1. Introduction

Solution-processed organic photovoltaic (OPV) cells have drawn tremendous interest in the past decade, for the prospect of a renewable energy source due to their eminent advantages such as light weight, high material utilization, solution process (roll to roll, spin coating), low cost, and high mechanical flexibility.\[1–3\] The performance of OPV has increased dramatically recently and power conversion efficiency (PCE) up to 7% has been achieved by using low-bandgap polymers in the bulk heterojunction (BHJ) structure solar cells.\[4–27\] Two different strategies are usually employed in developing new low-bandgap polymers.

The first and most common one is the donor-acceptor (D-A) approach through intramolecular charge transfer,\[18–20\] the second and much less explored approach to obtain low bandgap is through the quinoidal resonance structure stabilization.\[21–23\] Representative quinoidal units with its aromatic form were presented in Figure 1. Recently, Yu and co-workers\[21, 24\] have developed a series of new semiconducting polymers with thieno[3,4-b]thiophene (TT) and benzodithiophene (BDT) alternating units, with PCE over 8%.\[4\] These TT-based polymers can support the quinoidal structure and lead to a narrow polymer bandgap, which is crucial to efficiently harvest solar energy.

Thieno[3,4-b]pyrazine (TP) is another quinoidal building block,\[25\] which would reduce the significant steric interactions between the pyrazine nitrogen and neighboring thiophene thus facilitates to get planar backbone geometry.\[26\] TPs have been shown to be very successful in producing low-bandgap conjugated materials. However, the best devices for TP-based materials to date utilizing the aryl-alkyne copolymer gave only a moderate PCE of 2.37%.\[27\] Partial reason for this could be that most of the reported TP materials have low molecular weight due to the limits of solubility for the introduction of nitrogen atoms, and the lowest unoccupied molecular orbital (LUMO) of these materials is difficult to tune for their intrinsic strong electron-deficient nature of the TP block.\[25\]
Benzo[1,3]diazole (BD) is one of the most widely used quinoidal acceptor units in low-bandgap polymers, which is the isoelectronic species of PT. The lone pair of nitrogen atom in BD would interact with the hydrogen atom in adjacent unit thus could minimize the steric hindrance. The most famous PCDTTT (poly[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl]-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl]) and PSBTTT (poly[4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole]-2,6-diyl-alt-[2,1,3-benzothiadiazole-4,7-diyl]) have reached PCE of 7.2% (26,17) and 5.9%. (29)

Another important quinoidal unit is isothianaphthene (ITN, or benzo[c]-thiophene), (30) which was proved to have higher quinoidal resonance energy than TT. However, this unit is proved to be very unstable. Hillmyer and co-workers (32,33) had synthesized three types ITN-containing copolymer with fluorene (PITN-co-FI), thiophene (PITN-co-3HT and PITN-co-3DT), and BT (PITN-co-ThBTD). However, these polymers have low molecular weight and poor absorption in the visible region, except that polymer PITN-co-ThBTD exhibits a large red shift from solution to film with edge to 800 nm. OPV devices based on this polymer with PC61BM (1:4, w:w) exhibited only a PCE of 0.9%, which is the highest PCE for ITN-based polymers. (33) The low PCE and poor absorption of PITN-co-FI are ascribed to the large dihedral angle between two adjacent units (40.50° based on our calculation results), electron-rich nature of ITN and low molecular weight.

The non-planar structure (26,34) low molecular weight (35–40) and poorer film quality (41) therefore low crystallinity perhaps are the critical reasons for the poor OPV performance of ITN-based materials today. Inspired by Yu’s pioneer work, herein, we introduced two electron-withdrawing ester groups onto ITN, expecting to stabilize the quinoidal unit for solving the synthesis issues and obtaining high polymerization degree products with good solubility and thus achieve good film qualities during the device fabrication process. The initial results confirmed our design, OPV devices based on PBDT-DEAItN and PBDT-DOAItN as donors and PC61BM as the acceptor exhibit PCE around 1.2% under an AM1.5G simulated solar light at 100 mW cm−2, which is the best results for ITN-based OPV devices. The reasons behind the low PCEs, compared with other polymers, of these two polymers are investigated and the large dihedral angles between BDT and ITN units in the polymers are believed to be one of the major causes.

2. Experimental Section

2.1. Instruments

The 1H NMR spectra were recorded on a Bruker AV400 Spectrometer. Gel permeation chromatography (GPC) analysis was conducted on a Waters 510 system using polystyrene as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL min−1 at 40 °C. Thermal gravimetric analysis (TGA) was performed on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a 10 °C min−1 heating rate. The temperature of degradation (Td) corresponds to a 5% weight loss. X-ray diffraction (XRD) experiments were performed on a Rigaku D/max-2500 X-ray diffractometer with Cu-Kα radiation (λ = 1.5406) at a generator voltage of 40 kV and a current of 100 mA. Atomic force microscope (AFM) was performed using SII SPA-400 AFM in tapping mode. The UV-Vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with an LK98B II microcomputer-based electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. CH3CN was distilled over calcium hydride under dry argon immediately prior to use. Tetrabutylammonium hexafluorophosphate (Bu4NPF6, 0.1 M) in CH3CN was used as the supporting electrolyte, and the scan rate was 100 mV s−1.

2.2. Materials

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification. 2,6-Bis(trimethylsilyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b]dithiophene (1), (42) diethyl 1,3-dibromobenzo[c]thiophene-5,6-dicarboxylate (2), and diocyl 1,3-dibromobenzo[c]thiophene-5,6-dicarboxylate (3) (43,44) were prepared according to the reported methods. As shown in Scheme 1, the low-bandgap polymers PBDT-DEAItN and PBDT-DOAItN were synthesized by Stille coupling polymerization of the monomers of 2 or 3 with 1 using tris(dibenzylideneacetone)dipalladium(0) (Pd2(dba)3) and tr(o-toly)phosphine (P(o-toly)) as the catalyst in yields around 90%.
2.3. Polymer Synthesis

2.3.1. PBDT-DEAITN

Diethyl 1,3-dibromobenzene[c]thiophene-5,6-dicarboxylate (350 mg, 0.80 mmol), 2,6-bis(trimethylsilyl)-4,8-bis(2-ethylhexyl)benzene[1,2-b:4,5-b]dithiophene (621 mg, 0.80 mmol), and P(o-toly), (26.3 mg, 0.064 mmol) were dissolved in 10 mL dry chlorobenzene. The mixture was purged by argon, then bubbled with argon for 20 min. Pd(2dba)3 (15 mg, 0.016 mmol) was added. After being purged with argon, the mixture was refluxed at 110 °C for 24 h. After cooling to room temperature, the organic solution was added dropwise to 250 mL methanol to obtain precipitate, which was collected by filtration and washed with methanol and dried. Then the precipitate was subjected to Soxhlet extraction with methanol, hexane, and chloroform, respectively. The chloroform fraction was concentrated and obtained by precipitation from methanol. Then the residue was dried under vacuum and afforded a black solid powder. Yield: 523.4 mg, 90.3%, $\bar{M}_n = 27.54$ KDa, PDI = 2.14. $^1$H NMR (400M, CDCl3, $\delta$): 8.56 (m, 1H), 8.29 (m, 1H), 7.82 (m, 1H), 7.48 (m, 1H), 4.44 (br, 4H), 4.31 (br, 4H), 1.91–1.46 (m, 24H), 1.10 (m, 12H) ppm.

2.3.2. PBDT-DOAITN

The synthesis procedure was similar with that of PBDT-DEAITN except replacement of monomer diethyl 1,3-dibromobenzene[c]thiophene-5,6-dicarboxylate (2) with diotyl 1,3-dibromobenzene[c]thiophene-5,6-dicarboxylate (3). The polymer was obtained with yield of 90.9%, $\bar{M}_n = 16.74$ KDa, PDI = 2.38. $^1$H NMR (400M, CDCl3, $\delta$): 8.57 (m, 1H), 8.35 (m, 1H), 7.82 (m, 1H), 7.71 (m, 1H), 4.30 (br, 8H), 1.92–1.26 (m, 36H), 1.10–0.80 (m, 24H) ppm.

2.4. Polymer Solar Cell Fabrication and Testing

All the photovoltaic devices were fabricated by using a common solution process. An ITO-coated glass substrate was cleaned stepwise in detergent, distilled water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and subsequently dried by a nitrogen blow. A thin layer of PEDOT:PSS (Baytron P VP Al 4083, filtered at 0.45 μm) was spin-coated (4000 rpm, ca. 40 nm thick) onto ITO surface. After being baked at 150 °C for 20 min, the substrates were transferred into an argon-filled glove box. Subsequently, the active layer was spin-coated from different blend ratios (weight-to-weight) of donor and PC61BM in o-dichlorobenzene (ODCB) solution at 1500 rpm for 60 s on the ITO/PEDOT:PSS substrate without further special treatments. The active layer thickness was measured as ca. 80 nm using a Dektak 150 profilometer. Finally, 1 nm LiF layer and 80 nm Al layer were deposited on the active layer under high vacuum (<3 × 10⁻⁸ Pa). The effective area of each cell was 4 mm² defined by masks for all the solar cell devices discussed in this work.

2.5. Hole Mobility

Hole mobility was measured using a diode configuration of ITO/PEDOT:PSS/Polymer/Al by taking dark current in the range of 0–6 V and fitting the results to a space charge limited form, where the space charge limited current (SCLC) is described by:

$$J = \frac{9}{8} \frac{I C}{V_{bi} - V_{bi}} = kV_{appl} - kC$$

where $J$ is the current density, $V_{appl}$ is the applied voltage to the device, and $V = V_{appl} - V_{bi} - V_r$, where $V_{appl}$ is the applied voltage to the device, $V_{bi}$ is the voltage drop as a result of contact resistance and series resistance across the electrodes, and $V_r$ is the built-in voltage attributed to the relative work function difference of the two electrodes.

3. Results and Discussion

3.1. Polymer Synthesis and Characterization

The synthesis is outlined in Scheme 1, both PBDT-DEAITN and PBDT-DOAITN have readily good solubility in common organic solvents such as chloroform, chlorobenzene, and ODCB owing to the existence of four alkyl chains in each repeat unit. As shown in Table 1, the number-averaged molecular weight ($\bar{M}_n$) and polydispersity (PDI) were...
Isothianaphthene-Based Conjugated Polymers for Organic Photovoltaic Cells

The absorption spectra of PBDT-DEAITN and PBDT-DOAITN in dilute chloroform solution and in the solid state were shown in Figure 2 and summarized in Table 2. Both PBDT-DEAITN and PBDT-DOAITN exhibited two bands in the solution and solid state. The peaks at the shorter wavelength corresponding to the π–π* absorption of the two polymers nearly have no difference with maximum absorption peaks at 389 nm for solution and 403 nm for the solid. While PBDT-DEAITN showed less red shift compared with PBDT-DOAITN in both solution and film state at longer wavelength. Both polymers showed about 60 nm red-shift from solution to film, which were 56 nm (from 557 to 622 nm) for PBDT-DEAITN and 65 nm (from 557 to 622 nm) for PBDT-DOAITN. The optical bandgap of PBDT-DEAITN and PBDT-DOAITN in film state is comparable, which was estimated to be 1.52 and 1.58 eV by extrapolation of the low-energy edge of the absorption spectra.

Table 2. Optical and electrochemical data of PBDT-DEAITN and PBDT-DOAITN.

<table>
<thead>
<tr>
<th></th>
<th>UV –Visabsorption</th>
<th>Cyclic voltammetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_max [nm]</td>
<td>λ_max [nm]</td>
</tr>
<tr>
<td>PBDT-DEAITN</td>
<td>570</td>
<td>626</td>
</tr>
<tr>
<td>PBDT-DOAITN</td>
<td>557</td>
<td>622</td>
</tr>
</tbody>
</table>

Cyclic voltammograms (CVs) were recorded from thin films of PBDT-DEAITN and PBDT-DOAITN drop-casted from chloroform solutions as described in the Section 2. Figure 3 displays the CV curves for these two polymers, and the potentials were internally calibrated using the ferrocene/ferrocenium (Fc/Fc+) redox couple (4.8 eV below the vacuum level). From the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) of the polymers, HOMO and LUMO energy levels of the polymers were calculated according to the equations: HOMO = -e(E_{ox} + 4.8) (eV) and LUMO = -e(E_{red} + 4.8) (eV). The results of the electrochemical measurements are listed in Table 2, these two polymers exhibit deeper HOMO energy levels compared with reported ITN analogues, which are beneficial to achieve high V_{oc}. The HOMO level of PBDT-DEAITN (~5.42 eV) is 0.12 eV lower than that of PBDT-DOAITN (~5.30 eV), probably due to longer alkyl side chains, which would weaken the π-overlapping among individual conjugated polymer chains and therefore result in weaker intermolecular interaction. Based on the calculation structures of PBDT-DEAITN and PBDT-DOAITN discussed below, the two alkyl groups of ITN units tend to minimize the steric hindrance through arranging the two alkyl groups onto the different side of ITN plane (as shown in Scheme 1). The electrochemical bandgap of both polymers is somewhat larger than its optical bandgap, similar phenomena have been observed in the studies of other D-A

Figure 2. UV–Vis spectra of all polymers: PBDT-DEAITN, PBDT-DOAITN in chloroform and in solid film.

Figure 3. Cyclic voltammograms of the oxidation and reduction behavior of thin films of PBDT-DEAITN and PBDT-DOAITN.
for PBDT-DEAITN and PBDT-DOAITN, the electron density of LUMO is more localized on the ITN unit, which means that the introduction of electron-withdrawing groups onto ITN units has changed their electron-rich nature to electron-deficient. Meanwhile, the electron density of HOMO of these two polymers is delocalized over the whole conjugated backbone, and different alkyl groups have little effect on the electron-density distribution of frontier molecular orbital.

The dihedral angles between BDT and ITN units for PBDT-DEAITN and PBDT-DOAITN were 33.66° and 34.35°, which is obviously larger than other quinoidal-based polymers (19.01° for PBDTTT-CF, and only 0.82° for PBDT-TP[42]). The significantly larger dihedral angle of PBDT-DEAITN and PBDT-DOAITN is owing to the repulsion between sulfur atom (BDT) and hydrogen atom on the phenyl ring (ITN),[26,34] and this causes the polymer packing less ordered in solid state with low hole mobility, thus poor OPV performance. Recent experiment and theoretical results showed that large local dipole moment existing in one of the monomer units in the donor polymers plays an important role in charge separation and carrier generation, thus would facilitate to obtain high PCE.[56,57] As shown in Table 3, among all these polymers, PBDTTT-CF has the largest dipole moment and hole mobility, therefore the best OPV performance.

### 3.4. Photovoltaic Properties

The photovoltaic properties of PBDT-DEAITN and PBDT-DOAITN were explored based on BHJ devices with the standard sandwich structure ITO/PEDOT:PSS(40 nm)/polymer:PC 61 BM/LiF(1 nm)/Al(80 nm) using the simple solution process from their ODCB solutions. All OPV polymers,[42,49–51] presumably resulting from the interface barrier for charge injection.[42,52]

#### 3.3. Computational Study

Computational studies were employed to investigate the intrinsic properties and differences of PBDT-DEAITN, PBDT-DOAITN, and other representative quinoidal polymers (structures were shown in Figure S8, Supporting Information). To simplify the calculation, only one repeating unit of each polymer was subject to the calculation. All of the density functional theory calculations without special mention were performed with the Gaussian 09 program package[53] with the B3LYP function[54,55] and a 6–31g(d) basis set, and the frequency analysis was followed to assure that the optimized structures were stable states. The optimized geometry and simulated electron-density distributions were shown in Figure 4 and Supporting Information, and the calculated HOMO and LUMO levels are listed in Table 3. Compared with PBDT-ITN, PBDT-DEAITN, and PBDT-DOAITN, which have electron-withdrawing groups onto the ITN unit, the calculated HOMO levels of PBDT-ITN shifts from −4.84 to −5.03 eV, therefore increase the stability of ITN-based materials. As shown in Figure 4, theoretical results showed that large local dipole moment existing in one of the monomer units in the donor polymers plays an important role in charge separation and carrier generation, thus would facilitate to obtain high PCE.[56,57] As shown in Table 3, among all these polymers, PBDTTT-CF has the largest dipole moment and hole mobility, therefore the best OPV performance.

#### Table 3. Calculated results and measured mobility of representative quinoidal polymers.

<table>
<thead>
<tr>
<th></th>
<th>Dihedral [°]</th>
<th>Dipole [D]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>Mobility [cm² V⁻¹ s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT-DEAITN</td>
<td>33.66</td>
<td>0.81</td>
<td>−5.04</td>
<td>−2.15</td>
<td>2.36 × 10⁻⁵</td>
</tr>
<tr>
<td>PBDT-DOAITN</td>
<td>34.35</td>
<td>0.50</td>
<td>−5.03</td>
<td>−2.13</td>
<td>2.86 × 10⁻⁵</td>
</tr>
<tr>
<td>PBDT-ITN</td>
<td>35.89</td>
<td>0.45</td>
<td>−4.84</td>
<td>−1.74</td>
<td>None</td>
</tr>
<tr>
<td>PBDT-TP</td>
<td>0.82</td>
<td>0.03</td>
<td>−4.92</td>
<td>−2.43</td>
<td>None</td>
</tr>
<tr>
<td>PBDTTT-CF</td>
<td>19.01</td>
<td>3.11</td>
<td>−5.06</td>
<td>−2.09</td>
<td>7 × 10⁻⁴</td>
</tr>
</tbody>
</table>

*The mobilities were from SCLC results.*

![Figure 4. Optimized geometry and HOMO, LUMO electron-density distributions of PBDT-DEAITN (a) and PBDT-DOAITN (b).](image-url)
devices were tested under simulated AM1.5G illumination (100 mW cm\(^{-2}\)). Device optimizations were conducted by varying ratios of polymer versus PC\(_{61}\)BM, and film thicknesses. Typical current density-voltage (J–V) characteristics were shown in Figure 5 and summarized in Table 4. The optimized PCEs were 1.25% and 1.20% for PBDT-DEAITN and PBDT-DOAITN, respectively. Both polymers showed very low fill factor (FF) around 0.30, probably due to the low charge mobility. The hole mobility for PBDT-DEAITN and PBDT-DOAITN was 2.36 \times 10^{-5} and 2.86 \times 10^{-5} cm\(^2\) V\(^{-1}\) s\(^{-1}\) based on SCLC results.\(^{58,59}\) Both PBDT-DEAITN and PBDT-DOAITN films showed no clear peak in their XRD analysis (Figure S4, Supporting Information) and thus they exist as amorphous material in solid state. This is probably owing to the large dihedral between the adjacent units as calculated above, which is consistent with the measured low mobility. OPV devices based on PBDT-DOAITN showed larger \(V_{oc}\) than PBDT-DEAITN, which is in agreement with the CV data. Recent theoretical and experiment results showed that reducing the electronic coupling between the donors and acceptors will suppress the charge-transfer band oscillator strength and reduce dark saturation current, and thus increase \(V_{oc}\).\(^{60,61}\) Therefore, longer side chains such as the two octyl chains of PBDT-DOAITN would weaken the intermolecular interaction, which is beneficial to get higher \(V_{oc}\) for PBDT-DOAITN than PBDT-DEAITN.\(^{48}\)

In order to understand the effect of morphology of the active layers on their OPV device performance of these polymers, the surface morphology of blend film (w:w, 1:1.5) of PBDT-DEAITN or PBDT-DOAITN with PC\(_{61}\)BM spin-coated from ODCB solutions was studied by tapping-mode AFM, and the topography and phase images are shown in Figure S2 (Supporting Information). The root mean square (rms) roughness of blend films is 0.58 nm for PBDT-DEAITN/PC\(_{61}\)BM and 0.36 nm for PBDT-DOAITN/PC\(_{61}\)BM with the blend ratio of 1:1.5, indicating different miscibility between the copolymers and PC\(_{61}\)BM. In consistent with the XRD data above, the films of these two polymers did not show clear crystalline morphology from AFM images. This is in contrast to P3HT\(^{62,63}\) and other low-bandgap polymers with excellent charge mobilities.\(^{5,11,24,64-66}\) All these probably contributed to the low hole mobilities, short circuit currents (\(J_{sc}\)) and thus poor OPV performance for PBDT-DEAITN and PBDT-DOAITN.

### 4. Conclusion

In summary, two quinoidal copolymers PBDT-DEAITN and PBDT-DOAITN were successfully synthesized with high yields and characterized, these two polymers exhibited rather low optical bandgaps, number-averaged molecular weight

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**Table 4. OPV performances of PBDT-DEAITN and PBDT-DOAITN.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polymer:PC(_{61})BM</th>
<th>(V_{oc}) [V]</th>
<th>(J_{sc}) [mA cm(^{-2})]</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBDT-DEAITN</td>
<td>1:2</td>
<td>0.64</td>
<td>3.94</td>
<td>0.33</td>
<td>0.83</td>
</tr>
<tr>
<td>PBDT-DEAITN</td>
<td>1:3</td>
<td>0.62</td>
<td>4.19</td>
<td>0.34</td>
<td>0.88</td>
</tr>
<tr>
<td>PBDT-DEAITN</td>
<td>1:1.5</td>
<td>0.64</td>
<td>5.90</td>
<td>0.33</td>
<td>1.25</td>
</tr>
<tr>
<td>PBDT-DOAITN</td>
<td>1:2</td>
<td>0.72</td>
<td>3.97</td>
<td>0.26</td>
<td>0.74</td>
</tr>
<tr>
<td>PBDT-DOAITN</td>
<td>1:3</td>
<td>0.72</td>
<td>4.46</td>
<td>0.26</td>
<td>0.83</td>
</tr>
<tr>
<td>PBDT-DOAITN</td>
<td>1:1.5</td>
<td>0.78</td>
<td>4.65</td>
<td>0.33</td>
<td>1.20</td>
</tr>
</tbody>
</table>
more than 10 kDa and better film quality compared with other ITN-based polymers reported in literatures. Polymer solar cells based on these two polymers as donors and PCBM as the acceptor exhibit PCEs around 1.2%, which is the best performance for ITN-based OPV devices. The differences among the representative quinoidal polymers were discussed on the basis of theoretical calculations, which demonstrates that small dihedral angle between the adjacent units would result in a planar conjugated backbone, leading to low bandgap and high mobility, therefore better PCE. Future work should be focus on synthesizing planar polymers based on ITN units.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords: DFT calculations; dihedral; isothianaphthene; organic photovoltaics; quinoidal polymers


Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010, see supporting information for full citation.