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Pronounced Backbone Coplanarization by $\pi$-Extension in a Sterically Hindered Conjugated Polymer System Leads to Higher Photovoltaic Performance in Non-Fullerene Solar Cells

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ABSTRACT

Achieving both the backbone order and solubility of π-conjugated polymers, which are often in a trad-off relationship, is imperative for maximizing the performance of organic solar cells. Here, we studied three different π-conjugated polymers based on thiazolothiazole (PSTz1 and POTz1) and benzobisthiazole (PNBTz1) that were combined with a benzodithiophene unit in the backbone, where PNBTz1 was newly synthesized. Due to the steric hindrance between the side chains located on neighboring heteroaromatic rings, POTz1 had a much less coplanar backbone than PSTz1 in which such a steric hindrance is absent. However, POTz1 showed higher photovoltaic performance in solar cells that used Y6 as the acceptor material. This was likely due to the significantly higher solubility of POTz1 than PSTz1, resulting in a better morphology. Interestingly, PNBTz1 was found to have markedly higher backbone coplanarity than POTz1 despite having similar steric hindrance between the side chains, most likely owing to the more extended π-electron system, while PNBTz1 had good solubility comparable to POTz1. As a result, PNBTz1 exhibited higher photovoltaic performance than POTz1 in the Y6-based cells: specifically, the fill factor was significantly enhanced. Our results indicate that the backbone order and solubility can be achieved by the careful molecular design, which indeed leads to higher photovoltaic performance.

KEYWORDS: Conjugated polymers, Semiconducting polymers, Non-fullerene, Organic photovoltaics, Organic solar cells, Thiazolothiazole, Benzobisthiazole, Coplanar
INTRODUCTION

Organic solar cells have been widely and intensively investigated in the past few decades as next generation photovoltaic technology due to their lightweight, flexibility, and semi-transparency as well as low-cost and low-energy-consumption solution-processability.\(^1\) One of the largest issues in organic solar cells is to improve the power conversion efficiency (PCE), for which the development of the materials for both photoactive layers\(^2\)\(^-\)\(^4\) and interlayers\(^5\)\(^-\)\(^7\) as well as the optimization of fabrication conditions\(^8\)\(^-\)\(^10\) are crucial. A number of studies have been conducted to design and synthesize \(\pi\)-conjugated polymers in particular as the p-type semiconducting (donor) material for the photoactive layer, which has made remarkable progresses in the area.\(^11\)\(^-\)\(^16\) More recently, intensive studies on non-fullerene acceptor (NFA) materials have further resulted in improving the PCEs in excess of 18\%.\(^16\)\(^-\)\(^22\)

A promising approach for the development of high-performance \(\pi\)-conjugated polymers is to alternatively incorporate electron-rich and electron-poor rigid fused rings, which are often linked with some spacer heteroaromatic rings, in the polymer backbone.\(^11\)\(^-\)\(^16\),\(^23\)\(^-\)\(^25\) Such rigid-rod donor–acceptor motifs can coplanarize the polymer backbones, which facilitates the intermolecular \(\pi–\pi\) interactions and thus the polymer order in the thin film. However, this often results in poor solubility in organic solvents and thus poor solution processability. Thus, bulky side chains including branched alkyl groups are typically substituted in the polymer backbone to ensure sufficient solubility, which however could cause torsion of the backbone and/or could suppress the \(\pi–\pi\) interactions. Therefore, careful design of the backbones and side chains is crucial for achieving both the coplanarity and solubility of the polymers.

Thiazole-based fused rings such as thiazolo[5,4-\(d\)]thiazole (TzTz)\(^{26}\)\(^-\)\(^30\) and benzo[1,2-\(d\):4,5-\(d'\)]bisthiazole (BBTz),\(^{31}\)\(^-\)\(^34\) known as electron-poor fused rings, are promising building units for the development of high-performance polymers. We have been studying a series of \(\pi\)-conjugated polymers based on TzTz\(^{28}\)\(^,\)\(^35\)\(^-\)\(^39\) and BBTz\(^{32}\)\(^,\)\(^40\) for the use in organic field-effect transistors as well as organic solar cells. Based on their rigid fused-ring structure, TzTz and BBTz-based polymers exhibit coplanar
backbones and thus high $\pi-\pi$ stacking crystallinity, which have resulted in reasonably high charge carrier mobilities in transistor devices and/or photovoltaic performances in fullerene-based cells. More recently, while several other groups have reported that TzTz and BBTz-based polymers incorporating a benzo[1,2-\textit{b}:4,5-\textit{b'}]dithiophene (BDT) electron-rich fused ring nicely functioned in NFA-based cells,\textsuperscript{34,41-44} as BDT is one of the useful electron-rich building units for $\pi$-conjugated polymers,\textsuperscript{12,25,45-47} we independently have studied a series of TzTz-based polymers that combined with a BDT unit such as PSTz1 and POTz1 (Figure 1a).\textsuperscript{48} PSTz1, a BDT-TzTz polymer with the alkyl groups on the main chain thiophene ring heading toward the TzTz moiety, had a more coplanar backbone than POTz1 with the alkyl groups heading toward the BDT moiety. This was most likely because POTz1 has steric hindrance between the side chains while PSTz1 does not, as described in Figure 1b. Interestingly, however, POTz1 showed higher photovoltaic performance than PSTz1 in solar cells that used ITIC as the NFA material, in contrast to the case in the fullerene-based cells in which PSTz1 showed higher photovoltaic performance. We assumed that this was ascribed to the difference in the morphology of the blend film originating in the difference in the solubility: POTz1 had significantly higher solubility than PSTz1.

With this in mind, we here designed and synthesized PNBTz1, where the TzTz unit in POTz1 was replaced with the BBTz unit having extended $\pi$-electron system, expecting the improvement of the backbone coplanarity. We note here that the same polymer was reported by Wen and co-workers, in which the polymer showed PCEs as high as 13.3% combined with ITIC-F.\textsuperscript{34} In addition, Jefferies-EL and co-workers have reported a similar polymer with different alkyl groups, which was utilized in fullerene-based cells.\textsuperscript{49} Notably, PNBTz1 showed significantly enhanced backbone coplanarity compared to POTz1 despite having similar steric hindrance between the side chains (Figure 1b), without sacrificing the solubility. Furthermore, PNBTz1 exhibited a marked improvement in the fill factor (FF) compared to POTz1 in the solar cell that used Y6, a benchmark NFA (Figure 1c), thus resulting in PCEs of $\sim$14% that was higher than and POTz1 ($\sim$12%). We also discuss the correlation
between the molecular structure, polymer order and solar cell properties. The results show that the backbone torsion caused by steric hindrance between the side chains, being detrimental for the crystallinity and thereby charge transport, can be balanced by introducing an extended fused ring system.

Figure 1. (a) Chemical structure of PSTz1, POTz1 and PNBTz1. (b) Schematic for the steric effect between the side chains in PSTz1 (left) and POTz1 and PNBTz1 (right). Similar steric hindrance should exist in both POTz1 and PNBTz1. (c) Chemical structure of Y6.
RESULTS AND DISCUSSION

PNBTz1 was synthesized as depicted in Scheme 1, where the BBTz monomer (1) with 2-butyloctyl (BO) groups were copolymerized with the BDT monomer (2) with 2-ethylhexyl (EH) groups via the Stille coupling reaction. The number average and weight average molecular weights ($M_n/M_w$) and the polydispersity index ($D$), determined by gel-permeation chromatography measured at 140 °C, were 56,000/133,000 and 2.38 for PNBTz1. Solubility of the polymer was tested using the polymer solution with a concentration of approximately 5 g L$^{-1}$ in chloroform (CF). PNBTz1 dissolved completely at around 45 °C, while POTz1 with a similar molecular weight ($M_n/M_w = 56,800/214,000$, $D = 3.78$) dissolved at room temperature. We note that PNBTz1 kept dissolved after cooled to room temperature. Thus, the solubility of PNBTz1 is quite high and $\pi$-extension did not significantly decrease the solubility. In addition, PSTz1 was soluble in CF when the molecular weight was low such as $M_n/M_w$ of 11,200/19,400 ($D = 1.73$), but was insoluble in CF when $M_n$ was higher than 20,000: for example, PSTz1 with $M_n/M_w = 45,000/98,200$ ($D = 2.20$) was only soluble in high-boiling point solvents such as chlorobenzene (CB), o-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB) at around 100 °C. Hereafter, PSTz1 with $M_n$ of 11,200 was used for all the experiments if otherwise noted. In addition, we also synthesized a copolymer comprising BDT and BBTz having the alkyl side chains placed like PSTz1, which is called PKBTz1 (Figure S2). PKBTz1 with an $M_n$ of 40,700 ($M_w = 115,300$ and $D = 2.83$) was soluble in CF, thus had slightly higher solubility than PSTz1, but PKBTz1 with an $M_n$ of 63,300 ($M_w = 156,200$ and $D = 2.47$) was only soluble in chlorinated benzenes at around 100 °C. Both PKBTz1 batches with different molecular weights, unfortunately, exhibited even lower photovoltaic performance than PSTz1 (Figure S10). The polymers were found to be sufficiently thermally stable as no phase transition peak was observed in the differential scanning calorimetry measurements in the range of 20–350 °C (Figure S3).
Scheme 1. Synthesis of PNBTz1 (BO = 2-butyloctyl, EH = 2-ethylhexyl)
Energy levels for the highest occupied molecular orbital (HOMO), $E_{\text{HOMO}}$, and the lowest unoccupied molecular orbital (LUMO), $E_{\text{LUMO}}$, were determined by the oxidation and reduction onset potentials in the cyclic voltammograms of the polymer thin films (Figure S4). It was found that PNBTz1 had slightly lower energy levels than PSTz1 and POTz1: whereas $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ were $-5.37$ and $-3.35$ eV for PSTz1 and $-5.32$ and $-3.31$ eV for POTz1, those were $-5.44$ and $-3.46$ eV for PNBTz1, respectively (Table 1). The difference is mostly consistent with the calculated energy levels for the model compound of the polymers (Figure S5).

Polymer optical properties were investigated by UV–vis absorption spectroscopy in the CF solution and in the thin film fabricated from the CF solution (Figures 2a, Table 1). In the solution, PSTz1 and POTz1 showed absorption spectra similarly covering 300–630 nm with a vibrational structure with absorption maxima ($\lambda_{\text{max}}$) at around 590 and 540 nm, corresponding to the 0–0 and 0–1 transition bands, respectively. However, the intensity of the 0–0 band with respect to the 0–1 band was larger in PSTz1 than POTz1. This likely originates in the difference in the backbone coplanarity, where POTz1 should have significantly large backbone torsion due to the steric hindrance between the side chains compared to PSTz1 as illustrated in Figure 1b. This is consistent with the computation, in which the model compound for POTz1 had a significantly twisted geometry compared to PSTz1, in particular at the linkage between the BDT and alkylthiophene units: a dihedral angle was 6° for PSTz1 and was 43° for POTz1 (Figure 3). PNBTz1 gave absorption spectra covering 300–600 nm, which were slightly blue shifted compared to the spectra of POTz1. It is interesting to note that, in sharp contrast to POTz1, PNBTz1 showed a similar vibrational structure with $\lambda_{\text{max}}$’s of ca. 555 and 515 nm, but with a more intensified 0–0 band with respect to the 0–1 band compared to POTz1, suggesting that the PNBTz1 backbone is more coplanar than the POTz1 backbone despite having similar steric hindrance: the 0–1 band of the absorption for PNBTz1 was even more intensified compared to that for PSTz1 that do not have such steric hindrance. Interestingly, this contrasted the calculated structure of the model compound for PNBTz1, which had a twisted geometry similar to that for POTz1 (Figure 3).
implies that in PNBTz1 the backbones can partially aggregate due to the enhanced intermolecular interaction in the solution even the polymer is highly soluble.

In the thin film (Figure 2b), the spectrum of POTz1 exhibited 0–0 and 0–1 transition bands with \( \lambda_{\text{max}} \)’s of 580 and 545 nm. It is noted that the intensity of the 0–0 band was weaker than the 0–1 band, which contrasted to what was observed in the solution, suggesting that the backbone coplanarity was rather decreased. In PNBTz1, although the intensity of the 0–0 band with respect to the 0–1 band weakened relative to the case in the solution, the 0–0 band was still stronger than the 0–1 band, which was similar to the film absorption of PSTz1. Thus, the PNBTz1 backbone is more coplanar compared to the POTz1 backbone in the solid state as well as in the solution. These results clearly show that the extension of \( \pi \)-electron system can significantly enhance the backbone coplanarity even though there is a large torsion-susceptible steric hindrance.

We also measured the absorption spectra of the polymer/Y6 blend films with the polymer to Y6 weight ratio of 1:1.2, which is the optimal ratio for the OPV cells (Figure 2c). Both blend films gave similar absorption corresponding to Y6 in the range of approximately 600–900 nm. It is known that the shape of the absorption spectrum for Y6 is very sensitive to the film fabrication conditions, which is thought to be due to the difference in the local packing structure of Y6.\(^{50-52}\) The almost identical shape for the Y6 absorption suggests that Y6 molecules are locally packed in a similar fashion in these blend films. It should be noted that PNBTz1 provided a sharp spectrum in which the 0–0 band was slightly stronger than the 0–1 band, while POTz1 exhibited a weaker 0–0 band relative to the 0–1 band, as both similar to the case in the neat film. This indicates that the PNBTz1 backbone is more coplanar than the POTz1 backbone even when blended with Y6.

The enhanced backbone coplanarity in PNBTz1 compared to POTz1 seemingly originates in the higher intermolecular interactions caused by the more \( \pi \)-extended rigid structure of the BBTz unit than the TzTz unit. This consideration was further supported by the temperature dependence of the UV–vis absorption spectra measured in CB in the range of 20 to 100 °C (Figure 2d–f). Note that in the CB
solution, all the polymers exhibited less featured spectrum with weaker 0–0 transition band, compared to the case in the CF solution. In particular for POTz1, the 0–0 band appeared as shoulder. These results suggest that the polymer backbones can be more freely rotated in the CB solution than in the CF solution. The spectra of both PSTz1 and POTz1 became featureless as the temperature increased, even though the initial spectra at 20 °C were very different (Figures 2d and 2e), suggesting the significant disaggregation of the backbone and/or rotation of the linkages between the heteroaromatic rings in the backbone. The larger blue-shift of the spectrum with increase in temperature observed in POTz1 than in PSTz1 suggests that the backbone torsion is more significant in POTz1. On the other hand, the spectrum of PNBTz1 preserved vibrational structure with a certain intensity for the 0–0 band even at 100 °C compared to POTz1 and even PSTz1 (Figure 2f), thus the backbones of PNBTz1 still preserved coplanarity and/or aggregated to a certain extent.
Figure 2. (a–c) UV–vis absorption spectra of the polymers in (a) CF solution and (b) film, and those of (c) the polymer/Y6 blend film. Both polymer and polymer/Y6 blend films were fabricated from the CF solution. (d–f) Temperature-dependent absorption spectra measured in the CB solution for (d) PSTz1, (e) POTz1, and (f) PNBTz1.
Table 1. Polymer properties

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{LUMO}}$ (eV)$^a$</th>
<th>$E_{\text{HOMO}}$ (eV)$^a$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$E_g^{\text{opt}}$ (eV)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSTz1</td>
<td>−3.35</td>
<td>−5.37</td>
<td>544, 583</td>
<td>543, 590</td>
</tr>
<tr>
<td>POTz1</td>
<td>−3.31</td>
<td>−5.32</td>
<td>544</td>
<td>545, 580</td>
</tr>
<tr>
<td>PNBTz1</td>
<td>−3.46</td>
<td>−5.44</td>
<td>516, 556</td>
<td>514, 554</td>
</tr>
</tbody>
</table>

$^a$LUMO and HOMO energy levels ($E_{\text{LUMO}}$ and $E_{\text{HOMO}}$) Estimated using redox onset potentials determined by cyclic voltammetry. $^b$Optical bandgap determined from the onset in the film absorption spectrum.

Figure 3. Geometries of the model compounds for the polymers calculated by the DFT method at the B3LYP/6-31G(d) level. Dimers of the repeat units were used as the models, in which the alkyl groups were replaced by the methyl groups to simplify the calculation.
We fabricated OPV cells using both an inverted architecture (ITO/ZnO/active layer/MoO\textsubscript{x}/Ag) and a conventional architecture (ITO/PEDOT:PSS/active layer/PDINO\textsubscript{53}/Ag), where the polymers were used as the donor and Y6 was used as the acceptor in the active layer. We first optimized the photovoltaic performance using the inverted cell by changing the fabrication conditions, where chloroform was used as the solvent, and then adapted the best conditions to the conventional cell (Figures S6–S9, Tables S1–S4). The optimal polymer to Y6 weight ratio was found to be 1:1.2, and the thermal annealing of the active layer at 90 °C was found to slightly improve the performance for all the polymer/Y6 blends. Figures 4a and 4b show the current density (\(J\))–voltage (\(V\)) curves and external quantum efficiency (EQE) curves of the optimized inverted cells, respectively. The photovoltaic parameters are summarized in Table 2. Whereas PSTz1 showed a PCE of 11.0% with a \(J_{SC}\) of 18.7 mA cm\(^{-2}\), a \(V_{OC}\) of 0.83 V, and an FF of 0.70, POTz1 showed a PCE of 11.2% with a \(J_{SC}\) of 21.1 mA cm\(^{-2}\), a \(V_{OC}\) of 0.85 V, and an FF of 0.63. Although the PCEs for these polymers were similar, the photovoltaic parameters were different, \textit{i.e.}, POTz1 showed higher \(J_{SC}\) but lower FF than PSTz1. The higher \(J_{SC}\) in POTz1 is consistent with the higher EQEs in POTz1. On the one hand higher \(J_{SC}\) in the POTz1 cell than in the PSTz1 cell should be because POTz1 exhibited a better polymer-Y6 blended morphology as will be discussed later, likely due to the higher solubility and thus the higher miscibility with Y6. On the other hand, the lower FF in the POTz1 cell is attributable to the less ordered backbone structure as described above and the slightly lower charge carrier mobility as will be shown below. Notably, PNBTz1 exhibited a higher PCE of 13.0% (\(J_{SC} = 21.8\) mA cm\(^{-2}\), \(V_{OC} = 0.82\) V, FF = 0.72), in which \(J_{SC}\) and FF were slightly but higher than those of POTz1 and PSTz1, respectively. This is likely due to the fact that PNBTz1 had both high solubility and ordered coplanar backbone at the same time.

In addition, it is interesting to note that PSTz1 with higher molecular weight (\(M_n = 45,000\)), which had similar molecular weight to POTz1 and PNBTz1, showed lower photovoltaic performance, in particular FF, than PSTz1 with \(M_n = 11,200\) (Figures 5a and 5b, Table3). Although it is known that
some polymers such as PM6 show strong molecular-weight dependence of the performance in NFA-based cells,\textsuperscript{29, 54} a major reason of the lower performance observed for PSTz1 with an $M_n$ of 45,000 is possibly due to the solvent used for the active layer deposition. In this case, due to the insolubility of PSTz1 with an $M_n$ of 45,000 in CF, the solar cells were fabricated using CB. We note here that, in the UV–vis absorption spectra for the PSTz1/Y6 blend films, the absorption band of Y6 in the film with PSTz1 ($M_n = 45,000$) fabricated by CB significantly red-shifted and slightly weakened from that in the film with PSTz1 ($M_n = 11,200$) fabricated by CF (Figure 5c). This suggests that the aggregation structure, or local packing, of Y6 between these films were distinct, more specifically, Y6 did not form a favorable aggregation structure to perform well in the cell when fabricated by CB. We also fabricated PNBTz1/Y6 cell using CB, DCB, and TCB for the active layer deposition. These cells also showed significantly lower photovoltaic performances than that fabricated by CF (Figures 5d and 5e, Table 3), in which the Y6 absorption band in these blend films similarly red-shifted and weakened from that in the CF-fabricated film (Figure 5f). Solvents with the higher boiling point seemingly enhanced the shift and decreased the intensity of Y6 absorption band, which was consistent with the decrease in the photovoltaic performance. This implies that the drying process significantly affects the Y6 aggregation. In fact, transmission electron microscopy (TEM) also showed that the aggregation was significantly changed when the chlorinated benzenes were used as the solvent (Figure S11).

In all the polymers, the conventional cell exhibited higher photovoltaic performance than the inverted cell (Figures 4c and 4d). In fact, the PCEs for PSTz1 and POTz1 were slightly improved to approximately 12% (Table 2). In the conventional cell, the differences in the $J_{SC}$ and FF between the PSTz1- and POTz1-based cells become smaller. The PNBTz1-based conventional cell demonstrated the highest photovoltaic performance with PCEs as high as 14.0% ($J_{SC} = 23.8$ mA cm$^{-2}$, $V_{OC}$ was 0.84 V, and FF was 0.70), in which again the $J_{SC}$ and FF were even higher than those observed in the PSTz1- and POTz1-based conventional cells.
Figure 4. (a) $J-V$ curves of the polymer/Y6 cells with the inverted architecture (ITO/ZnO/(polymer/Y6)/MoO$_3$/Ag). (b) EQE spectra of the polymer/Y6 cells with the inverted architecture. (c) $J-V$ curves of the polymer/Y6 cells with the conventional architecture (ITO/PEDOT:PSS/(polymer/Y6)/PDINO/Ag). (d) EQE spectra of the polymer/Y6 cells with the conventional architecture.

Table 2. Photovoltaic properties of the polymer/Y6 cells.

<table>
<thead>
<tr>
<th>polymer$^a$</th>
<th>device structure$^b$</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$J_{SC}^{EQE}$ (mA cm$^{-2}$)$^c$</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSTz1</td>
<td>inverted</td>
<td>18.7</td>
<td>18.7</td>
<td>0.83</td>
<td>0.70</td>
<td>11.0 [10.5]</td>
</tr>
<tr>
<td></td>
<td>conventional</td>
<td>20.7</td>
<td>19.8</td>
<td>0.84</td>
<td>0.69</td>
<td>12.1 [11.5]</td>
</tr>
<tr>
<td>POTz1</td>
<td>inverted</td>
<td>21.1</td>
<td>20.7</td>
<td>0.85</td>
<td>0.63</td>
<td>11.2 [10.6]</td>
</tr>
<tr>
<td></td>
<td>conventional</td>
<td>21.0</td>
<td>20.8</td>
<td>0.84</td>
<td>0.68</td>
<td>12.0 [11.4]</td>
</tr>
<tr>
<td>PNBTz1</td>
<td>inverted</td>
<td>21.8</td>
<td>21.5</td>
<td>0.82</td>
<td>0.72</td>
<td>13.0 [12.1]</td>
</tr>
<tr>
<td></td>
<td>conventional</td>
<td>23.8</td>
<td>23.4</td>
<td>0.84</td>
<td>0.70</td>
<td>14.0 [13.4]</td>
</tr>
</tbody>
</table>

$^a$PSTz1: $M_n = 11,200$, POTz1: $M_n = 56,800$, PNBTz1: $M_n = 56,000$. $^b$inverted: ITO/ZnO/(polymer/Y6)/MoO$_3$/Ag, conventional: ITO/PEDOT:PSS/(polymer/Y6)/PDINO/Ag. $^c$$J_{SC}$ calculated from EQE spectrum. $^d$maximun PCE and average PCE in the bracket
Figure 5. (a) $J$–$V$ curves and (b) EQE spectra of the PSTz1/Y6 cells with the inverted architecture, and (c) UV–vis absorption spectra of PSTz1/Y6 blend films, in which different molecular weight PSTz1 samples were used. The blend films were fabricated using chloroform (CF) and chlorobenzene (CB) for the PSTz1 samples with $M_n = 11,200$ and $45,000$, respectively. (d) $J$–$V$ curves and (e) EQE spectra of the PNBTz1/Y6 cells with the inverted architecture, and (f) UV–vis absorption spectra of PNBTz1/Y6 blend films, in which the films were fabricated using CF, CB, $o$-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene (TCB).
Table 3. Photovoltaic properties of the PSTz1/Y6 and PNBTz1/Y6 cells with the inverted architecture fabricated using different solvents.

<table>
<thead>
<tr>
<th>polymer</th>
<th>solvent</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$J_{SC}^{EQE}$ (mA cm$^{-2}$)$^d$</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSTz1</td>
<td>CF$^b$</td>
<td>18.7</td>
<td>18.7</td>
<td>0.83</td>
<td>0.70</td>
<td>11.0 [10.5]</td>
</tr>
<tr>
<td></td>
<td>CB$^c$</td>
<td>18.4</td>
<td>18.9</td>
<td>0.85</td>
<td>0.56</td>
<td>8.7 [8.3]</td>
</tr>
<tr>
<td>PNBTz1</td>
<td>CF</td>
<td>21.8</td>
<td>21.5</td>
<td>0.82</td>
<td>0.72</td>
<td>13.0 [12.1]</td>
</tr>
<tr>
<td></td>
<td>CB</td>
<td>11.7</td>
<td>11.9</td>
<td>0.73</td>
<td>0.63</td>
<td>5.5 [5.3]</td>
</tr>
<tr>
<td></td>
<td>DCB</td>
<td>9.4</td>
<td>9.6</td>
<td>0.68</td>
<td>0.55</td>
<td>3.6 [3.0]</td>
</tr>
<tr>
<td></td>
<td>TCB</td>
<td>5.2</td>
<td>5.8</td>
<td>0.64</td>
<td>0.47</td>
<td>1.6 [1.2]</td>
</tr>
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</table>

$^a$Solvents used for the active layer fabrication. CF: chloroform, CB: chlorobenzene, DCB: o-dichlorobenzene, TCB: 1,2,4-trichlorobenzene. $^b$PSTz1 with $M_n = 11,200$ was used. $^c$PSTz1 with $M_n = 45,000$ was used. $^d$$J_{SC}$ calculated from EQE spectrum. $^e$maximun PCE and average PCE in the bracket.
To understand the difference in the photovoltaic performance of these polymers, we first studied the photoluminescence (PL) quenching efficiencies of the blend films. As a result, all the blend films similarly showed very high PL quenching efficiencies with 100% and ca. 90% when excited at 500 and 800 nm, which correspond to the polymer and Y6 excitation, respectively (Figure 6): quenching efficiencies for the PSTz1, POTz1, and PNBTz1 blend films for the 800 nm excitation were 91%, 89%, and 92%, respectively. This indicates that both the electron/energy transfer from the polymer to Y6 and the hole transfer from Y6 to the polymer were highly efficient for all the blend films, and there is no difference in the charge generation process, in particular, exciton diffusion and charge transfer processes. We thus assume that the differences in the photovoltaic performances, more specifically $J_{SC}$ and FF, would be due to the difference in the charge dissociation and/or charge transport processes.

We then fabricated hole-only and electron-only devices for the blend films (Figure S15), and estimated the hole and electron mobilities, respectively, on the basis of space-charge limited current model. While the POTz1/Y6 blend film showed a hole mobility $1.7 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, which was lower than the PSTz1/Y6 blend film ($5.4 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$). However, the PNBTz1/Y6 blend film showed a hole mobility of $4.5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, which was higher than the POTz1/Y6 blend film and is comparable to the PSTz1/Y6 blend film. On the other hand, these blend films exhibited almost the same electron mobilities: $1.7 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for the PNBTz1/Y6 film, $1.2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for the POTz1/Y6 film, and $1.5 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ for the PSTz1/Y6 film. Therefore, the difference in the hole mobility agrees well with the trend in FF for these polymer-based cells.
Figure 6. Photoluminescence spectra for (a) the polymer neat films and polymer/Y6 blend films excited at 500 nm (polymer excitation) and (b) the Y6 neat film and polymer/Y6 blend films excited at 800 nm (Y6 excitation).
The grazing incidence X-ray diffraction (GIXD) measurements were carried out to investigate the structural order of the polymers. Figure 7 displays the two-dimensional (2D) GIXD patterns (Figures 7a–c and 7e–g) and the diffraction profiles (Figures 7d and 7h) of the polymer neat films and polymer/Y6 blend films. In the neat films (Figure 7a–d), all the polymers provided 2D GIXD patterns with a diffraction corresponding to the lamellar structure along the \( q_{xy} \) axis and a diffraction corresponding to the \( \pi-\pi \) stacking structure along the quasi \( q_z \) axis, thus the polymer backbones are oriented in a face-on fashion. However, there was a notable difference in the \( \pi-\pi \) stacking structure. The \( \pi-\pi \) stacking distance \( (d_{\pi}) \) of PO\( Tz1 \) was ca. 4.1 Å, which was slightly wider than that of PS\( Tz1 \) (ca. 4.0 Å). Further, the coherence length of the \( \pi-\pi \) stacking structure for PO\( Tz1 \), estimated by the Scherrer equation,\(^{55} \) was ca. 9 Å, which was slightly smaller than that for PS\( Tz1 \) (ca. 12 Å). This is consistent with the fact that PO\( Tz1 \) had less coplanar backbone structure compared to PS\( Tz1 \), as evidenced by the UV–vis absorption measurements, which should originate in the larger steric hindrance between the side chains. Notably, on the other hand, PNBTz1 exhibited a \( d_{\pi} \) of 3.76 Å, which was markedly narrower than PO\( Tz1 \) (even narrower than PS\( Tz1 \)) despite the fact that there is similar steric hindrance between the side chains (larger steric hindrance). This clearly indicates that PNBTz1 had significantly improved \( \pi-\pi \) stacking structure, which agrees well with the enhanced backbone coplanarity. Thus, the introduction of the extended \( \pi \)-conjugated system is highly beneficial for coplanarizing the backbone and improving the structural order in \( \pi \)-conjugated polymers with such sterically hindered molecular structure.

In contrast, in the blend film (Figure 7e–g), all the polymers gave similar diffraction patterns with diffractions at the smaller \( q_{xy} \) region with a \( d \)-spacing of 21 Å \( (q_{xy} \approx 0.3 \text{ Å}^{-1}) \) and at the larger \( q_z \) region with a \( d \)-spacing of around 3.6 Å \( (q_z \approx 1.7 \text{ Å}^{-1}) \). Considering that the \( d \)-spacing of the diffraction at the quasi-\( q_z \) axis is different from that observed in all the polymer neat films, the diffractions seemingly correspond to the molecular order of Y6, rather than the polymers. In fact, the 2D GIXD patterns for the blend films closely resemble to that for the Y6 neat film (Figure S12). This means that there were
no diffractions corresponding to the polymers and thus the polymers were mostly in amorphous form in the blend film. In addition, the coherence lengths for the π–π stacking structure most likely corresponding to Y6, estimated from the diffraction at around 1.7 Å−1, were similar for all the blend films: 16.8 Å for PSTz1/Y6, 14.5 Å for POTz1/Y6, and 17.9 Å for PNBTz1/Y6 blend films. This is consistent with the fact that the electron mobilities for these blend films were similar. Therefore, it is assumed that the ordering structure understood from the 2D GIXD patterns should not account for the difference in the photovoltaic performance.

We also conducted atomic force microscopy (AFM) and TEM to investigate the surface and internal morphology of the blend film, respectively. Whereas the AFM measurement did not show significant differences in the surface morphology (Figure S14), the TEM measurement provided some differences in the internal morphology (Figure 8). The PSTz1 blend film (Figure 8a) provided larger nanofibrillar structures than the POTz1 and PNBTz1 blend films (Figures 8b and 8c), implying that the PSTz1/Y6 blend formed slightly large phase separation, which may originate in the higher backbone order of PSTz1. In general, the larger phase separation is often detrimental to the exciton diffusion, which gives rise to lower JSC. In these cases, however, the exciton diffusion and charge transfer processes were similarly efficient as discussed above. Therefore, the larger phase separation in the PSTz1/Y6 blend film could have led to slightly inefficient charge dissociation and thereby lower JSC than the others. On the other hand, the blend films of POTz1 and PNBTz1 provided similar TEM textures with finely mixed nanofibrils. This implies that the morphology is not the factor determining the difference in the photovoltaic performance of these two polymers. Overall, we conclude that the difference in the backbone coplanarity in the blend film, as evidenced by the UV–vis absorption measurement, would be a key factor determining the difference in the photovoltaic performance, in particular FF, between POTz1 and PNBTz1. In fact, as discussed above the PNBTz1/Y6 blend film showed higher hole mobility than the POTz1/Y6 blend film, reflecting the higher backbone coplanarity in PNBTz1. It is
possible that even though the long-range order is absent, the higher local order in PNBTz1 than in POTz1 can give higher charge carrier mobility.

Figure 7. 2D GIXD patterns of the (a–c) polymer neat films and (e–g) polymer/Y6 blend films: (a) PSTz1, (b) POTz1, (c) PNBTz1, (e) PSTz1/Y6, (f) POTz1/Y6, and (g) PNBTz1/Y6. GIXD profiles of the (d) polymer neat films and (h) polymer/Y6 blend films.

Figure 8. TEM images of the (a) PSTz1/Y6, (b) POTz1/Y6, and (c) PNBTz1/Y6 blend films.
CONCLUSION

In this study, we studied the impact of the size of a fused π-electron system in a series of π-conjugated polymers, PSTz1, POTz1, and PNBTz1, in which a TzTz unit and a BBTz unit were copolymerized with a BDT unit, respectively. Despite the similar steric hindrance originating in the side chain placement, PNBTz1 had a more coplanar and ordered backbone relative to POTz1 both in the polymer neat film and the polymer/NFA (Y6) blend film as evidenced by the optical absorption measurements. Notably, the backbone coplanarity of PNBTz1 was comparable to that of PSTz1 with much lesser steric hindrance. Such a high coplanarity in PNBTz1 likely originates in the more extended π-electron system of the BBTz moiety than the TzTz moiety. Interestingly, the solubility of PNBTz1 was similar to that of POTz1 despite the improved backbone coplanarity and was markedly higher than that of PSTz1. The GIXD measurements for the polymer neat films also showed that PNBTz1 showed higher structural order than POTz1 and even PSTz1. Although the GIXD measurements for the blend films did not provide the information of the polymer structural order, optical absorption measurements polymers revealed that the backbone of PNBTz1 was more coplanar and/or locally ordered than POTz1 in the blend film. Reflecting the difference in the structural order of the polymers and Y6 between the blend films that used PNBTz1 and POTz1, the OPV cells based on the PNBTz1/Y6 blend showed PCEs as high as 14%, which was higher than that for the cells based on the PSTz1/Y6 and POTz1/Y6 blends (12%), in which the increased PCE was due to the enhanced $J_{SC}$ and FF. The results indicate that the extension of the π-electron system can improve the backbone order, even though there is steric hindrance that could cause backbone torsion, without significantly sacrificing the solubility, ultimately leading to the higher photovoltaic performance. We believe that this study would be a guideline for the design of π-conjugated polymers for efficient OPVs.
EXPERIMENTAL SECTION

Materials.

All chemicals were used as purchased. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (1) was purchased from Ossila Ltd. 2,6-Bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)benzo[1,2-d:4,5-d’]bis(thiazole) (2) was synthesized according to the published procedure.\(^{28}\) PSTz1 and POTz1 were synthesized according to the reported procedure.\(^{48}\)

Synthesis.

PNBTz1. To a reaction tube equipped with a stirring bar, 1 (45.3 mg, 0.05 mmol), 2 (42.5 mg, 0.05 mmol), Pd(PPh\(_3\))\(_4\) (1.1 mg, 0.001 mmol), and toluene (2 mL) were added. The tube was purged with argon and sealed, and then was heated at 200 °C for 2 hour in a microwave reactor (Biotage Initiator). After cooling to room temperature, the reaction solution was poured into 100 mL of methanol containing 5 mL of hydrochloric acid, and stirred for 5 hours. Then the precipitated solid was subjected to the sequential Soxhlet extraction with methanol, hexane, dichloromethane to remove low molecular weight fractions. The residue was then extracted with chloroform, and reprecipitated in 100 mL of methanol to yield dark red solids (51.0 mg, yield = 80%). Anal. Calcd for C\(_{74}\)H\(_{96}\)N\(_2\)S\(_8\): C, 69.98, H, 7.62, N, 2.21. Found: C, 68.14, H, 7.16, N, 2.22.

Supporting Information

Experimental procedures, \(^1\)H-NMR spectrum for PNBTz1, DSC curves, cyclic voltammograms, HOMO and LUMO geometries, solar cells data, TEM and AFM images, 2D GIXD patterns, hole- and electron-only devices data.

ACKNOWLEDGEMENTS

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REFERENCES


TOC graphic

High coplanarity
Low solubility
PCE = 12.1%

High coplanarity
High solubility
PCE = 12.0%

High coplanarity
High solubility
PCE = 14.0%