Supporting Information

Introducing an alternative oxidant for Spiro-OMeTAD with the reduction product to passivate perovskite defects

Xing Gao\textsuperscript{a}, Fei Wu\textsuperscript{a,*}, Ye Zeng\textsuperscript{a}, Kaixing Chen\textsuperscript{a}, Xiaorui Liu\textsuperscript{b,*}, Linna Zhu\textsuperscript{a,*}

\textsuperscript{a} Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energy, School of Materials & Energy, Southwest University, Chongqing 400715, P. R. China.

\textsuperscript{b} Key Laboratory of Luminescence Analysis and Molecular Sensing, Ministry of Education, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P. R. China.

**Corresponding Author:** Linna Zhu, School of Materials & Energy, Southwest University, Chongqing, China, E-mail address: lnzhu@swu.edu.cn.

Fei Wu, School of Materials & Energy, Southwest University, Chongqing, China, E-mail address: feiwu610@swu.edu.cn.

Xiaorui Liu, School of Chemistry and Chemical Engineering, Southwest University, Chongqing, China, E-mail address: liuxiaorui@swu.edu.cn.

Table of Contents

1. Experimental Section

2. Calculation formulas
3. Figures:

**Figure S1.** Photograph of different spiro-OMeTAD solutions undergoing thin-film chromatography.

**Figure S2.** $^1$H NMR spectrum of the reduction product of IBX.

**Figure S3.** XPS spectra of the I 3d of the perovskite film and perovskite/2-Iodobenzoic acid film.

**Figure S4.** XPS spectra of the I 3d of the 2-Iodobenzoic acid film.

**Figure S5.** XPS spectra of the C 1s of different films.

**Figure S6.** SEM images of spiro-OMeTAD films without (a) and with IBX (b).

**Figure S7.** $J-V$ curve of hole-only devices based on unoxidized Spiro-OMeTAD.

**Figure S8.** TRPL spectra of perovskite substrate with different HTL films.

**Figure S9.** $J−V$ curves of the devices based on spiro-OMeTAD with different concentrations of IBX.

**Figure S10.** Statistical distribution of photovoltaic parameters of the PSCs doped with or without IBX: $J_{sc}$ (a), $V_{oc}$ (b), FF (c) and PCE (d).

**Figure S11.** TPV of the PSCs with and without IBX.

4. Tables:

**Table S1.** Conductivity of spiro-OMeTAD films with different treatments.

**Table S2.** Specific values of series resistance ($R_s$), and recombination resistance ($R_{rec}$) of PSCs with and without IBX.

**Table S3.** Photovoltaic parameters of the devices with different concentrations of IBX.

**Table S4.** Photovoltaic data of the PSCs based on spiro-OMeTAD with and without IBX scanned from different directions.
Experimental Section

Materials

Spiro-OMeTAD, Li-TFSI, tBP, Cesium iodide (CsI, 99.90%), Formamidinium iodide (FAI, 99.90%), Lead iodide (Pbl2, 99.99%) and Lead bromide (PbBr2, 99.99%) were purchased from Youxuan Tech.. N,N-Dimethylformamide (DMF, 99.80%), Dimethyl sulfoxide (DMSO, 99.80%), Chlorobenzene (CB, 99.80%) and Acetonitrile (ACN) were purchased from Sigma-aldrich. 30 NR-D transparent Titania paste was purchased from Xi’an Polymer Light Technology Corp. 2-Iodoxybenzoic acid (IBX, 97.00%) was purchased from Energy Chemical.

Solution preparation

The perovskite precursor solution was prepared by dissolving 1.30 M Pbl2, 1.19 M FAI, 0.14 M PbBr2, 0.14 M MABr, and 0.07 M CsI into the DMSO/DMF (1/4, v/v) mixture. The hole transport material solution was prepared by dissolving 72.5 mg of spiro-OMeTAD in 1mL of CB, with the additives of 28.5 µL t-BP, 17.5 µL Li-TFSI (520 mg mL⁻¹ in ACN). For the spiro-OMeTAD solution with IBX, IBX was added into HTL precursor solution, the concentration of IBX were 1.0 mg mL⁻¹, 1.5 mg mL⁻¹, 2.0 mg mL⁻¹, 2.5 mg mL⁻¹, and 3.0 mg mL⁻¹, respectively.

Fabrication of perovskite solar cells

The FTO glass substrates (14 Ω per square) were ultrasonically cleaned with detergent, deionized water and ethanol for 20 min in sequence, and dried by nitrogen flow. Then the dry FTO substrates were treated by O₂-plasma for 180 s before using.
After that, a compact TiO$_2$ layer was deposited on the cleaned FTO glass by spray pyrolysis from a precursor solution of 0.2 M titanium isopropoxide and 2 M acetylacetone in isopropanol. The mesoporous TiO$_2$ was prepared by diluting a commercial TiO$_2$ paste (30 NR-D) with anhydrous ethanol at a weight ratio of 1/6. After sintering the compact TiO$_2$, the mesoporous TiO$_2$ layer was spin-coated onto the TiO$_2$ compact layer at 5000 rpm for 30 s, and sintered. The perovskite film was deposited by a consecutive two-step spin-coating process at 2000 rpm for 10 s and then at a speed of 6000 rpm for 30 s on the surface of mesoporous TiO$_2$ layer. At the time of 15 s prior to the program end, 100 μL of chlorobenzene was dripped on the spinning substrate, and then the film was annealed at 120 °C for 1 h. The spiro-OMeTAD solution (with or without IBX) was spin-coated on the perovskite film at 6000 rpm for 30 s. Finally, 60 nm thick Au film was thermally evaporated on the HTL in vacuum environment (\(<10^{-5}\)Pa) to accomplish the whole fabrication of device.

**Characterizations**

UV-vis absorption spectra were measured on a Shimadzu UV-2550 absorption spectrophotometer. Fluorescence emission spectra was measured by fluorescence spectrophotometer (RF-5301PC). The space-charge limited current (SCLC) measurements were performed by collecting the $J$–$V$ characteristics of devices in dark conditions. The Fourier-transform infrared spectroscopy (FTIR) spectroscopy was carried out using Thermo Nicolet 6700. The current-voltage ($J$-$V$) characteristics were measured under 100 mW cm$^{-2}$ (AM 1.5G illumination) using a Newport solar simulator (model 91160) and a Keithley 2400 source/meter. PL and TR-PL spectra
were obtained via using the Pico Quant Fluotime 300 with a 510 nm picosecond pulsed laser. The surface morphology of films was characterized by FE-SEM images (JSM-7800F), and atomic force microscope (AFM) was used for characterizing the morphology using a CSPM5500. X-ray photoelectron spectroscopy (XPS) was performed using a scanning XPS microprobe (K-Alpha). The EIS were measured with CHI 6500 in the dark. Film thickness were measured with Surfcorder ET150. Transient photocurrent (TPC) and transient photovoltage (TPV) were recorded using a ZAHNE® MEISSSTEME (Instrument model: PP211).

**Hole Mobility Measurements**

Devices structure: FTO/PEDOT:PSS/Spiro-OMeTAD with or without IBX/MoO₃/Ag

The hole mobilities (μ) were measured by using space charge limited current (SCLC) method with an equation as follows:

\[
J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8L^3}
\]

where \(\varepsilon_0\) and \(\varepsilon_r\) are the vacuum permittivity (8.85 × 10⁻¹² F/m) and relative permittivity, respectively. \(J\) is the current density, \(\mu\) is the hole mobility, \(V\) is voltage, and \(L\) is the film thickness.

**Conductivity Measurements**

Devices structure: FTO/Spiro-OMeTAD with or without IBX/Ag

The conductivity of spiro-OMeTAD films with or without IBX is characterized by \(J-V\) curves. The conductivity was calculated according to the following equation:

\[
\sigma = \frac{Id}{AV}
\]

where \(A\) is the active area of the device, \(d\) is the thickness of the films, \(I\) is the current, and \(V\) is the voltage.
TRPL Analysis

The TRPL results are fitted through the biexponential equation as below:

\[ f(t) = A_1 \exp \left( \frac{-t}{\tau_1} \right) + A_2 \exp \left( \frac{-t}{\tau_2} \right) \]

And the average value of lifetime (\( \tau_{ave} \)) is calculated by the following equation:

\[ \tau_{ave} = \frac{A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2}{A_1 \cdot \tau_1 + A_2 \cdot \tau_2} \]

\( \tau_1 \) and \( \tau_2 \) represent the fast and slow decay times, which are derived from the charge carriers quenching and the radiative recombination, respectively.

Figure S1. Photograph of different spiro-OMeTAD solutions undergoing thin-film chromatography.
**Figure S2.** $^1$H NMR spectrum of the reduction product of IBX.

**Figure S3.** XPS spectra of the I 3d of the perovskite film and perovskite/2-Iodobenzoic acid film.
Figure S4. XPS spectra of the I 3d of the 2-iodobenzoic acid film.

Figure S5. XPS spectra of the C 1s of different films.

Figure S6. SEM images of spiro-OMeTAD films without (a) and with IBX (b).
Figure S7. J-V curve of hole-only devices based on unoxidized Spiro-OMeTAD.

Figure S8. TRPL spectra of perovskite substrate with different HTL films.
Figure S9. $J-V$ curves of the devices based on spiro-OMeTAD with different concentrations of IBX.

Figure S10. Statistical distribution of photovoltaic parameters of the PSCs doped with or without IBX: $J_{sc}$ (a), $V_{oc}$ (b), FF (c) and PCE (d).
Figure S11. TPV of the PSCs with and without IBX.

Table S1. Conductivity of spiro-OMeTAD films with different treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S·cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>spiro+Li+tBP</td>
<td>3.8×10⁻⁵</td>
</tr>
<tr>
<td>spiro+Li+tBP+O₂</td>
<td>8.7×10⁻⁵</td>
</tr>
<tr>
<td>spiro+Li+tBP+IBX</td>
<td>1.5×10⁻⁴</td>
</tr>
</tbody>
</table>

Table S2. Specific values of series resistance ($R_s$), and recombination resistance ($R_{rec}$) of PSCs with and without IBX.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$R_s$ (Ω)</th>
<th>$R_{rec}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without IBX</td>
<td>23</td>
<td>2135</td>
</tr>
<tr>
<td>with IBX</td>
<td>20</td>
<td>4180</td>
</tr>
</tbody>
</table>
Table S3. Photovoltaic parameters of the devices with different concentrations of IBX.

<table>
<thead>
<tr>
<th>Doping concentration (mg/mL)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>23.54</td>
<td>1.11</td>
<td>0.78</td>
<td>20.42</td>
</tr>
<tr>
<td>1.0</td>
<td>23.88</td>
<td>1.12</td>
<td>0.79</td>
<td>21.25</td>
</tr>
<tr>
<td>1.5</td>
<td>24.01</td>
<td>1.14</td>
<td>0.81</td>
<td>22.22</td>
</tr>
<tr>
<td>2.0</td>
<td>24.13</td>
<td>1.14</td>
<td>0.82</td>
<td>22.45</td>
</tr>
<tr>
<td>2.5</td>
<td>23.80</td>
<td>1.13</td>
<td>0.80</td>
<td>21.55</td>
</tr>
<tr>
<td>3.0</td>
<td>23.42</td>
<td>1.10</td>
<td>0.76</td>
<td>19.70</td>
</tr>
</tbody>
</table>

Table S4. Photovoltaic data of the PSCs based on spiro-OMeTAD with and without IBX scanned from different directions.

<table>
<thead>
<tr>
<th>Doping</th>
<th>Scan direction</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without IBX</td>
<td>Forward</td>
<td>23.54</td>
<td>1.11</td>
<td>0.78</td>
<td>20.42</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>23.49</td>
<td>1.10</td>
<td>0.75</td>
<td>19.29</td>
</tr>
<tr>
<td>With IBX</td>
<td>Forward</td>
<td>24.13</td>
<td>1.14</td>
<td>0.82</td>
<td>22.45</td>
</tr>
<tr>
<td></td>
<td>Reverse</td>
<td>24.11</td>
<td>1.13</td>
<td>0.79</td>
<td>21.66</td>
</tr>
</tbody>
</table>