A polymer acceptor with an optimal LUMO energy level for all-polymer solar cells†

Zicheng Ding,‡a Xiaojing Long,‡ab Chuandong Dou,*a Jun Liu,*a and Lixiang Wanga

A key parameter for polymer electron acceptors is the lowest unoccupied molecular orbital (LUMO) energy level \( E_{\text{LUMO}} \). For state-of-the-art polymer electron acceptors based on the naphthalene diimide (NDI) unit, their \( E_{\text{LUMO}} \) are low-lying and cannot be tuned, leading to a low open-circuit voltage \( (V_{\text{oc}}) \) of the resulting all-polymer solar cells (all-PSCs). We report that polymer electron acceptors based on the double B–N bridged bipyrinide (BNBP) unit exhibit tunable \( E_{\text{LUMO}} \) because of their delocalized LUMOs over polymer backbones. The \( E_{\text{LUMO}} \) of the copolymer of the BNBP unit and selenophene unit \( (\text{P-BNBP-Se}) \) is lower by 0.16 eV than that of the copolymer of the BNBP unit and thiophene unit \( (\text{P-BNBP-T}) \). As a result, the energy levels of P-BNBP-Se match well with the widely-used polymer donor, poly(ethylenedioxythiophenyl)-benzodithiophene-2-ethylenyl-thienothiophene \( (\text{PTB7-Th}) \). The electron mobility of P-BNBP-Se \( (\mu_e = 2.07 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \) is also higher than that of P-BNBP-T \( (\mu_e = 7.16 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \). While the all-PSC device based on the PTB7-Th:P-BNBP-T blend shows a moderate power conversion efficiency (PCE) of 2.27%, the corresponding device with P-BNBP-Se as the acceptor exhibits a PCE as high as 4.26%. Moreover, owing to the suitable \( E_{\text{LUMO}} \) of P-BNBP-Se, the all-PSC device of P-BNBP-Se shows a \( V_{\text{oc}} \) of 1.03 V, which is higher by 0.22 V than that with the conventional NDI-based polymer acceptor. These results indicate that BNBP-based polymers can give all-PSCs with high PCEs, remarkably high \( V_{\text{oc}} \) values and small photon energy losses.

Introduction

All-polymer solar cells (all-PSCs), which utilize polymers as both the electron donor and electron acceptor, have attracted much attention recently because of their great advantages over conventional polymer/fullerene PSCs. These advantages include enhanced light absorption of polymer acceptors, low cost, and improved mechanical/thermal stability. Great progress in all-PSCs has been made by using absorption-complementary polymer donor/acceptors, optimizing the blend morphologies, or developing new polymer acceptors. However, the further development of all-PSCs is severely limited by the lack of excellent polymer acceptors. To date, only several specific polymer acceptors based on the naphthalene diimide (NDI) unit, perylenediimide (PDI) unit and B–N bridged thienylthiazole (BNTT) unit can work as polymer acceptors for efficient all-PSCs with power conversion efficiencies (PCEs) exceeding 4%.†

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‡ Electronic supplementary information (ESI) available: Experimental details, thermal property, theoretical calculations, as well as all-PSC device fabrications and characterizations. See DOI: 10.1039/c6sc01756h
‡ Z. Ding and X. Long contributed equally to this work.

A key parameter for polymer acceptors is the lowest unoccupied molecular orbital (LUMO) energy level \( E_{\text{LUMO}} \). In all-PSCs, the \( E_{\text{LUMO}} \) difference between the acceptor and donor \( (\Delta E_{\text{LUMO}}) \) is regarded as the driving force for the charge separation. The difference between the \( E_{\text{LUMO}} \) of the acceptor and the highest occupied molecular orbital (HOMO) energy level \( (E_{\text{HOMO}}) \) of the donor is related to the open-circuit voltage \( (V_{\text{oc}}) \) of all-PSCs. Therefore, to get a large \( \Delta E_{\text{LUMO}} \) for effective charge separation and to maximize \( V_{\text{oc}} \), the \( E_{\text{LUMO}} \) of the polymer acceptor must be carefully optimized. The state-of-the-art polymer acceptors are the NDI-based conjugated polymers. Unfortunately, the \( E_{\text{LUMO}} \) of these polymers are fixed at ca. –3.85 eV and cannot be effectively tuned, leading to a low \( V_{\text{oc}} \) of the resulting all-PSCs. According to a study by Takimiya et al.,7 the fixed \( E_{\text{LUMO}} \) of NDI-based polymers are due to the localized LUMOs on the NDI units. The \( E_{\text{LUMO}} \) of the NDI-based conjugated polymers are determined by the NDI unit and are not affected by the copolymerization units. Thus, it is important but challenging to develop polymer acceptors with tunable \( E_{\text{LUMO}} \).

Following our strategy to develop polymer acceptors using the B–N unit, we have reported a new electron-deficient building block based on the B–N unit, double B–N bridged bipyrinide (BNBP), to develop a polymer acceptor. In this manuscript, we report that BNBP-based polymer acceptors show tunable \( E_{\text{LUMO}} \) because of their delocalized LUMOs over the polymer backbones. The \( E_{\text{LUMO}} \) of the copolymer of the BNBP
unit and selenophene unit (P-BNBP-Se) is lower by 0.16 eV than
that of the copolymer of the BNBP unit and thiophene unit (P-
BNBP-T) (Fig. 1). As a result, the energy levels of P-BNBP-Se
match well with the widely-used polymer donor, poly[[ethyl-
hexyl-thiophenyl]-benzothiophene-[ethylhexyl]-thieno-thio-
phene] (PTB7-Th). While the all-PSC device based on the PTB7-
Th:P-BNBP-T blend shows a moderate PCE of 2.27%, the cor-
responding device with P-BNBP-Se as the acceptor exhibits
a PCE as high as 4.26% with a remarkably high $V_{oc}$ of 1.03 V.
These results indicate that BNBP-based polymer acceptors have
different electronic structures from those of the classical NDI-
based polymer acceptors and that they can give all-PSCs with
remarkably high $V_{oc}$ values and high PCEs.

**Results and discussion**

Scheme 1 shows the synthetic route of P-BNBP-Se and P-BNBP-
T. The three monomers were prepared following literature
methods and the two polymers were synthesized in Stille-poly-
merization conditions. Their chemical structures are con-
firmed 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 ($M_n$) and polydispersity (PDI) are 26.3 kDa and 1.93 for P-BNBP-
Se and 46.2 kDa and 1.81 for P-BNBP-T, respectively. According
to the thermogravimetric analysis (TGA), P-BNBP-T and P-BNBP-
Se show a good thermal stability with thermal decomposition
 temperatures ($T_d$) of over 350 °C (ESI†). In addition, the two
polymers show a good solubility in common organic solvents,
including chlorobenzene (CB), chloroform (CHCl$_3$) and o-
dichlorobenzene (o-DCB).

To elucidate the molecular orbitals of the two polymers,
density functional theory (DFT) calculations at the B3LYP/6-31G*
level of theory were performed with the model compounds con-
taining six repeating units with the long alkyl chains replaced by
methyl groups. For comparison, we also show the DFT calcu-
lation result of the state-of-the-art polymer acceptor, [poly((N,N-
bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl-
alt-5,5’-(2,2-bithiophene))] (N2200 or P[NDI2ODT2]) (Fig. 1a). As shown in Fig. 2, the calculated LUMO of the model
compound of N2200 is localized on the NDI units, indicating
that its $E_{LUMO}$ is determined by the NDI unit and cannot be
effectively tuned by changing the co-monomer units. This is
consistent with the DFT calculation and experimental results of
NDI-based conjugated polymers in the literature. In contrast,
the calculated LUMOs of the model compounds of P-BNBP-Se/P-
BNBP-T are delocalized over the BNBP units and the sen-
elophene/thiophene units. Therefore, the LUMO levels of BNBP-
based polymers are determined by both the BNBP unit and the
c-co-monomer unit. The LUMO levels of BNBP-based polymers
should be effectively tuned by changing the co-monomer units.

Cyclic voltammetry was employed to estimate the LUMO/
HOMO energy levels of the two polymers (ESI†). As shown in
Fig. 3a, P-BNBP-Se exhibits irreversible reduction and oxidation
waves with onset potentials of $E_{onset} = -1.14$ V and $E_{onset} = +1.04$ V, respectively. Accordingly, the $E_{LUMO}$/HOMO of P-BNBP-Se
are estimated to be $-3.66$ eV/$-5.84$ eV (Table 1). Similarly, the
$E_{LUMO}$/HOMO of P-BNBP-T are estimated to be $-3.50$ eV/$-5.77$ eV (Table 1). As reported previously, the model compound of the
BNBP unit itself has an $E_{LUMO}$ of $-3.19$ eV. The $E_{LUMO}$ of the two
BNBP-based polymers are much lower than that of the BNBP
unit. Moreover, the $E_{LUMO}$ of P-BNBP-Se is lower than that of P-
BNBP-T by 0.16 eV. These results confirm that the LUMO levels
of BNBP-based polymers can be effectively tuned by changing

**Scheme 1** Synthetic route of P-BNBP-Se and P-BNBP-T.
Fig. 2 Kohn–Sham LUMOs of model compounds of P-BNBP-Se, P-BNBP-T and N2200, based on calculations at the B3LYP/6-31G* level.

Fig. 3 (a) Cyclic voltammogram of P-BNBP-Se and P-BNBP-T in thin films using a Ag/AgCl reference electrode, Fc = ferrocene; (b) UV/Vis absorption spectra of P-BNBP-Se and P-BNBP-T in o-DCB solutions and in thin films.

The co-monomer units. This is consistent with the delocalized LUMOs in the DFT calculation results. The lower-lying $E_{LUMO}$ of P-BNBP-Se is attributed to the lower electronegativity of the Se atom (2.4) than the S atom (2.5) and the empty orbital of the Se atom.13

Fig. 3b shows the absorption spectra of P-BNBP-Se and P-BNBP-T in dilute o-DCB solutions and in thin films. Both of the two polymers in solutions show broad absorption bands around $\lambda = 580$ nm. The absorption spectrum is slightly redshifted for P-BNBP-Se compared to P-BNBP-T. In thin film, P-BNBP-Se exhibits a maximum absorption at 635 nm, while P-BNBP-T shows the absorption peak at 622 nm. Both of the two films show high absorption coefficients ($\epsilon$), suggesting their intense light absorption. According to the onset absorption wavelength in thin films, the optical band gaps ($E_g$) of P-BNBP-Se and P-BNBP-T are estimated to be 1.87 eV and 1.92 eV, respectively. The electron mobilities ($\mu_e$) of P-BNBP-Se and P-BNBP-T were estimated using the space-charge-limited current (SCLC) method with the current density-voltage curves of the electron-only devices (device structure: ITO/PEIE/polymer/Ca/Al).14 The electron mobility of P-BNBP-Se ($\mu_e = 2.07 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) is higher than that of P-BNBP-T ($\mu_e = 7.16 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) (ESI†). The higher electron mobility of P-BNBP-Se is due to the stronger intermolecular interactions in Se-containing polymers because of the larger and more polarizable radii of the selenium atom than the sulfur atom. This is confirmed by the smaller $\pi$$-\pi$ stacking distance of P-BNBP-Se ($d_{\pi\pi} = 3.77$ Å) than that of P-BNBP-T ($d_{\pi\pi} = 3.81$ Å) (ESI†). The electron mobility of P-BNBP-Se is comparable to the hole mobilities of typical polymer electron donors, which is very favourable for its application as a polymer electron acceptor in all-PSCs.

To investigate the application of P-BNBP-Se and P-BNBP-T as electron acceptors in all-PSCs, we select a widely-used polymer donor, PTB7-Th. All-PSC devices were fabricated with a configuration of ITO/PEDOT:PSS/PTB7-Th:P-BNBP-Se or P-BNBP-T/Ca/Al (ESI†). The active layer was spin-coated from the blend in o-DCB solution without any additives. Fig. 4 shows the current density–voltage ($J$–$V$) curves under AM 1.5G illumination (100 mW cm$^{-2}$) and the external quantum efficiency (EQE) spectra of the optimal devices. The photovoltaic parameters are summarized in Table 2. The PTB7-Th : P-BNBP-T (3 : 1, w:w) device shows a PCE of 2.27%, which is very favourable for its application as a polymer electron acceptor in all-PSCs.

Table 1 Molecular weights, photophysical and electronic properties, and electron mobilities of P-BNBP-Se and P-BNBP-T

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_a$ (kDa)</th>
<th>PDI</th>
<th>$\lambda_{ab}^a$ (nm)</th>
<th>$\lambda_{ab}^b$ (nm)</th>
<th>$\epsilon^b$ (cm$^{-1}$)</th>
<th>$E_{HOMO}^b$ (eV)</th>
<th>$E_{LUMO}^b$ (eV)</th>
<th>$E_{LUMO}^d$ (eV)</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-BNBP-Se</td>
<td>26.3</td>
<td>1.93</td>
<td>600</td>
<td>635</td>
<td>1.49 $\times 10^5$</td>
<td>1.87</td>
<td>+1.04</td>
<td>−1.14</td>
<td>−5.84</td>
</tr>
<tr>
<td>P-BNBP-T</td>
<td>46.0</td>
<td>2.01</td>
<td>593</td>
<td>622</td>
<td>1.45 $\times 10^5$</td>
<td>1.92</td>
<td>+0.97</td>
<td>−1.30</td>
<td>−5.77</td>
</tr>
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</table>

$^a$ Measured in o-DCB solution. $^b$ Measured in thin film. $^c$ Onset potential vs. Fe/Fe$^+$. $^d$ $E_{HOMO}$/$E_{LUMO} = -(4.80 + E_{\text{onset}} + E_{\text{red}})^{\text{oxidized}} \text{eV}$. 

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that of N2200. The much increased $J_{sc}$ of the P-BNBP-Se device than that of the P-BNBP-T device is in accordance with their EQE values ($\text{EQE}_{\text{max}} = 0.47$ for P-BNBP-Se and $\text{EQE}_{\text{max}} = 0.25$ for P-BNBP-T) (Fig. 4b). The $J_{sc}$ calculated from the integration of the EQE spectra agrees well with the $J_{sc}$ values obtained from the $J$–$V$ scans within an error of 5%.

The charge carrier mobilities of the two blends were investigated using the SCLC method with the electron-only and hole-only devices (ESI†). The electron mobility and hole mobility ($\mu_a$) of the PTB7-Th:P-BNBP-Se blend are estimated to be $3.34 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $2.38 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. In comparison, the PTB7-Th:P-BNBP-T blend exhibits $\mu_a = 5.96 \times 10^{-6}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $\mu_h = 7.28 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The higher electron mobility and the balanced electron/hole mobilities of the PTB7-Th:P-BNBP-Se blend are due to the enhanced electron mobility of P-BNBP-Se. We also investigated the bimolecular charge recombination in the all-PSC devices using the light-intensity dependence of the $J$–$V$ curves (Fig. 5). The $J_{sc}$ follows a power-law dependence on the illumination intensity ($J_{sc} \propto P_{\text{light}}^\alpha$), where $P_{\text{light}}$ is light intensity and $\alpha$ is the calculated power-law exponent. The $\alpha$ values are 0.93 for the PTB7-Th:P-BNBP-Se device and 0.94 for the PTB7-Th:P-BNBP-T device, which are close to unity, suggesting that the bimolecular charge recombination is weak in the two devices at a short circuit condition. Both the weak bimolecular recombination and the high and balanced electron/hole mobilities of PTB7-Th:P-BNBP-Se can explain its excellent device performance.

Fig. 4 (a) $J$–$V$ curves and (b) EQE spectra of the all-PSC devices based on the PTB7-Th:P-BNBP-Se, PTB7-Th:P-BNBP-T and PTB7-Th:N2200 blends, respectively.

The morphologies of the PTB7-Th:P-BNBP-Se and PTB7-Th:P-BNBP-T blends were characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM). As shown in Fig. 6, the TEM images exhibit similar nano/microstructures without large-size aggregation. The AFM images of the two blends similarly reveal smooth surface morphologies with the same root-mean-square (RMS) roughness of 1.47 nm and domain sizes of around 20–40 nm. The phase separation morphologies of the two blends are beneficial for good all-PSC devices.

In organic photovoltaics (OPVs), the $\Delta E_{\text{LUMO}}$ of the donor and acceptor is regarded as the driving force for charge separation. The $\Delta E_{\text{LUMO}}$ should be larger than a specific value for efficient charge separation. If $\Delta E_{\text{LUMO}}$ is too large, there is a lot of

Fig. 5 Short-circuit current density ($J_{sc}$) versus light intensity ($P_{\text{light}}$) data and power-law ($J_{sc} \propto P_{\text{light}}^\alpha$) fittings for the all-PSC devices.

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>EQE$_{\text{max/ave}}$</th>
<th>$E_{\text{loss}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-BNBP-Se</td>
<td>1.03</td>
<td>10.02</td>
<td>0.42</td>
<td>4.26/4.11</td>
<td>0.47/0.56</td>
</tr>
<tr>
<td>P-BNBP-T</td>
<td>1.12</td>
<td>5.24</td>
<td>0.39</td>
<td>2.27/2.08</td>
<td>0.25/0.47</td>
</tr>
<tr>
<td>N2200</td>
<td>0.81</td>
<td>10.55</td>
<td>0.53</td>
<td>4.37/4.30</td>
<td>0.50/0.67</td>
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* The average EQE value is calculated from eight devices.
of energy loss in the charge separation process, leading to a low
$V_{oc}$ because the $V_{oc}$ of the donor and $E_{LUMO}$ of the acceptor. In our
previous report, an all-PSC device based on the PTB7:P-BNBP-T
blend ($\Delta E_{LUMO} = 0.19$ eV) showed a good PCE of 3.38%. As
shown in Fig. 1b, the $\Delta E_{LUMO}$ is only 0.06 eV for PTB7-Ph-P,
and thus the all-PSC device shows a high $V_{oc}$ but produces a low
PCE due to the insufficient charge separation. As the $E_{LUMO}$ of
P-BNBP-Se is lower than that of P-BNBP-T, the $\Delta E_{LUMO}$ for
PTB7-Th:P-BNBP-Se is increased to 0.22 eV and ensures an
efficient charge separation, resulting in higher $J_{sc}$ and PCE values.
Moreover, due to the suitable $E_{LUMO}$ of P-BNBP-Se, the PTB7-Ph:
P-BNBP-Se device produces a high $V_{oc}$ of 1.03 V, which is higher
than that of the PTB7-Th:N2200 device by 0.22 V. These results
indicate that the suitable $E_{LUMO}$ of P-BNBP-Se plays an
important role in enhancing the all-PSCs device performance.

It is worthy to note the remarkably low photon energy losses
($E_{loss}$) of the all-PSCs based on P-BNBP-Se and P-BNBP-T. $E_{loss}$
is defined as the difference between the lowest optical bandgap
of the donor/acceptor and the $e^{-}$ of the organic photovoltaic
(OPV) device ($E_{loss} = E_g - e^{-}V_{oc}$). Typically, OPVs have large $E_{loss}$
values of 0.7–1.0 eV. It has been proposed that the lowest
$E_{loss}$ of OPVs is 0.6 eV, despite several exceptional examples. As
listed in Table 2, the $E_{loss}$ for the device of PTB7-Ph:
P-BNBP-Se and PTB7-Th:P-BNBP-T is 0.56 eV and 0.47 eV,
respectively. To our best knowledge, the $E_{loss}$ of 0.47 eV is the
lowest one for OPVs reported so far. A small $E_{loss}$ is always
observed for all-PSCs with BNBP-based polymers as electron
acceptors and the exact reason is as yet unknown. We speculate
that the small $E_{loss}$ is related to the high-lying LUMO levels of
the BNBP-based polymers.

Conclusions
In summary, we have developed a polymer acceptor based on
the BNBP unit and selenophene unit with an optimal $E_{LUMO}$ to
simultaneously enable charge separation and maximize $V_{oc}$.
BNBP-based polymers have delocalized LUMOs over the poly-
mer backbones, so their $E_{LUMO}$ can be tuned by changing the
comonomer unit. The $E_{LUMO}$ of P-BNBP-Se is lower by 0.16 eV
under that of P-BNBP-T and consequently matches well with that
of the polymer donor, PTB7-Th. While the all-PSC device based
on PTB7-Ph:P-BNBP-Se shows a moderate PCE of 2.27%, the
corresponding device with P-BNBP-Se as the acceptor exhibits
a PCE as high as 4.26%. Moreover, the device of P-BNBP-Se shows
a $V_{oc}$ of up to 1.03 V and $E_{loss}$ as small as 0.56 eV. These
results indicate that polymers-based polymer acceptors have
different electronic structures from those of classical NDI-based
polymer acceptors and that they can give all-PSCs with remar-
kably high $V_{oc}$ values and high PCEs.

Experimental section
Synthesis of P-BNBP-Se
The dibromo-substituted BNBP monomer was synthesized
according to the previous report. The starting materials of the
dibromo-substituted BNBP monomer (220 mg, 0.248 mmol),
2,5-bis(trimethylstannyl)selenophene (114.1 mg, 0.248 mmol),
$P_{(db)}$ (4.05 mg, 0.0050 mmol) and $P_{(o-tol)}$ (12.1 mg,
0.04 mmol) were placed in a two-necked flask under argon, and
then dried toluene (11 mL) was added. After the mixture was
stirred at 115 °C for 48 h, an end-capping reaction was carried
out by adding 2,5-bis(trimethylstannyl)selenophene (3 mg) and
then bromobenzene (200 mg). After cooling, the resulting
organic phase was extracted with CHCl$_3$ (150 mL) and washed
with water. After the solvents were removed, the residue was
dispersed in methanol and the precipitate was collected. The
obtained dark solid was dispersed in acetonitrile, and was
collected and dried in a vacuum overnight. Yield: 213 mg (95%).

<table>
<thead>
<tr>
<th>Synthesis of P-BNBP-Se</th>
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<tr>
<td><strong>PTB7-Th:</strong></td>
</tr>
<tr>
<td><strong>Ph</strong></td>
</tr>
<tr>
<td><strong>BNBP-Se</strong></td>
</tr>
<tr>
<td><strong>PTB7-Th:</strong></td>
</tr>
<tr>
<td><strong>BNBP-T</strong></td>
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Notes and references
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10 DFT calculations were performed using Gaussian 09 program: M. J. Frisch, et al., Gaussian 09, revision A.02, Gaussian, Inc., Wallingford, CT, 2009. For details, see ESI.†


