Supplementary Information

Efficient Hole Transport Layers with Widely Tunable Work Function for Deep HOMO Level Organic Solar Cells

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Fig. S1. Molecular structure of a) F5BnPA, b) SMPV1 and PC71BM.
Fig. S2 Surface potential images of a) GO, b) GO:F5BnPA, c) MoOₓ, d) MoOₓ:F5BnPA. e-f) corresponding pixel analysis.
Fig. S3 Schematic of chemisorption of F5BnPA on oxide surface and dipole moment.
The thickness of GO and MoO<sub>x</sub> are optimized through P3HT:PCBM based OSCs. The device structure is ITO/GO or MoO<sub>x</sub>/P3HT:PCBM/Ca/Al. The devices are fabricated according to the details in the experimental section. The GO solution is diluted into a series of concentration (0.8, 0.6, 0.4, 0.2, 0.1 mg mL<sup>-1</sup>). The synthesized molybdenum bronze solution is diluted by ethanol in a series of v/v ratio (1:2.5, 1:5, 1:7.5, 1:10, 1:12.5). The optimized concentration of GO solution in ethanol was 0.2 mg mL<sup>-1</sup>, and the optimized ratio of molybdenum bronze solution was 1:7.5. The respective thickness are 2 nm and 8 nm, as measured by ellipsometer.

Fig. S4. J-V characteristics of P3HT:PCBM based OSCs using different thickness of a) GO and b) MoO<sub>x</sub>. 
Fig. S5. $J$-$V$ characteristics of P3HT:PCBM based OSCs using different HTLs (the concentrations of F5BnPA are both 0.5 mg mL$^{-1}$) under illumination of simulated 100 mW cm$^{-2}$ AM 1.5G irradiation.

Table S1. Device performance of OSCs with the structure of ITO/HTL/SMPV1:PC$_{71}$BM/Ca/Al.

<table>
<thead>
<tr>
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<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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</thead>
<tbody>
<tr>
<td>GO</td>
<td>11.03 ± 0.27</td>
<td>0.65 ± 0.01</td>
<td>43.28 ± 0.76</td>
<td>3.10 ± 0.14</td>
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<tr>
<td>GO:F5BnPA</td>
<td>11.96 ± 0.11</td>
<td>0.92 ± 0.01</td>
<td>46.59 ± 1.00</td>
<td>5.13 ± 0.18</td>
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<tr>
<td>MoO$_x$</td>
<td>10.96 ± 0.20</td>
<td>0.88 ± 0.01</td>
<td>50.81 ± 0.30</td>
<td>4.92 ± 0.10</td>
</tr>
<tr>
<td>MoO$_x$:F5BnPA</td>
<td>11.69 ± 0.27</td>
<td>0.91 ± 0.01</td>
<td>55.92 ± 0.90</td>
<td>5.96 ± 0.19</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>11.27 ± 0.47</td>
<td>0.94 ± 0.01</td>
<td>52.42 ± 2.40</td>
<td>5.54 ± 0.30</td>
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Fig. S6. EQE of the OSC structure of ITO/HTLs/Active layers/Ca/Al.
Fig. S7. J-V characteristics of hole only devices with the structure of ITO/HTL/SMPV1:PC$_{71}$BM/MoO$_x$/Ag.