobility. The resulting all-PSC devices exhibit power conversion efficiencies of 1.50%–2.47%.

Keywords All-polymer solar cells; Polymer acceptor; Boron; B←N coordination bond

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INTRODUCTION

All-polymer solar cells (all-PSCs) use conjugated polymers as both electron donor and electron acceptor. Compared with conventional polymer/fullerene solar cells, all-PSCs have great advantages, including enhanced solar light absorption, tunable energy levels and bandgaps of acceptors and improved morphology stability^[1–4]. The power conversion efficiency (PCE) of all-PSCs has exceeded 8% and is fairly comparable to that of polymer/fullerene solar cells^[5]. Although significant progress has been made for all-PSCs recently, the development of all-PSCs are limited by the lack of efficient polymer electron acceptors^[6–10]. Only some specific conjugated polymers based on naphthalene diimide (NDI) or perylenediimide (PDI) building blocks containing imide unit can be used as efficient polymer acceptors^[11–20].

Organoboron compounds have been demonstrated as promising opto-electronic materials^[21–25]. For example, Pei *et al.* developed BN-embedded aromatics that showed high hole mobilities in organic field-effect transistors (OFETs)^[26, 27]. B←N coordination bond can greatly decrease both LUMO and HOMO energy levels ($E_{\text{LUMO/HOMO}}$) of organic small molecules^[28–30]. We have recently proposed to design polymer electron acceptors using B←N unit. When B←N bridged thienylthiazole (BNTT) building block is incorporated into conjugated

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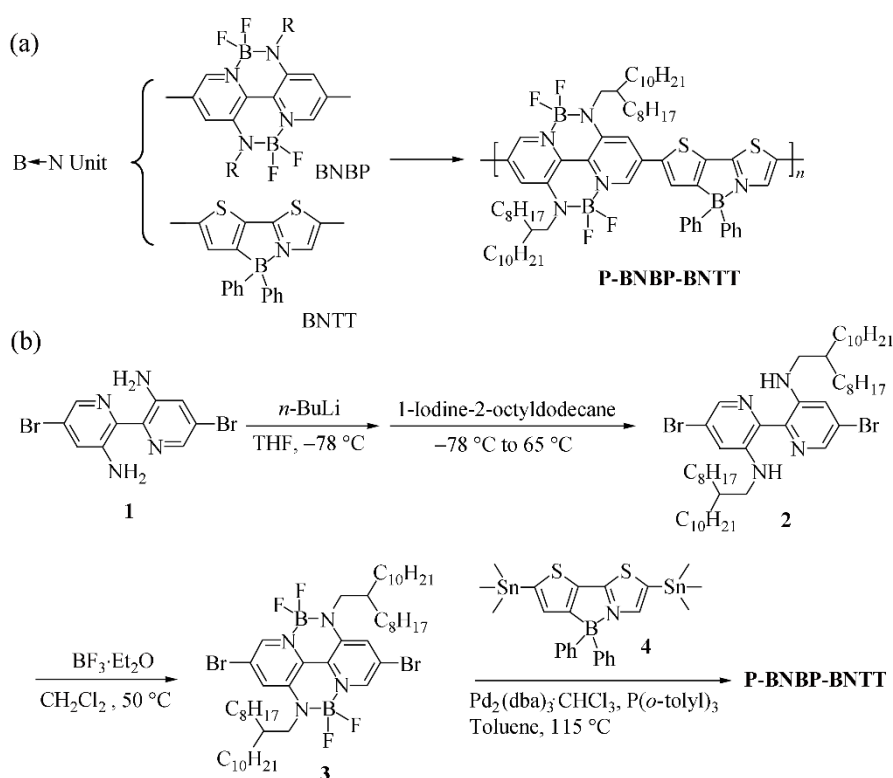
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polymers, it can transform typical polymer electron donors to electron acceptors^[31, 32]. In another example, a novel electron-deficient building block based on B←N unit, double B←N bridged bipyridine (BNBP), has been developed to design polymer electron acceptors^[33–35]. All-PSC devices based on these polymer acceptors containing B←N unit exhibit PCEs of exceeding 5%, which is comparable to that of the analogous all-PSCs using the state-of-the-art polymer acceptors based on NDI unit^[11–20]. These results encourage us to design new polymer acceptors using B←N unit.

In this paper, we report a new alternating conjugated polymer of two building blocks based on B←N unit, which is denoted as **P-BNBP-BNTT** as shown in Scheme 1(a). **P-BNBP-BNTT** exhibits strong light absorption in the visible range, low-lying LUMO/HOMO energy levels and moderate electron mobility. The versatile applications of **P-BNBP-BNTT** as polymer acceptor in all-PSCs are demonstrated and PCE of 2.47% is achieved.



Scheme 1 (a) Schematic illustration of the molecular design of **P-BNBP-BNTT**, (b) synthetic route of **P-BNBP-BNTT** (Ph = Phenyl)

EXPERIMENTAL

Materials

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Ether, toluene, THF and CH_2Cl_2 were dried using sodium or calcium hydroxide before use. $n\text{-BuLi}$ (2.5 mol/L in hexane) was purchased from J&K Chemical Industries and used as received.

5,5'-Dibromo-N3,N3'-di-2-octyldodecyl-[2,2'-bipyridine]-3,3'-diamine **2**

To a solution of **1** (500 mg, 1.46 mmol) in THF (45 mL) under argon was added $n\text{-BuLi}$ (2.5 mol/L in hexane, 1.23 mL, 3.07 mmol) dropwise at $-78\text{ }^{\circ}\text{C}$. After the mixture being stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, 1-iodine-2-octyldodecane (2.38 g, 5.84 mmol) was added under argon. The mixture was stirred for 4 h at $75\text{ }^{\circ}\text{C}$. After

removing the solvents under reduced pressure, the brown oil was purified by silica gel column chromatography (CH_2Cl_2 :hexane = 1:10, *V:V*). **2** was obtained as a yellow oil in 37% yield (490 mg, 0.54 mmol). ^1H -NMR (400 MHz, C_6D_6 , 25 °C, δ): 10.29 (t, J = 4.4 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 2.79 (t, J = 5.2 Hz, 2H), 1.68–1.62 (m, 1H), 1.41–1.31 (m, 32H), 0.95–0.91 (m, 6H). ^{13}C -NMR (100 MHz, C_6D_6 , 25 °C, δ): 147.28, 138.27, 132.01, 120.23, 119.32, 46.15, 37.73, 32.98, 32.38, 30.50, 30.18, 30.17, 30.11, 30.05, 29.86, 29.84, 27.28, 23.16, 14.42. Anal. Calcd for $\text{C}_{50}\text{H}_{88}\text{Br}_2\text{N}_4$: C, 66.35; H, 9.80; Br, 17.66; N, 6.19. Found: C, 66.23; H, 9.73; N, 6.30.

Dibromo-substituted BNBP **3**

Under argon, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ solution (1.78 mL, 10.4 mmol) was added to a solution of **2** (476 mg, 0.53 mmol) and Et_3N (0.72 mL, 5.2 mmol) in dry CH_2Cl_2 (23 mL). The mixture was stirred at 50 °C for 1 h with the color changing from yellow to orange. After removing the solvents, the orange solid was purified by silica gel column chromatography (CH_2Cl_2 :hexane = 1:4, *V:V*). **3** was obtained as an orange solid in 83% yield (430 mg, 0.43 mmol). ^1H -NMR (400 MHz, C_6D_6 , δ): 8.22 (d, J = 1.6 Hz, 1H), 7.28 (d, J = 1.6 Hz, 1H), 3.41 (d, J = 6.8 Hz, 2H), 1.78 (s, 1H), 1.39–1.28 (m, 32H), 0.94–0.90 (m, 6H). ^{13}C -NMR (100 MHz, C_6D_6 , δ): 144.69, 128.56, 125.64, 125.37, 122.28, 48.63, 36.02, 32.37, 32.34, 32.15, 30.52, 30.50, 30.14, 30.07, 29.86, 29.79, 26.87, 23.16, 23.14, 14.41. Anal. Calcd for $\text{C}_{50}\text{H}_{86}\text{B}_2\text{Br}_2\text{F}_4\text{N}_4$: C, 60.01; H, 8.66; B, 2.16; Br, 15.97; F, 7.59; N, 5.60. Found: C, 60.13; H, 8.48; N, 5.48.

Polymer P-BNBP-BNTT

Starting materials of **3** (153 mg, 0.153 mmol), **4** (100.3 mg, 0.153 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (3.17 mg, 0.00306 mmol) and $\text{P}(o\text{-tolyl})_3$ (7.45 mg, 0.02448 mmol) were placed in a two-necked flask under argon, and then dried toluene (20 mL) was added. After the mixture being stirred at 120 °C for 36 h, end-capping reaction was carried out by adding BNTT (10 mg, 0.015 mmol) and then bromobenzene (0.1 mL, 0.425 mmol). After cooling, the resulting organic phase was extracted with CHCl_3 (150 mL) and washed with water. After the solvents being removed, the residue was dispersed in acetonitrile and the precipitate was collected. The obtained dark solid was purified by Soxhlet extraction in acetone, hexane and CHCl_3 . The solid from CHCl_3 solution was dispersed in acetonitrile, then collected and dried under vacuum overnight. Yield: 145 mg (81%). ^1H -NMR (400 MHz, $\text{C}_6\text{D}_4\text{Cl}_2$, 100 °C, δ): 8.72 (br, 2H), 8.50 (br, 2H), 8.30 (br, 1H), 8.00 (br, 1H), 7.66 (br, 10H), 3.95 (br, 4H), 2.27 (br, 2H), 1.76–1.30 (br, 64H), 1.07 (br, 12H). GPC (TCB, polystyrene standard, 150 °C): M_n = 13700, PDI = 2.22. Anal. Calcd for $\text{C}_{49}\text{H}_{98}\text{B}_3\text{F}_4\text{N}_5\text{S}_2$: C, 70.7; H, 8.55; B, 2.77; F, 6.48; N, 5.97; S, 5.47. Found: C, 68.79; H, 8.87; N, 6.25; S, 5.59.

RESULTS AND DISCUSSION

Synthesis and Thermal Stability

Scheme 1(b) shows the synthetic route of **P-BNBP-BNTT**. The two monomers were prepared following reported procedures^[31–35]. **P-BNBP-BNTT** was synthesized by Stille-polymerization of the two monomers with $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3/\text{P}(o\text{-tolyl})_3$ as the catalyst system. Owing to the asymmetric BNTT building block, **P-BNBP-BNTT** should be regiorandom because both head-to-head and head-to-tail connections of the two building blocks could coexist. The chemical structure of **P-BNBP-BNTT** was confirmed by ^1H -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 weight (M_n) of **P-BNBP-BNTT** was 13.7 kDa with polydispersity index (PDI) of 2.2. **P-BNBP-BNTT** was readily soluble in common organic solvents, such as chloroform, chlorobenzene and *o*-dichlorobenzene. Thermogravimetric analysis (TGA) showed that **P-BNBP-BNTT** had good thermal stability with thermal decomposition temperature (T_d) at 287 °C for 5% mass loss (Fig. S1 in supporting information).

Theoretical Calculations

To elucidate the configuration and molecular orbitals of **P-BNBP-BNTT**, geometry optimization and Kohn-

Sham molecular orbital calculation were performed with the model compound at the B3LYP/6-31G* level of theory (in the supporting information, SI). As shown in Fig. S2 (in SI), the two pendent phenyl groups of BNTT unit adopt an average dihedral angle of 75.0° with thienylthiazole skeleton, suggesting that the two pendent phenyl groups serve as steric hindrance to prevent the close stacking of polymer backbone in solid state. The backbone of **P-BNBP-BNTT** shows a twisted conformation with the dihedral angle of about 24.5° between BNBP and BNTT building blocks. As shown in Fig. 1, while the HOMO of **P-BNBP-BNTT** is localized on the BNBP building block, the LUMO of **P-BNBP-BNTT** is delocalized over both the BNBP and BNTT building blocks, which are fully consistent with that of the reported BNBP-based polymers^[33–35].

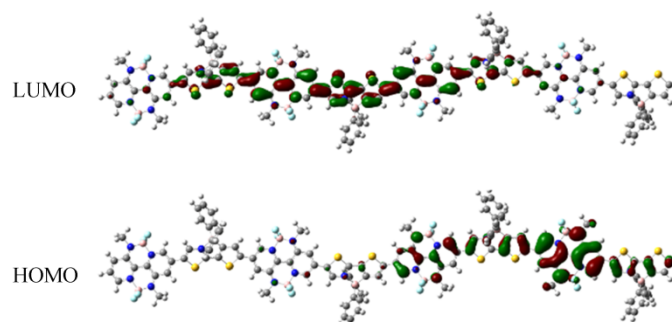


Fig. 1 Kohn-Sham molecular orbitals of the model compound of **P-BNBP-BNTT** (B3LYP/6-31G*)

XRD Measurements

In grazing incident X-ray diffraction (GI-XRD) pattern of **P-BNBP-BNTT** (Fig. 2), we can see a lamellar (100) peak at $2\theta = 4.5^\circ$ and a π - π stacking (010) peak at $2\theta = 20.0^\circ$, indicating a lamellar packing distance of 1.96 nm and a π - π stacking distance of 0.44 nm. The short lamellar packing distance of **P-BNBP-BNTT** indicates interdigitation of the alkyl chains. The large π - π stacking distance is attributed to the large steric hindrance effect of the two pendant phenyl groups of the BNTT building block. This is consistent with the geometry optimization results.

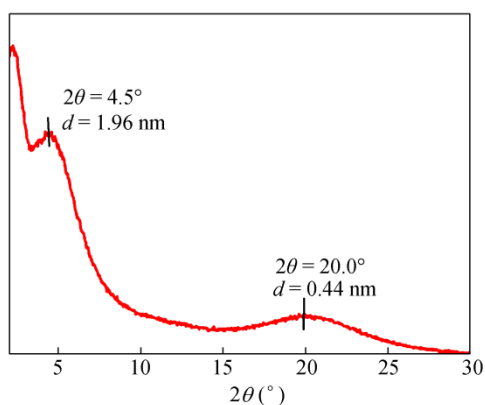


Fig. 2 GI-XRD pattern of the drop-cast film of **P-BNBP-BNTT**

Photophysical Properties

Figure 3(a) shows the UV-Vis absorption spectra of **P-BNBP-BNTT** in dilute chlorobenzene solution and in thin film. The absorption spectrum of **P-BNBP-BNTT** in solution shows a strong absorption band peak at 597 nm with molar absorption coefficient of $5.94 \times 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$. This strong absorption in the visible range is expected to improve the solar light absorption of the active layer of all-PSCs. The absorption spectrum in thin film is red-shifted by 16 nm compared to that in solution due to intermolecular interactions in the solid state. According to the onset absorption wavelength in the thin film, the optical band gap (E_g) of **P-BNBP-BNTT** is estimated to be 1.91 eV.

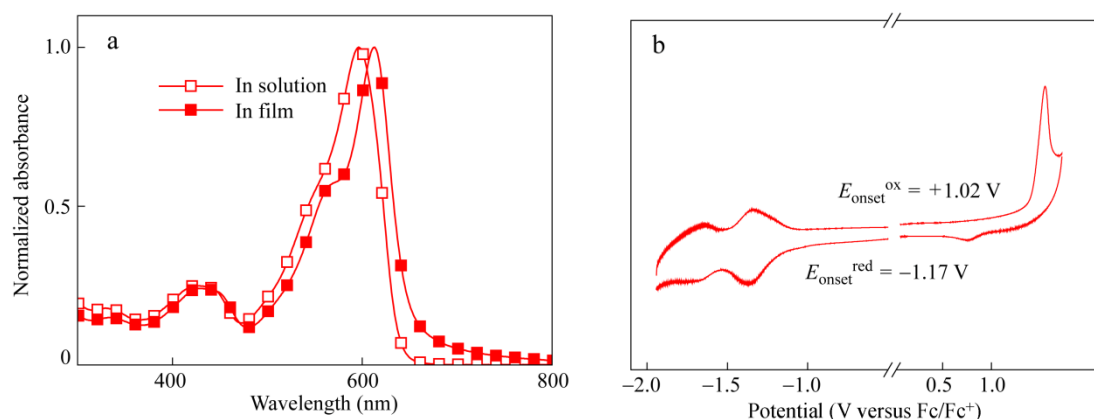


Fig. 3 (a) UV/Vis absorption spectra of **P-BNBP-BNTT** in chlorobenzene and in film, (b) Cyclic voltammogram of **P-BNBP-BNTT**, Fc = ferrocene

Electrochemical Properties and Electron Mobility

To estimate the LUMO/HOMO energy levels, cyclic voltammetry (CV) measurements were carried out with the thin film of **P-BNBP-BNTT**, which show an irreversible oxidation band and two quasi-reversible reduction bands (Fig. 3b). Based on the onset potentials of the reduction and oxidation processes, the $E_{\text{LUMO/HOMO}}$ of **P-BNBP-BNTT** are calculated to be -3.63 eV/ -5.82 eV.

Electron mobility of **P-BNBP-BNTT** was estimated using space-charge-limited current (SCLC) method with current density-voltage (J - V) curve of the electron-only device (Fig. S4 in SI). **P-BNBP-BNTT** exhibits a moderate electron mobility of $1.49 \times 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, which is attributed to large π - π stacking distance in polymer backbones. The low-lying LUMO/HOMO energy levels and moderate electron mobility of **P-BNBP-BNTT** suggest that it can be used as polymer electron acceptor in efficient all-PSCs.

Photovoltaic Properties

To investigate the application of **P-BNBP-BNTT** as polymer acceptor, all-PSCs were fabricated with the configuration of ITO/PEDOT:PSS (40 nm)/polymer donor:**P-BNBP-BNTT**/Ca (20 nm)/Al (100 nm). Three typical polymer donors are selected, including poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT), poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl]] (PTB7) and poly[(ethylhexyl-thiophenyl)-benzodithiophene-(ethylhexyl)-thieno thiophene] (PTB7-Th)^[36–38]. Their chemical structures are given in Fig. 4(a) and their LUMO/HOMO energy level alignments are shown in Fig. 4(b). The $E_{\text{LUMO/HOMO}}$ of **P-BNBP-BNTT** match well with those of PCDTBT and PTB7 because of their adequate LUMO energy level offsets (ΔE_{LUMO}), which can ensure efficient photo-induced charge separation. The ΔE_{LUMO} between **P-BNBP-BNTT** and PTB7-Th is less than 0.3 eV, which may lead to inefficient charge separation. Figure S3 (in SI) shows the absorption spectra of the three polymer donors and the polymer acceptor **P-BNBP-BNTT**. The absorption spectrum of **P-BNBP-BNTT** is complementary with those of PTB7 and PTB7-Th, which is good for light-harvesting of the blend. The narrow absorption spectrum of PCDTBT may produce weak light absorption.

Figure 5 shows the J - V curves and external quantum efficiency (EQE) spectra for the three all-PSC devices under AM1.5G illumination ($100 \text{ mW} \cdot \text{cm}^{-2}$). The photovoltaic parameters are summarized in Table 1. Among the three blends, PTB7:**P-BNBP-BNTT** exhibits the best photovoltaic performance with open-circuit voltage (V_{oc}) of 1.04 V, short-circuit current density (J_{sc}) of $6.21 \text{ mA} \cdot \text{cm}^{-2}$, fill factor (FF) of 0.38, corresponding to a PCE of 2.47%. PCDTBT:**P-BNBP-BNTT** device shows PCE of 1.50% ($V_{\text{oc}} = 1.08 \text{ V}$, $J_{\text{sc}} = 4.15 \text{ mA} \cdot \text{cm}^{-2}$, FF = 0.34) and PTB7-Th:**P-BNBP-BNTT** device has PCE of 2.37% ($V_{\text{oc}} = 1.02 \text{ V}$, $J_{\text{sc}} = 7.32 \text{ mA} \cdot \text{cm}^{-2}$, FF = 0.32). These results suggest that **P-BNBP-BNTT** is a versatile good polymer electron acceptor to match well with various polymer electron donors for efficient all-PSCs. The lower J_{sc} and PCE of the PCDTBT:**P-BNBP-BNTT**

device than those of the other two devices may be assigned to its narrow absorption band shown in their EQE curves (Fig. 5b). J_{sc} values calculated from the integration of EQE spectra with AM1.5G spectrum are consistent with those obtained from $J-V$ scans within 10% error.

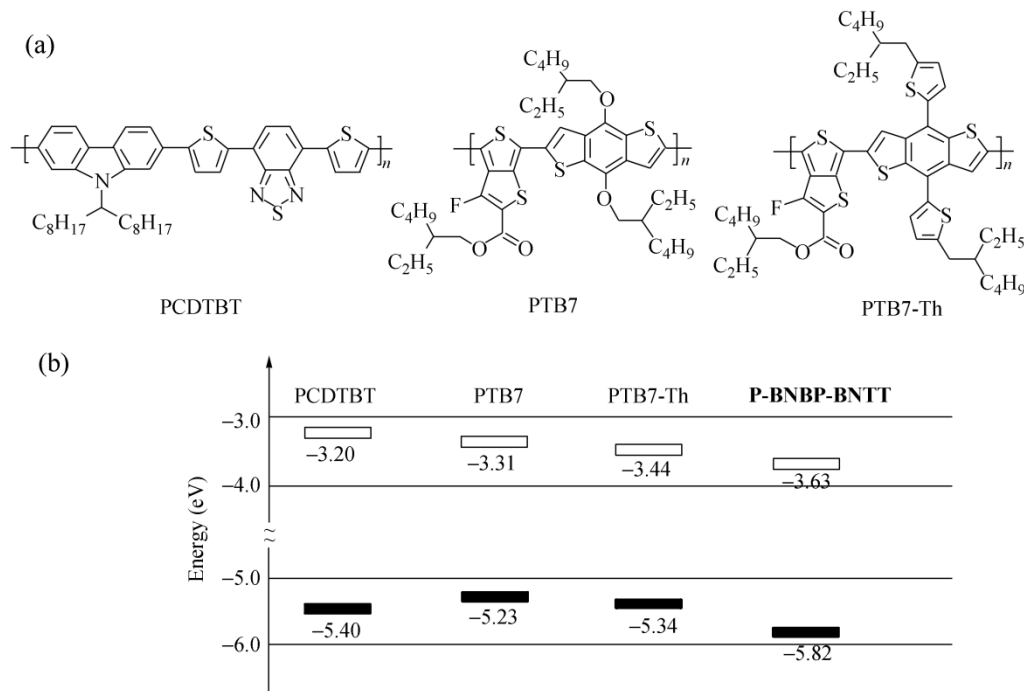


Fig. 4 (a) Chemical structures of polymer donors used in this study; (b) Schematic of LUMO/HOMO energy level alignments of polymer donors and acceptor

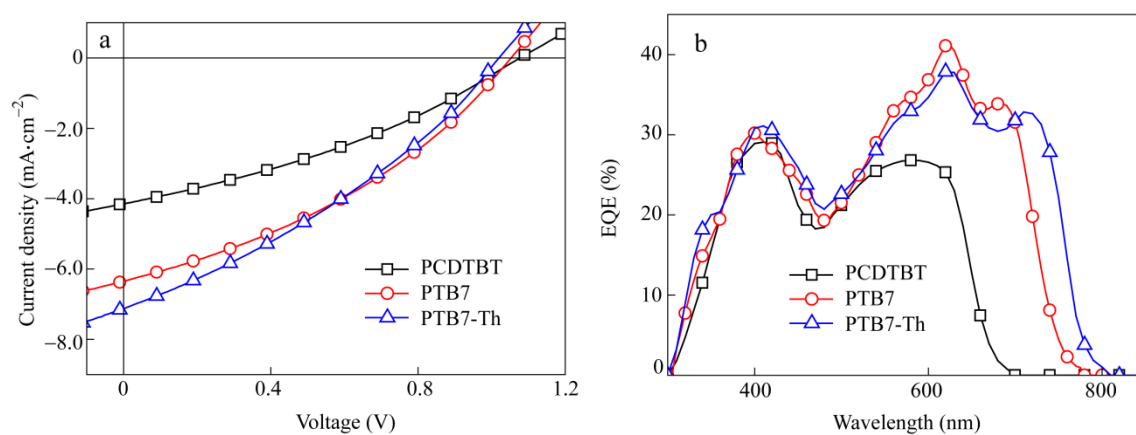


Fig. 5 (a) $J-V$ curves and (b) EQE spectra of the all-PSC devices with **P-BNBP-BNTT** as electron acceptor and PCDTBT/PTB7/PTB7-Th as electron donor

Electron and hole mobility of the three blends are measured using SCLC method with electron-only devices (ITO/PEIE/active layer/Ca/Al) and hole-only devices (ITO/PEDOT:PSS/active layer/MoO₃/Ag), respectively. The results are listed in Table 1 and shown in Fig. S5. All the three devices show the low electron mobility in the order of 10^{-7} – 10^{-6} cm²·V⁻¹·s⁻¹, leading to the unbalanced electron/hole mobility. This may be attributed to both the moderate electron mobility of **P-BNBP-BNTT** itself and the poor phase separation morphology (*vide infra*). PCDTBT:**P-BNBP-BNTT** and PTB7-Th:**P-BNBP-BNTT** blends exhibiting low FF values are probably due to

their both low electron and hole mobility, though PCDTBT:**P-BNBP-BNTT** blend has a relatively balanced electron/hole mobility. Among the three blends, PTB7:**P-BNBP-BNTT** blend shows the highest electron and hole mobility, which is in accordance with its best photovoltaic performance.

Table 1 Summary of the all-PSC devices performance and charge transport properties

Donor	V_{oc} (V)	J_{sc} ($\text{mA}\cdot\text{cm}^{-2}$)	FF	PCE_{max} (%)	$\text{PCE}_{\text{ave}}^a$ (%)	EQE	μ_h ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	μ_e ($\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$)	μ_h/μ_e
PCDTBT	1.08	4.15	0.34	1.50	1.38	0.29	4.25×10^{-6}	8.03×10^{-7}	5/1
PTB7	1.04	6.21	0.38	2.47	2.41	0.42	8.63×10^{-5}	1.39×10^{-6}	62/1
PTB7-Th	1.02	7.32	0.32	2.37	2.30	0.38	3.49×10^{-5}	4.57×10^{-7}	76/1

^a The average PCE value is calculated from six devices.

Nanoscale phase-separation morphology of polymer donor/polymer acceptor blend plays an important role in all-PSC device performance. The morphologies of the active layers of the three all-PSCs are measured by transmission electron microscopy (TEM) and the atomic force microscopy (AFM). As shown in TEM images (Figs. 6a–6c), isolated domains with size of about 100 nm without interpenetrating network are observed for all the three blends. These morphologies are detrimental for charge transport and can explain the relatively low J_{sc} and FF for the three all-PSC devices. Figures 6(d)–6(f) give AFM height images of the three blends, which all show smooth surfaces. PTB7:**P-BNBP-BNTT** shows the root-mean-square (RMS) roughness of 1.33 nm, which is smaller than 1.71 nm for PCDTBT:**P-BNBP-BNTT** blend and 2.27 nm for PTB7-Th:**P-BNBP-BNTT** blend. This is consistent with the best photovoltaic performance of the device of PTB7:**P-BNBP-BNTT**. The non-ideal nanoscale morphologies of the three blends indicate that there is much room for all-PSC device efficiency improvement *via* optimization of active layer film-formation process.

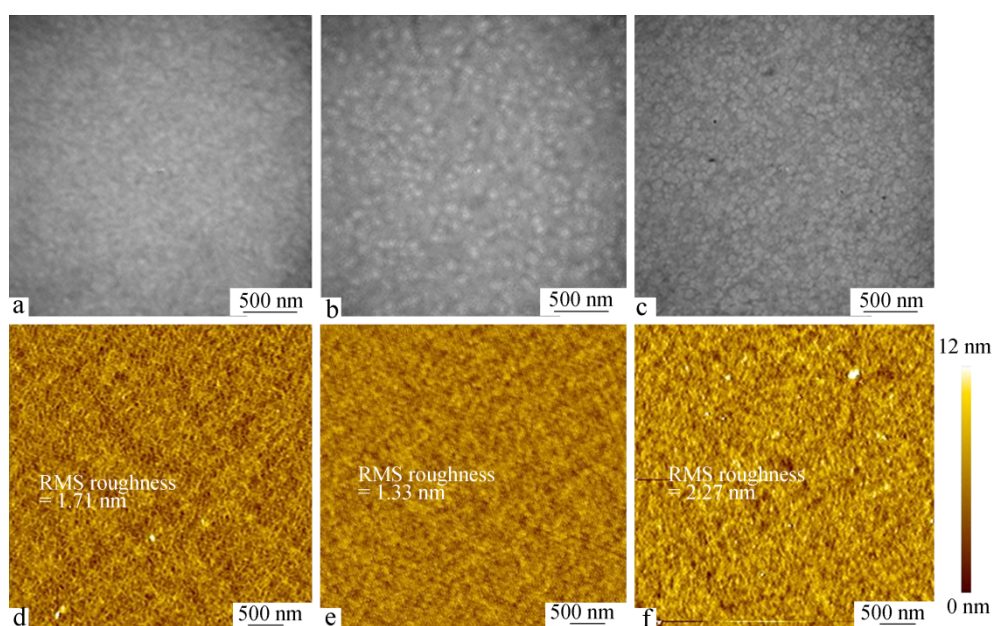


Fig. 6 TEM images (top) and AFM height images (bottom) of PCDTBT/PTB7/PTB7-Th:**P-BNBP-BNTT** blends: (a) and (d) PCDTBT:**P-BNBP-BNTT**; (b) and (e) PTB7:**P-BNBP-BNTT**; (c) and (f) PTB7-Th:**P-BNBP-BNTT**

CONCLUSIONS

In conclusion, we have developed a new conjugated polymer composed of alternating BNBP and BNTT units

based on B←N unit. **P-BNBP-BNTT** exhibits low-lying LUMO/HOMO energy levels, strong absorption in the visible range, and moderate electron mobility. For the blends of **P-BNBP-BNTT** with typical polymer donors, despite of the un-optimized nanoscale morphology, the all-PSC devices exhibit good photovoltaic performance. Further study on developing promising polymer acceptors using B←N unit for all-PSCs is in progress in our laboratory.

REFERENCES

- 1 Kim, T., Kim, J.H., Kang, T.E., Lee, C., Kang, H., Shin, M., Wang, C., Ma, B., Jeong, U., Kim, T.S. and Kim, B.J., *Nat. Commun.*, 2015, 6: 8547
- 2 Facchetti, A., *Mater. Today*, 2013, 16: 123
- 3 Yu, G., Gao, J., Hummelen, J.C., Wudl, F. and Heeger, A.J., *Science*, 1995, 270: 1789
- 4 Lin, Y. and Zhan, X., *Acc. Chem. Res.*, 2016, 49: 175
- 5 Gao, L., Zhang, Z.G., Xue, L., Min, J., Zhang, J., Wei, Z. and Li, Y., *Adv. Mater.*, 2016, 28: 1884
- 6 Song, H., Tong, H., Xie, Z., Wang, L. and Wang, F., *Chinese J. Polym. Sci.*, 2013, 31: 1117
- 7 Lu, L., Zheng, T., Wu, Q., Schneider, A.M., Zhao, D. and Yu, L., *Chem. Rev.*, 2015, 115: 12666
- 8 Zhang, S., Ye, L., Zhao, W., Tang, B., Wang, Q. and Hou, J., *Sci. China Chem.*, 2015, 58: 248
- 9 Lu, Z., Li, C., Du, C., Gong, X. and Bo, Z., *Chinese J. Polym. Sci.*, 2013, 31: 901
- 10 Liao, X.F., Wang, J., Chen, S.Y., Chen, L. and Chen, Y.W., *Chinese J. Polym. Sci.*, 2016, 34: 491
- 11 Ye, L., Jiao, X., Zhou, M., Zhang, S., Yao, H., Zhao, W., Xia, A., Ade, H. and Hou, J., *Adv. Mater.*, 2015, 27: 6046
- 12 Zhou, N., Lin, H., Lou, S.J., Yu, X., Guo, P., Manley, E.F., Loser, S., Hartnett, P., Huang, H., Wasielewski, M.R., Chen, L.X., Chang, R.P.H., Facchetti, A. and Marks, T.J., *Adv. Energy Mater.*, 2014, 4: 1300785
- 13 Mu, C., Liu, P., Ma, W., Jiang, K., Zhao, J.B., Zhang, K., Chen, Z.H., Wei, Z.H., Yi, Y., Wang, J.N., Yang, S.H., Huang, F., Facchetti, A., Ade, H. and Yan, H., *Adv. Mater.*, 2014, 26: 7224
- 14 Li, W.W., Roelofs, W.S.C., Turbiez, M., Wienk, M.M. and Janssen, R.A.J., *Adv. Mater.*, 2014, 20: 3304
- 15 Schubert, M., Collins, B.A., Mangold, H., Howard, I.A., Schindler, W., Vandewal, K., Roland, S., Behrends, J., Krafft, F., Steyrlleuthner, R., Chen, Z., Fostiropoulos, K., Bittl, R., Salleo, A., Facchetti, A., Laquai, F., Ade, H.W. and Neher, D., *Adv. Funct. Mater.*, 2014, 24: 4068
- 16 Hwang, Y.J., Earmme, T., Courtright, B.A.E., Eberle, F.N. and Jenekhe, S.A., *J. Am. Chem. Soc.*, 2015, 137: 4424
- 17 Kang, H., Uddin, M.A., Lee, C., Kim, K.H., Nguyen, T.L., Lee, W., Li, Y.X., Wang, C., Woo, H.Y. and Kim, B., *J. Am. Chem. Soc.*, 2015, 137: 2359
- 18 Cheng, P., Ye, L., Zhao, X., Hou, J., Li, Y. and Zhan, X., *Energy Environ. Sci.*, 2014, 7: 1351
- 19 Zhan, X., Tan, Z., Domercq, B., An, Z., Zhang, X., Barlow, S., Li, Y., Zhu, D., Kippelen, B. and Marder, S.R., *J. Am. Chem. Soc.*, 2007, 129: 7246
- 20 Zhou, Y., Kurosawa, T., Ma, W., Guo, Y., Fang, L., Vandewal, K., Diao, Y., Wang, C., Yan, Q., Reinspach, J., Mei, J., Appleton, A.L., Koleilat, G.I., Gao, Y., Mannsfeld, S.C.B., Salleo, A., Ade, H., Zhao, D. and Bao, Z., *Adv. Mater.*, 2014, 26: 3767
- 21 Dou, C., Saito, S., Matsuo, K., Hisaki, I. and Yamaguchi, S., *Angew. Chem. Int. Ed.*, 2012, 51: 12206
- 22 Rao, Y.L. and Wang, S., *Inorg. Chem.*, 2011, 50: 12263
- 23 Tanaka, K. and Chujo, Y., *Macromol. Rapid Commun.*, 2012, 33: 1235
- 24 Jäkle, F., *Chem. Rev.*, 2010, 110: 3985
- 25 Yamaguchi, S. and Wakamiya, A., *Pure Appl. Chem.*, 2006, 78: 1413
- 26 Wang, X., Zhuang, F., Wang, R., Wang, X., Cao, X., Wang, J. and Pei, J., *J. Am. Chem. Soc.*, 2014, 136: 3764
- 27 Wang, X.Y., Lin, H.R., Lei, T., Yang, D.C., Zhuang, F.D., Wang, J.Y., Yuan, S.C. and Pei, J., *Angew. Chem. Int. Ed.*, 2013, 52: 3117
- 28 Li, D., Zhang, H. and Wang, Y., *Chem. Soc. Rev.*, 2013, 42: 8416

- 29 Zalar, P., Henson, Z.B., Welch, G.C., Bazan, G.C. and Nguyen, T.Q., *Angew. Chem. Int. Ed.*, 2012, 51: 7495
- 30 Wakamiya, A., Taniguchi, T. and Yamaguchi, S., *Angew. Chem. Int. Ed.*, 2006, 45: 3170
- 31 Zhao, R., Dou, C., Xie, Z., Liu, J. and Wang, L., *Angew. Chem. Int. Ed.*, 2016, 55: 5313
- 32 Dou, C., Ding, Z., Zhang, Z., Xie, Z., Liu J. and Wang, L., *Angew. Chem. Int. Ed.*, 2015, 54: 3648
- 33 Dou, C., Long, X., Ding, Z., Xie, Z., Liu, J. and Wang, L., *Angew. Chem. Int. Ed.*, 2016, 55: 1436
- 34 Long, X., Ding, Z., Dou, C., Zhang, J., Liu, J. and Wang, L., *Adv. Mater.*, 2016, 28: 6504
- 35 Ding, Z., Long, X., Dou, C., Liu, J. and Wang, L., *Chem. Sci.*, 2016, 7: 6197
- 36 Blouin, N., Michaud, A. and Leclerc, M., *Adv. Mater.*, 2007, 19: 2295
- 37 Liao, S.H., Jhuo, H.J., Cheng, Y.S. and Chen, S.A., *Adv. Mater.*, 2013, 25: 4766
- 38 He, Z., Zhong, C., Su, S., Xu, M., Wu, H. and Cao, Y., *Nat. Photon.*, 2012, 6: 591