Supplementary Information

Incorporating deep electron traps in perovskite devices: towards high efficiency solar cells and fast photodetectors

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Experimental details

Materials
The PEDOT:PSS, lead iodine (PbI₂) and methylammonium iodide (CH₃NH₃I) were attained from Xi'an p-OLED Co. (China). The m-MTDATA, BCP and C₆₀ were purchased from Lumtec corp. (Taiwan). F4-TCNQ was got from Sigma-Aldrich (UK). All materials were used as received.

Fabrication of devices
The pre-cleaned ITO substrates were firstly treated with UV-ozone for 10 min before use. The m-MTDATA was dissolved into chlorobenzene (CB) with the concentration of 4 mg mL⁻¹, and different contents of F4-TCNQ were added to get the composite solutions with the concentrations of 0.002, 0.005, 0.01, 0.02 and 0.05 mg mL⁻¹ for F4-TCNQ, respectively. The pristine m-MTDATA solution and m:F composite solutions were deposited onto the ITO substrates at 3000 rpm for 50 s, and then annealed at 100 °C for 10 min. The PEDOT:PSS HTL was prepared on the ITO electrode and annealed at 120 °C for 20 min. Subsequently, the perovskite layer was spin-coated onto different HTLs at 4000 rpm and cleaned by anhydrous ether. Finally, the devices were completed by successively evaporating the C₆₀ (30 nm), BCP (9 nm) and Ag (80 nm) onto the perovskite layer. The effective area of device is 0.044 cm².

Film and Device Characterization
The light transmission and absorbance spectra were measured on a Shimadzu UV-1700 spectrophotometer. The surface morphologies were analyzed by a Bruker Dimension Icon AFM. The surface WFs were measured by extracting 100 points in a size of 50×50 μm using a Kelvin probe system. The light J-V characteristics were carried out using a Keithley 2601 source meter with an Oriel 300 W solar simulator intensity of ~100 mW cm⁻². The EQE spectra were measured using a Crowntech QTest Station 1000 AD. The surface and cross-sectional morphologies were characterized by a JEOL JSM-7500 field-emission SEM. The contact angles were carried out on a Powereach JC2000D contact angle goniometer. The Nyquist plots were measured by a Precision Impedance Analyzer 6500B Series of Wayne Kerr Electronics. The TPC measurements were carried out using a 550 nm nanosecond laser with repeating frequency of 10 Hz.
**Fig. S1** Chemical structures of m-MTDATA and F4-TCNQ.

**Fig. S2** Electron trapping process in the m:F composite HTL.
**Fig. S3** $J$-$V$ characteristics of devices based on m:F composite HTLs with different doping concentration.

**Fig. S4** Dark current-voltage characteristics of devices with m:F-3, m:F-4 and m:F-5, and inset is the charge transport process.
Fig. S5 SEM image of small grains region with higher magnification.

Fig. S6 Contact angles of DMF on PEDOT:PSS, pristine m-MTDATA and m:F-2.
Fig. S7  $J$-$V$ characteristics of electron-only device, and inset is the device structure.

Fig. S8  Multiple time response characteristics of device based on m:F-2 HTL.
**Fig. S9** Spectral $R$ of devices with PEDOT:PSS, pristine m-MTDATA and m:F-2 HTLs.

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**Table S1** Detail photovoltaic parameters of all devices fabricated here.

<table>
<thead>
<tr>
<th>HTLs</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>Integrated $J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>0.898</td>
<td>19.33</td>
<td>18.91</td>
<td>78.5</td>
<td>13.63</td>
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<td>m-MTDATA</td>
<td>1.026</td>
<td>21.30</td>
<td>20.91</td>
<td>78.4</td>
<td>17.13</td>
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<td>M:F-1</td>
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<td>21.61</td>
<td>21.14</td>
<td>78.6</td>
<td>17.63</td>
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<td>M:F-2</td>
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<td>78.8</td>
<td>18.35</td>
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<td>21.16</td>
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<td>M:F-5</td>
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<td>19.58</td>
<td>19.09</td>
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<td>14.44</td>
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