Abstract: Compared with the dominant aromatic conjugated materials, photovoltaic applications of their quinoidal counterparts featuring rigid and planar molecular structures have long been unexplored despite their narrow optical bandgaps, large absorption coefficients, and excellent charge-transport properties. The design and synthesis of dithienoindophenine derivatives (DTIPs) by stabilizing the quinoidal resonance of the parent indophenine framework is reported here. Compared with the bipolar indophenine derivatives, DTIPs with the fixed molecular configuration are found to be p-type semiconductors exhibiting excellent unipolar hole mobilities up to 0.22 cm²V⁻¹s⁻¹, which is one order of magnitude higher than that of the parent IP-O and is even comparable to that of QQT(CN)₄-based single-crystal field-effect transistors (FET). DTIPs exhibit better photovoltaic performance than their aromatic bithieno[3,4-b]thiophene (BTI) counterparts with an optimal power-conversion efficiency (PCE) of 4.07%.

Organic photovoltaics (OPVs) has been developed into a promising photo-electric conversion technique in terms of its potential advantages of low cost, large area manufacture, and flexibility. To maximize sunlight utilization, a variety of donor materials with low optical bandgaps have been designed by the “donor–acceptor” (D–A) approach, most of which are based on the aromatic frameworks. Surprisingly, donor materials with purely quinoidal frameworks have rarely been reported to date, with low PCEs of ≤1.1%. Generally, quinoidal oligothiophenes (QOT) with rigid and planar Kekulé structures show unique optoelectronic properties such as narrow optical bandgaps with large absorption coefficients, singlet-fission property, near-infrared fluorescence, and excellent charge-transport properties, which are highly desirable for OPV applications. However, the most well-known dicyanomethylene-terminated QOTs such as quinoidal bithiophene (QBT) are typically n-type semiconductors because of their high electron affinities. Indophenine derivatives (QBT with 1-alkylindolin-2-one terminals) known for over one century have recently been found to show promising ambipolar properties (Figure 1). To demonstrate the potential of QOTs for OPV applications, p-type QOTs with suitable HOMO and LUMO energy levels should be developed preferentially to match [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) acceptors.

Figure 1. n-Type, ambipolar, and p-type quinoidal bithiophenes: QBT (n-type), IP-O (ambipolar), DTIP-i-O (p-type; R¹: n-dodecyl; R²: n-octyl).

Thieno[3,4-b]thiophene (Tbt) can efficiently reduce optical bandgaps by enhancing quinoidal resonance of aromatic conjugated systems, that is, destabilization of aromatic resonance. Thus, we envisioned that Tbt may also elevate the LUMO energy level of indophene derivatives by stabilizing the quinoidal resonance. With the introduction of Tbt into the indophenine framework, we designed and synthesized dithienoindophenine derivatives, DTIP-i-O and DTIP-o-O, with proximal and distal sulfur orientations (Figure 1). DTIPs inherit the advantages of QOTs, and meanwhile are endowed with new characteristics such as stable E-configuration, large π-surface, and intermolecular S–S interaction that especially benefits hole transport. Compared with the parent N-octylindophene (IP-O), the frontier orbital energies of DTIPs increased slightly for HOMO and considerably for LUMO, indicating that the aromatization tendency of the QBT framework are restrained. According to OTFT (organic thin-film transistor) measurements, we found that DTIPs are p-type semiconductors with hole mobility...
of 0.22 cm$^2$V$^{-1}$s$^{-1}$, which is higher than that of parent IP-O by one order of magnitude. Furthermore, DTIPs were successfully employed as donor materials in bulk heterojunction (BHJ) solar cells and delivered decent power conversion efficiency (PCE) of 4.07%, which is much higher than their aromatic counterparts, BTTs, and should not be underestimated if we consider the low PCEs obtained at the similarly early stage of small-molecule solar cells utilizing aromatic donor materials.$^{[13]}$

Instead of the traditional ‘indophenine reaction’,$^{[10]}$ the new synthetic route was utilized for the synthesis of isomeric DTIPs because of the unsymmetrical Tbt (Scheme 1). Bithieno[3,4-b]thiophene and tributyl(2-octylthieno[3,4-b]thiophenes, compound 2, were then synthesized from bithieno[3,4-b]thiophene/4-iodo-2-octylisatin, which was synthesized using a similar procedure. The stereochemistry of dialkylated indophenine was clarified by Tormos et al. in 2016.$^{[8]}$ The hydrogens at 3-position of DTIP-o and compound 2 were then synthesized from bithieno[3,4-b]thiophene and tributyl(2-octylthieno[3,4-b]thiophen-6-yl)-stannane/stribyl(2-octylthieno[3,4-b]thiophen-4-yl)-stannane in 60 and 85% yields, respectively.$^{[11]}$ Diols, compound 2 and compound 2', were then synthesized from bithieno[3,4-b]thiophenes by deprotonation and selective nucleophilic reaction with N-octylisatin in 70 and 80% yields, respectively. Finally, diols were reduced using SnCl$_4$ to give DTIP-i-O and DTIP-o-O in 40 and 80% yields as blue solids. For comparison, IP-O was synthesized using a similar procedure. The stereochemistry of diallylated indophenine was clarified by Tormos et al. in 1996.$^{[14]}$ which revealed the existence of up to six stereoisomers. In contrast to IP-O, dithienoindophenines show well-defined $^1$H NMR spectra, revealing the absence of any isomer. In Figure 2, all hydrogens in the aromatic region of IP and DTIPs are assigned. The hydrogens at 3-position of DTIP-i-O were significantly more downfield-shifted than those of DTIP-o-O, (δ: 8.76 vs. 7.39 ppm), which points the intramolecular O–H interaction and confirms the explicit configurations, as shown in Scheme 1. It has been previously assumed that the isomeric phenomenon might not affect the device performance; however, we believe that the configurationally fixed DTIPs may avoid the energetic and morphology disorders, which is favorable for enhancing device performance. In addition, the aromatic counterparts, BTT-i-O and BTT-o-O, were synthesized by the Knoevenagel condensation between dialdehyde intermediates and 1-octylindolin-2-one as blue solids.

The photophysical and electrochemical properties of DTIPs, IP-O, and BTTs were examined in dichloromethane and are summarized in Table 1. DTIPs show structured absorption spectra with maximum absorptions at 665 nm (DTIP-i-O) and 639 nm (DTIP-o-O) that are similar to that of IP-O (634 nm; see Figure 3a) with comparable absorption coefficients and are consistent with only the E-configuration. In thin films, the maximum absorptions of DTIPs are hypsochromically shifted by 49 and 39 nm, respectively. Meanwhile, a new shoulder peak (707 and 696 nm) was observed at the long-wavelength side, which suggests the possibility of coexistence of H- and J- packing patterns. Based on the absorption onsets in thin films, the op-
tical bandgaps of DTIPs were estimated to be 1.56 and 1.65 eV, respectively. The electrochemical properties of DTIPs were examined by cyclic voltammogram (Figure S2 in the Supporting Information). DTIPs show reversible or quasi-reversible oxidative and reductive processes, according to which the HOMO and LUMO energy levels were determined to be $5.10/3.58$ eV for DTIP-$i$-O and $5.13/3.49$ eV for DTIP-$o$-O. Compared with IP-$O$ ($5.16/3.70$ eV), DTIPs show slightly elevated HOMO and considerably elevated LUMOs. The LUMOs of DTIPs match the PCBM acceptor better than that of IP-$O$ in BHJ solar cells.

BTTs show structured absorption spectra with maximum absorptions at 659 nm (BTT-$i$-O) and 661 nm (BTT-$o$-O) with comparable absorption coefficients. In thin films (Figure 3b), the maximum absorption of BTT-$i$-O is bathochromically shifted by 30 nm, whereas that of BTT-$o$-O is hypsochromically shifted by 34 nm, which implies $J$-aggregation for BTT-$i$-O film and main $H$-aggregation in BTT-$o$-O film. Accordingly, the optical bandgaps of BTTs were estimated to be 1.69 (BTT-$i$-O) and 1.57 eV (BTT-$o$-O), respectively, which shows the opposite tendency to DTIPs based on sulfur orientations. In addition, BTTs show obviously higher HOMO and LUMO energy levels, $-4.97/3.38$ eV for BTT-$i$-O and $-5.01/3.39$ eV for BTT-$o$-O than those of DTIPs, implying the effectiveness of lowering HOMO and LUMO energy levels with quinoidal cores.

The potential of DTIPs as p-type semiconductors was investigated by bottom-gate bottom-contact (BGBC) OTFT (organic thin-film transistor) devices that were fabricated on octadecyltrichlorosilane (OTS)-modified SiO$_2$ (300 nm)/Si substrates. Thin films were spin-coated as the organic semiconductor layer and 30 nm gold served as the source-drain electrodes. The optimized thin films were obtained by annealing at 120 °C. Figure 4 shows the $I-V$ characteristics of the best DTIP-based OTFTs. In accordance with the alignment of frontier orbital energy levels, DTIP-based OTFT devices showed p-type transport property with negligible n-type behavior. Devices based on DTIP-$i$-O showed higher hole mobilities ($\mu_{h,m} = 0.15 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $V_{th} = 3.1 \text{ V}$, $I_{on}/I_{off} = 10^5$) than those of DTIP-$o$-O ($\mu_{h,m} = 0.055 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $V_{th} = 6.3 \text{ V}$, $I_{on}/I_{off} = 10^4$; see Table S2 in the Supporting Information). A maximum mobility of $0.22 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was obtained at 120 °C for DTIP-$i$-O, which is nearly one order of magnitude higher than that of ambipolar IP ($\mu_{h,m} = 0.031 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) and is comparable to that of single-crystal FETs based on QQT(CN)$_4$.[15] From AFM (atomic force microscopy) investigations (Figure S3 in the Supporting Information), we found that DTIP-$i$-O can form better continuous thin films with less defects than DTIP-$o$-O. In DTIP-$i$-O, there are intramolecular O-H hydrogen bonds, suggesting the enhanced rigidity of DTIP-$i$-O compared with DTIP-$o$-O. Accordingly, we observed that DTIP-$i$-O possessed better crystallinity than DTIP-$o$-O according to the thin-film X-ray diffraction images (Figure S4 in the Supporting Information), which may also have contributed to its higher hole mobility. In addition, the hole-transport properties of BTTs have also been examined, $0.014$ and $0.036 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for BTT-$i$-O and BTT-$o$-O, respectively, which is significantly lower than those of the corresponding quinoidal counterparts.
To investigate the potential of DTIPs for photovoltaic applications, solution-processed BHJ solar cell devices were fabricated with a conventional configuration of ITO/PEDOT:PSS/active layer/PFN[Ti]/Al. Table 2 and Figure 5 summarize the optimal photovoltaic parameters for such devices, all of which were tested under AM 1.5 G, 100 mW cm\(^{-2}\) simulated illumination. Comparatively, the DTIP-o-O device shows a higher \(V_{oc}\) (0.92 eV) than that of the DTIP-i-O device (0.86 eV), which relates with the former donor’s relatively deeper HOMO. Meanwhile, the DTIP-o-O device also obtained a larger \(J_{sc}\) than that of the DTIP-i-O, which can be attributed to its better phase separation. In the DTIP-o-O:PC\(_{70}\)BM blend, smaller aggregates were observed using atomic force microscopy (AFM), as shown in Figure S5 (see the Supporting Information), which favors the charge separation and transport. DTIP-o-O device displays a superior PCE (4.07\%) to that of DTIP-i-O device (3.41\%), whereas devices based on BTTs both show low optimal PCEs, 2.47\% (BTT-i-O) and 1.00\% (BTT-o-O).

In summary, dithienoindophenine derivatives DTIPs with fixed molecular configuration were designed and synthesized together with the reference aromatic BTTs. DTIPs exhibited excellent unipolar hole mobility up to 0.22 cm\(^2\)V\(^{-1}\)s\(^{-1}\), which is one order of magnitude higher than that of the parent IP-O and is even comparable to that of single-crystal FETs based on QQT(CN)\(_4\). DTIP-based solar cells delivered a decent PCE of 4.07\%, which is significantly higher than those of aromatic BTT counterparts. From this study on DTIPs, we believe that OPV applications of quinoidal semiconductors should be investigated further.

### Experimental Section

**DTIP-o-O**: 2,2'–Dioctyl-4,4'-bithieno[3,4-b]thiophene (0.27 g, 0.53 mmol) was dissolved in anhydrous THF (20 mL) under a nitrogen atmosphere and cooled to –35 °C. After \(N,N,N,N\)-tetramethyl-

<table>
<thead>
<tr>
<th>Cpd.(^{[a]})</th>
<th>(V_{oc}) [V]</th>
<th>(J_{sc}) [mA cm(^{-2})]</th>
<th>FF [%]</th>
<th>PCE (average) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTIP-i-O</td>
<td>0.86</td>
<td>6.99</td>
<td>56.70</td>
<td>3.41 (3.35)</td>
</tr>
<tr>
<td>DTIP-o-O</td>
<td>0.92</td>
<td>7.97</td>
<td>55.66</td>
<td>4.07 (4.05)</td>
</tr>
<tr>
<td>BTT-i-O</td>
<td>0.73</td>
<td>6.82</td>
<td>49.52</td>
<td>2.47 (2.23)</td>
</tr>
<tr>
<td>BTT-o-O</td>
<td>0.54</td>
<td>3.76</td>
<td>48.69</td>
<td>1.00 (0.95)</td>
</tr>
</tbody>
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\(^{[a]}\) Structure of ITO:PEDOT:PSS/donors:PC\(_{70}\)BM (weight ratio: 1:0.5)/PFN/Al.

**Figure 5.** Characteristic \(J-V\) curves (a) and EQE curves (b) of the optimized solar cell devices based on DTIPs and BTTs.
C_{60}H_{78}N_{2}O_{2}S_{4}: C 72.97, H 7.96, N 2.84; found: C 72.00, H 7.99, N 2.84.

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