Supporting Information

Fine-Tuning Device Performances of Small Molecule Solar Cells via the More Polarized DPP-Armed Donor Units

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1. Experimental section

1.1. Materials

PC$_{61}$BM was purchased from American Dye Source (ADS) Inc. All other reagents and chemicals were purchased from commercial sources (TCI, Acros, Sigma, or Alfa) and used without further purification except statements. Solvents (toluene and tetrahydrofuran) were distilled by standard procedures before used.

1.2. Instruments, methods and measurements

$^1$H NMR and $^{13}$C NMR spectrums were recorded by a Bruker DMX-400 spectrometer with CDCl$_3$ as a solvent and tetramethylsilane as an internal reference. MALDI-TOF mass spectra were recorded by a Bruker BIFLEXIII. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The pristine films on quartz plate used for the UV measurements were prepared by spin-coating a 1 mg/mL chloroform solution of the samples. To compare with the EQE characteristics of the best devices, the blending films used for absorption spectrum measurements were prepared on ITO/PEDOT: PSS substrate under the same conditions (e.g. donor/acceptor ratio, spin-coating speed, solvent) to the preparation of photovoltaic devices that afford the best performances. The electrochemical cyclic voltammetry (CV) was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) dichloromethane (DCM) solution with a scan speed at 0.1 V/s. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The concentration of DPPT, DPPSe and DPPTT is adjusted as 1 mg/mL in chromatographic pure DCM solution) for the measurements cyclic voltammetry (CV). XRD samples were prepared under the same conditions to the preparation of photovoltaic active-layers (e.g. donor/acceptor ratio, spin-coating speed, solvent) that afford the best performances with silica as substrates. The film thickness was measured as about 150 nm. Atom force microscopy (AFM) was investigated by SPI 3800N using tapping-mode with a scan speed of 1Hz.

1.3. Fabrication and characterizations of OSCs

OSCs with a typical configuration of ITO/PEDOT: PSS/DPPT (DPPSe or DPPTT): PC$_{61}$BM/Ca/Al was fabricated as follows. The ITO glass was pre-cleaned with deionized water, CMOS grade acetone and isopropanol in turn for 15 min. The organic residues were further removed by treating
with UV-ozone for 1 h. Then the ITO glass was modified by spin-coating PEDOT: PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) layer, 45 nm) on it. After the ITO glasses were dried in oven at 150°C for 15 min, the active layer was spin-coated on the ITO/PEDOT:PSS using a blend solution of 
DPPT, DPPSe and DPPTT, respectively, and PC_{61}BM (40 mg/mL in o-
dichlorobenzene (o-CB) for DPPT and DPPSe and CHCl_{3} for DPPTT, variants with donor/acceptor weight ratio of 1:2, 1:1, 2:1, 3:1 and 4:1, respectively). Ca (12 nm) and Al (120 nm) electrode was then subsequently thermally evaporated on the active layer under the vacuum of 1×10^{-6} Torr. The active area of the device was 0.04 cm^2, and the thickness of the active films were in the range of 70~200 nm. The devices were characterized in nitrogen atmosphere under the illumination of simulated AM 1.5 G, 100 mW/cm^2 using a xenon-lamp-based solar simulator. The current-voltage (I-V) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. The IPCE measurements of the encapsulated devices were performed in air (PV Measurements Inc., Model QEX7).

1.4. Tests of the hole mobilities of the small molecule and PC61BM blending films

The devices were fabricated with configuration of ITO/PEDOT:PSS/small molecule: PC_{61}BM/Au with the donor/acceptor ratio of 3:1 (DPPT:PC_{61}BM), 3:1 (DPPSe:PC_{61}BM), and 2:1 (DPPTT:PC_{61}BM). The active layers were spin-coated under the conditions that afford the best photovoltaic results. The following equation was applied to estimate the hole mobilities:\footnote{1, 2} \[ \ln(JL^3/V^2) = 0.89(J/E_0)^{0.5}(V/L)^{0.5} + \ln(9\varepsilon\varepsilon_0\mu_0/8), \] where \( \varepsilon \) is the dielectric constant of the polymer, \( \varepsilon_0 \) the permittivity of the vacuum, \( \mu_0 \) the zero-field mobility, \( E_0 \) the characteristic field, \( J \) the current density, \( L \) the thickness of the films, and \( V = V_{\text{appl}}-V_{\text{bi}} \); \( V_{\text{appl}} \) is the applied potential, and \( V_{\text{bi}} \) the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, \( V_{\text{bi}} = 0.2 \) V). The \( \ln(JL^3/V^2) \) vs \( (V/L)^{0.5} \) plots of the small molecules based on SCLC method are shown in Figure 3. The hole mobility of the blending films were deduced from the intercept value \( \ln(9\varepsilon\varepsilon_0\mu_0/8) \). Herein \( \varepsilon = 3 \), \( \varepsilon_0 \) is 8.85419×10^{-12} CV^{-1}m^{-1}. 

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2. Synthesis

Scheme S1 The synthetic routes toward the DPP-based small molecules.

2.1 Synthesis of protocols

The synthetic routes towards DPPT, DPPSe, and DPPTT are showed in Scheme S1.

**Trimethyl(5-octylthieno[3,2-b]thiophen-2-yl)stannane (2):** 2-octylthiophene (1, 400 mg, 2 mmol) and 10 ml anhydrous tetrahydrofuran (THF) were put into to a flask tube in nitrogen atmosphere and cooled down to −78°C. Subsequently, butyllithium (1 ml, 2.2 M in hexane) was added to the flask tube dropwise. After stirred at −78 °C for 30 min, trimethyltin chloride (2.2 ml, 1 M in hexane) was added in one portion. And then the reaction was stirred at room temperature for another 2 h and then was poured into water and extracted by diethyl ether twice. After being dried by anhydrous magnesium sulfate (MgSO₄) and removing the solvent, the product of 2 was used in the next step without any further purification.

**1-(Selenophen-2-yl)octan-1-one (4):** Aluminum chloride (AlCl₃, 400 mg, 3 mmol) was added to a solution of selenophene (3, 262 mg, 2 mmol) in anhydrous DCM. The solution was stirred at room
temperature for 1 h, then cooled to 0 °C. Octanoyl chloride (358 mg, 2.2 mmol) was carefully added to the solution for 10 min. After the addition was completed, the mixture was stirred at room temperature for another 2 h. Water was added to the reaction solution to quench the reaction and then the solution was extracted with DCM. The organic phase was dried with anhydrous MgSO₄ and solvent was removed under vacuum. The crude residue was purified by silica gel chromatography (petroleum ether) to yield 4 (340 mg, 1.3 mmol, 65%). $^1$H NMR (400 MHz, CDCl₃): 8.35(d, 1H, $J=5.32$Hz), 7.91(d, 1H, $J=3.28$ Hz), 7.38(t, 1H, $J=4.44$ Hz), 2.90(t, 2H, $J=7.4$ Hz), 1.74(m, 2H), 1.28–1.34(m, 8H), 0.87(m, 3H). $^{13}$C NMR (100 MHz, CDCl₃): 194.2, 151.6, 139.5, 134.0, 130.7, 38.8, 31.7, 29.3, 29.1, 25.0, 22.6, 14.1.

2-Octylselenophene (5): AlCl₃(400 mg, 3 mmol) was carefully added to a solution of LiAlH₄ (285 mg, 7.5 mmol) in anhydrous ether (10 ml) at 0 °C, then 1-(selenophen-2-yl)octan-1-one (4, 271 mg, 1 mmol) was added to the solution. Then the mixture was stirred at room temperature for 1 h. Cool water was added slowly to the solution in ice-bath to quench the reaction and then the solution was extracted with DCM. The organic phase was dried with anhydrous MgSO₄ and solvent was removed under vacuum. The crude residue was purified by silica gel chromatography (petroleum ether) to produce 5 (155 mg, 0.6 mmol, 60%). $^1$H NMR (400 MHz, CDCl₃): 7.79(d, 1H, $J=5.35$Hz), 7.13(t, 1H, $J=3.78$Hz), 6.95(d, 1H, $J=3.62$Hz), 2.89(t, 2H, $J=7.40$Hz), 1.69(m, 2H), 1.28—1.38(m, 10H), 0.89(m, 3H). $^{13}$C NMR (100 MHz, CDCl₃): 153.5, 129.1, 127.9, 126.2, 32.7, 32.6, 31.9, 29.4, 29.2, 29.1, 22.7, 14.1.

Trimethyl (5-octylselenophen-2-yl) stannane (6): The experimental procedure is similar to that of 2 except for altering the starting material to 2-octylselenophene (5, 260 mg, 1 mmol) and the product 6 was used in the next step without any further purification.

1-(Thieno[3,2-b]thiophen-2-yl)octan-1-one (8): The experimental procedure is similar to that of 4 except for altering the starting material to thieno[3,2-b] thiophene (7, 280 mg, 2 mmol). The crude residue was purified by silica gel chromatography (petroleum ether) to yield 8 (400 mg, 1.5 mmol, 75%). $^1$H NMR (400 MHz, CDCl₃): 7.90(s, 1H), 7.61(d, 2H, $J=5.12$Hz), 7.29(d, 2H, $J=5.08$Hz), 2.92(t, 2H, $J=7.36$Hz), 1.77(m, 2H), 1.37-1.29(m, 8H), 0.87(t, 3H). $^{13}$C NMR (100 MHz, CDCl₃): 193.8, 145.5, 144.6, 138.5, 131.8, 123.7, 119.6, 38.6, 31.2, 28.9, 28.6, 24.5, 22.1, 13.6.

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2-Octylthieno[3,2-b]thiophene (9): The experimental procedure is similar to that of 5 except for altering the starting material to 1-(selenophen-2-yl)octan-1-one (8, 266 mg, 1 mmol). The crude residue was purified by silica gel chromatography (petroleum ether) to yield 9 (200 mg, 0.8 mmol, 80%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.24(d, 1H, \(J=4.52\)Hz), 7.19(t, 1H, \(J=4.28\)Hz), 6.96(s, 1H), 2.88(t, 2H, \(J=7.48\)Hz), 1.72(m, 2H), 1.38-1.27(m, 10H), 0.88(m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 148.6, 138.8, 137.3, 119.5, 116.2, 31.9, 31.6, 31.2, 29.4, 29.2, 29.1, 22.7, 14.1.

Trimethyl(5-octylthieno[3,2-b]thiophen-2-yl)stannane (10): The experimental procedure is similar to that of 2 except for altering the starting material to 2-octylthieno[3, 2-b]thiophene (9, 252 mg, 1 mmol) and the product 10 was used in the next step without any further purification.

2.2 Synthesis of DPPT, DPPSe and DPPTT

A general synthetic procedure for synthesis of DPPT, DPPSe and DPPTT is as follows. A 10 ml anhydrous toluene solution of 3,6-bis(5-bromothiophen-2-yl)-2-(2-ethylheptyl)-5-(2-ethylhexyl) pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (11, 134 mg, 0.2 mmol) and Trimethyl stannane compounds (2, 6, or 10) in a molar ratio of 1: 2.2 were put into a flask under nitrogen atmosphere. After 10 min nitrogen-blowing of the solution, catalyst of Pd(PPh\(_3\))\(_4\) (0.1 eq) was added to the reaction and the reactant was heated to reflux at 130 \(^\circ\)C for 24 h. Then the reactant was cooled to room temperature. Subsequently, the solvent was removed under vacuum and the reactant was purified by silica gel chromatography (petroleum ether: DCM=2:1).

2,5-Bis(2-ethylhexyl)-3,6-bis(5'-octyl-[2,2'-bithiophen]-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPPT): DPPT is obtained as a dark blue powder (146 mg, 0.16 mmol, 80%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): 8.91(d, 2H, \(J=3.24\)Hz), 7.26(d, 2H, \(J=4.32\)Hz), 7.17(d, 2H, \(J=3.20\)Hz), 6.90(d, 2H, \(J=3.62\)Hz), 4.03(m, 4H), 2.88(m, 4H), 1.92(m,2H), 1.69(m, 4H), 1.26-1.38(m, 36H), 0.88(m, 18H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 161.7, 147.8, 143.4, 139.4, 136.8, 136.7, 127.5, 125.4, 125.0, 124.0, 108.2, 46.0, 39.3, 31.9, 31.6, 30.4, 30.3, 29.3, 29.2, 29.1, 28.3, 26.8, 23.7, 23.1, 22.7, 14.1, 10.6. MALDI-TOF MS: 913.4 (M+H\(^+\)). Elemental Analysis for C\(_{54}\)H\(_{76}\)N\(_2\)O\(_2\)S\(_4\): Calcd: C, 71.00%; H, 8.39%; N, 3.07%. Found: C, 70.72%; H, 8.39%; N, 2.93%.
2,5-Bis(2-ethylhexyl)-3,6-bis(5-(5-octylselenophen-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPPSe): DPPSe is obtained as a dark green powder (171 mg, 0.17 mmol, 85%).

$^1$H NMR (400 MHz, CDCl$_3$): 8.91(d, 2H, $J$=3.26Hz), 7.26(d, 2H, $J$=3.66Hz), 7.17(d, 2H, $J$=3.20Hz), 6.90(d, 2H, $J$=3.16Hz), 4.03(m, 4H), 2.88(t, 4H), 1.92(m, 2H), 1.69(m, 4H). $^{13}$C NMR(100 MHz, CDCl$_3$): 161.7, 155.6, 145.5, 139.5, 138.4, 136.8, 127.7, 127.5, 127.1, 124.8, 108.3, 46.0, 39.3, 33.0, 32.5, 31.9, 30.4, 29.7, 29.3, 29.2, 29.1, 28.6, 23.7, 23.1, 22.7, 14.1, 10.6. MALDI-TOF MS: 1007.8 (M+H$^+$). Elemental Analysis for C$_{54}$H$_{76}$N$_2$O$_2$S$_2$Se$_2$: Calcd: C, 64.39%; H, 7.61%; N, 2.78%. Found: C, 64.00%; H, 7.52%; N, 2.79%.

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(5-octylthieno[3,2-b]thiophen-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPPTT): DPPTT is obtained as a dark blue powder (174 mg, 0.17 mmol, 83%). $^1$H NMR (400 MHz, CDCl$_3$): 8.94(d, 2H, $J$=1.36Hz), 7.38(s, 2H), 7.26(d, 2H, $J$=2.40Hz), 6.91(s, 2H), 4.02(m, 4H), 2.86(m, 4H), 1.93(m, 2H), 1.71(m, 4H), 1.38-1.28(m, 36H), 0.92(m, 18H). $^{13}$C NMR(100 MHz, CDCl$_3$): 161.6, 150.3, 143.3, 139.2, 139.0, 128.1, 136.8, 135.9, 127.9, 124.3, 117.3, 116.4, 108.3, 46.0, 39.3, 39.3, 31.9, 31.5, 31.3, 30.4, 29.3, 29.2, 29.1, 28.6, 23.7, 23.2, 22.7, 14.1, 10.6. MALDI-TOF MS: 1025.4 (M+H$^+$). Elemental Analysis for C$_{58}$H$_{76}$N$_2$O$_2$S$_6$: Calcd: C, 67.92%; H, 7.47%; N, 2.73%. Found: C, 67.81%; H, 7.16%; N, 2.43%.

3. Supporting figures

Figure S1. Performances of standard P3HT/PCBM device.
Figure S2. Tapping mode AFM images of DPPT (a), DPPSe (b), and DPPTT (c) pristine films. Note: scan area: 5×5 µm, Ra roughness = 1.30 nm (a), 1.43 nm (b), and 6.15 nm (c).

4. Supporting tables

Table S1. Optoelectronic properties of the DPP-based small molecules.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Solution</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt;/10&lt;sup&gt;4&lt;/sup&gt; (M&lt;sup&gt;−1&lt;/sup&gt;·cm&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>fwhm (cm&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>fwhm (cm&lt;sup&gt;−1&lt;/sup&gt;)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;edge&lt;/sub&gt;(nm)&lt;sup&gt;e&lt;/sup&gt;/E&lt;sub&gt;g&lt;/sub&gt;&lt;sup&gt;elec&lt;/sup&gt; (eV)&lt;sup&gt;h&lt;/sup&gt;</th>
<th>Electrochemical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPPT</td>
<td>583, 621</td>
<td>44.8, 47.6</td>
<td>3078.1</td>
<td>597, 659</td>
<td>4036.8</td>
<td>737/1.68</td>
<td>0.66/5.06</td>
<td>−1.02/−3.38</td>
</tr>
<tr>
<td>DPPSe</td>
<td>589, 627</td>
<td>46.1, 48.0</td>
<td>3117.4</td>
<td>606, 669</td>
<td>4229.6</td>
<td>746/1.66</td>
<td>0.61/5.01</td>
<td>−1.02/−3.38</td>
</tr>
<tr>
<td>DPPTT</td>
<td>601, 639</td>
<td>47.1, 48.6</td>
<td>3145.1</td>
<td>617, 680</td>
<td>4452.2</td>
<td>778/1.59</td>
<td>0.58/4.98</td>
<td>−1.02/−3.38</td>
</tr>
</tbody>
</table>

Note: <sup>a</sup> absorption maximum; <sup>b</sup> molar extinction coefficient; <sup>c</sup> the full width at half maximum (fwhm) is calculated following this equation of fwhm = 1/λ<sub>1</sub>hm - 1/λ<sub>2</sub>hm, where λ<sub>1</sub>hm and λ<sub>2</sub>hm are the wavelengths at the half maxima of the absorption, respectively, localizing at the blue and the red edge of the absorption band; <sup>d</sup> absorption edge; <sup>e</sup> optical bandgap calculated from the absorption edge with 1240/λ<sub>edge</sub>; <sup>f</sup> onset voltage of the oxidation/reduction processes; <sup>g</sup> calculated from the onset of oxidation/reduction voltage; <sup>h</sup> electrochemical bandgaps calculated from LUMO-HOMO.

Table S2. XRD diffraction peaks and d-spacing of the pristine small molecule films and small molecule/PC61BM blending films with the donor/acceptor ratio of 3:1 (DPPT:PC<sub>B</sub>BM), 3:1 (DPPSe:PC<sub>B</sub>BM), and 2:1 (DPPTT:PC<sub>B</sub>BM), respectively.

<table>
<thead>
<tr>
<th>Film</th>
<th>2θ(deg) (d-spacing (Å))</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>I/I&lt;sub&gt;b&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPPT</td>
<td>4.47 (19.7) 7.27 (12.1)</td>
<td>23.86 (3.72)</td>
<td>3.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPSe</td>
<td>4.45 (19.8) 6.95 (12.7)</td>
<td>23.22 (3.83)</td>
<td>2.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPTT</td>
<td>4.86 (19.2) 6.78 (13.0)</td>
<td>21.78 (4.08)</td>
<td>17.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPT:PCBM</td>
<td>4.45 (19.8) 7.29 (12.1)</td>
<td>23.60 (3.76)</td>
<td>14.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPSe:PCBM</td>
<td>4.48 (19.7) 6.97 (12.6)</td>
<td>23.80 (3.73)</td>
<td>3.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DPPTT:PCBM</td>
<td>4.65 (19.0) 6.60 (13.4)</td>
<td>20.43 (4.03)</td>
<td>3.46</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: a, b, and c represent the different packing direction as shown in Figure 7b; I/I<sub>b</sub> denotes the relative intensity ratio of a reflection versus b reflection.

5. References