ELECTRONIC SUPPLEMENTARY INFORMATION

Small Molecule Dopant-Free Dual Hole Transporting Material for Conventional and Inverted Perovskite Solar Cells
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Solar cells fabrication and characterization

Pre-patterned ITO substrates (Naranjo) were cleaned by means of sequential sonication in acetone, sodium dodecyl sulfate solution (99%, Acros), deionised water and isopropanol (15 minutes per step). ITO substrates were dried with a nitrogen flow and treated with UV-ozone for 30 minutes before using. Devices with inverted architecture were fabricated following the protocol previously described.[1]

For perovskite solar cells with conventional architecture, an aqueous SnO$_2$ solution (15 wt%, Alfa Aesar) stirred overnight at room temperature was deposited via spin-coating (2800 rpm, 60 seconds) on clean ITO substrates. After cleaning the electrode contacts with water, an annealing step was performed at 150 °C for 30 minutes followed by an UV-ozone treatment for 10 minutes. Next, the substrates were transferred to a nitrogen-filled glovebox to spin coat (2000 rpm, 30 seconds) a solution of [60]PCBM in chlorobenzene (10 mg mL$^{-1}$) which was stirred overnight at 60 °C. The resulting thin film was annealed at 100 °C for 30 minutes. The active layer was prepared using a two-step methodology. First, a solution of PbI$_2$ (0.93 M) in a DMF:DMSO (5:1) mixture, which was stirred overnight at 70 °C, was casted by static spin-coating (2000 rpm, 40 seconds). Subsequently, a CH$_3$NH$_3$I solution (0.30 M) in isopropanol, which was stirred overnight at room temperature, was deposited via dynamic spin-coating (2000 rpm, 40 seconds). The resulting films were annealed at 130 °C for 10 minutes. Next, ADI and ADAI hole transporting materials were deposited by thermal evaporation ($10^{-7}$-$10^{-8}$ mbar) until a nominal thickness of ~10-20 nm. For the reference Spiro-MeOTAD, BuPy (28.5 µL) and LiTFSI (17.5 µL from a 520 mg mL$^{-1}$ solution in acetonitrile) were added to a solution of Spiro-MeOTAD (80 mg mL$^{-1}$) in chlorobenzene and the resulting mixture was stirred overnight at room temperature. Before using it (~1 hour), 20 µL of the complex FK209 (500 mg mL$^{-1}$ in acetonitrile) were added and the mixture was stirred at room temperature before casting (2000 rpm, 50 seconds) onto the perovskite active layer. Devices were completed by the sequential thermal evaporation through a mask of MoO$_3$ (10 nm) and Au (110 nm) under high vacuum conditions ($3 \times 10^{-7}$ mbar).

The device area for all perovskite-based devices was estimated by the aperture of a black shadow mask (0.0676 cm$^2$ and 0.1296 cm$^2$). $J$–$V$ characteristics were acquired by using a Keithley 2400 source meter under nitrogen atmosphere. The devices were illuminated using a tungsten-halogen lamp (~100 mW cm$^{-2}$) that included a Schott GG385 UV filter and a Hoya LB120 daylight filter. Fast forward and reverse $J$–$V$ scans were measured between −0.5 V and 1.5 V at a scan rate of 0.25 V s$^{-1}$. The stabilised $J$–$V$ (slow scan) curves were acquired in reverse direction, from $V_{OC}+0.02\text{ to }0.04$ V to −0.02-0.04 V, with steps of 0.02 V. Before each measurement, devices were light soaked at $V_{OC}$ for 5 minutes. The $J$–$V$ curves were obtained using the final value achieved after registering the current density during 10 seconds at every step. External quantum efficiency spectra were measured under nitrogen atmosphere using a high-power LED with a bias light of 530. The device was irradiated with modulated monochromatic light from a 50 W tungsten-halogen lamp (Osram 64610) and a monochromator (Oriel, Cornerstone 130) using a mechanical chopper. The response was acquired as a voltage from a preamplifier (SR570) based on a lock-in amplifier (SR830). A calibrated silicon cell was employed as reference to determine the corrected values of $J_{SC}$ and PCE.
light intensity dependence measurements were carried out by using a Keithley 2400 SMU and high-power LEDs (Thorlabs) that emitted at 405 nm and 730 nm (1-1000 mA).

Molecular packing

![Figure S1. Projection across the long axis of π-π stacked molecules in ADI (left) and ADAI (right) packing.](image)

Space charge limited current and hole mobility

Single carrier devices with the architecture: ITO / MoO\(_3\) (10 nm) / HTL (120 nm) / MoO\(_3\) (10 nm) / Ag (100 nm) were fabricated by thermal evaporation under high vacuum. J-V curves were measured using a Keithley 2636A SMU. These curves were fitted to estimate the space charge limited hole mobility according to the Murgatroyd equation:\(^\text{[2]}\)

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \left( \frac{V^2}{L^3} \right) \exp \left[ 0.89 \beta \left( \frac{V}{L} \right)^{1/2} \right],
\]

where \(J\) is the current density, \(\varepsilon_0\) the vacuum permittivity (8.85 \(\times\) 10\(^{-14}\) F cm\(^{-1}\)), \(\varepsilon_r\) the relative permittivity of the organic layer (approximated to a value of 3), \(\mu_0\) the zero-field mobility, \(L\) the thickness of the organic layer, and \(\beta\) the field-activation factor. The hole mobility was determined using the Poole-Frenkel relationship, \(\mu = \mu_0 \exp(\beta E^{1/2})\), at an electric field of 10\(^5\) V cm\(^{-1}\), using the values of \(\mu_0\) and \(\beta\) obtained by the non-linear fitting of the J-V curves.

![Figure S2. J-V characteristics of the hole-only devices. The solid line represents the fit of the data to the Murgatroyd relation for space charge limited current with a field-dependent mobility. Below 1 V, the current density is dominated by an Ohmic leakage current, explaining the discrepancy with fit in that region.](image)
**Solar cells J-V characteristics**

**Figure S3.** Forward and reverse J-V scans of the optimized devices with (a) p-i-n and (b) n-i-p architectures.

**Thin film UV-vis spectra**

**Figure S4.** UV–vis absorption spectra of ADI and ADAI thin films before and after DMF treatment.
**Time Correlated Single Photon Counting**

Figure S5. Time-resolved photoluminescence decay profiles registered at PL maximum.

Table S1. Time Correlated Single Photon Counting fitting parameters.

<table>
<thead>
<tr>
<th>Material Combination</th>
<th>A1</th>
<th>τ1 (ns)</th>
<th>A2</th>
<th>τ2 (ns)</th>
<th>τavg. (ns)</th>
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<tr>
<td>glass / MAPI</td>
<td>0.58</td>
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<td>140</td>
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<td>glass / MAPI / ADI</td>
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<td>3.20</td>
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<td>26</td>
<td>12</td>
</tr>
<tr>
<td>glass / MAPI / ADAl</td>
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<td>1.91</td>
<td>0.18</td>
<td>21</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*τavg. = ΣAiτi² / ΣAiτi*

References