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_3NH_3I 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, ^{t}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 though a mask of MoO_3 (10 nm) and Au (110 nm) under high vacuum conditions (~3 × 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} +0.02-0.04 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. The

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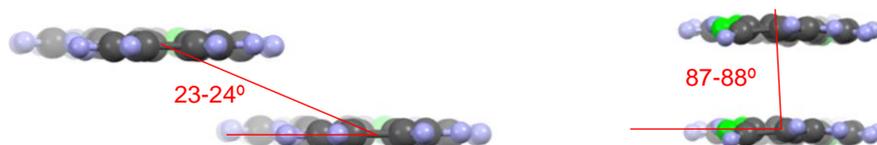
Figure S1. Projection across the long axis of π-π stacked molecules in ADI (left) and ADAI (right) packing.

Space charge limited current and hole mobility

Single carrier devices with the architecture: ITO / MoO₃ (10 nm) / **HTL** (120 nm) / MoO₃ (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:[2] $J = (9/8)\varepsilon_0\varepsilon_r\mu_0(V^2/L^3)\exp[0.89\beta(V/L)^{1/2}]$, where J is the current density, ε_0 the vacuum permittivity (8.85×10^{-14} F cm⁻¹), ε_r the relative permittivity of the organic layer (approximated to a value of 3), μ_0 the zero-field mobility, L the thickness of the organic layer, and β 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 μ_0 and β obtained by the non-linear fitting of the *J-V* curves.
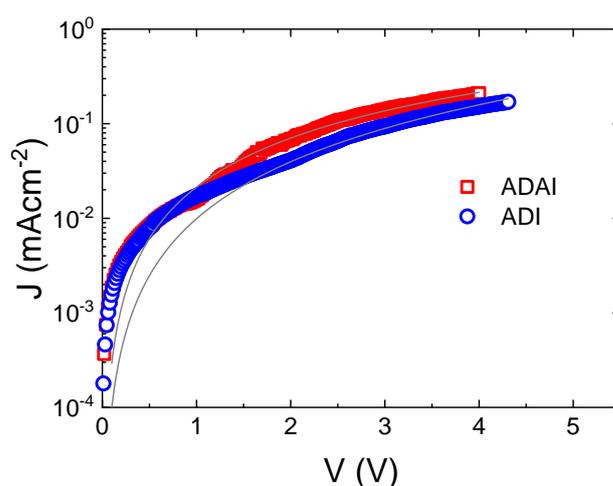
Figure S2. *J-V* characteristics of the hole-only devices. The solid line represents the fit of the data to the Murgatroyd relation for space charge limited current with a field-dependent mobility. Below 1 V, the current density is dominated by an Ohmic leakage current, explaining the discrepancy with fit in that region.

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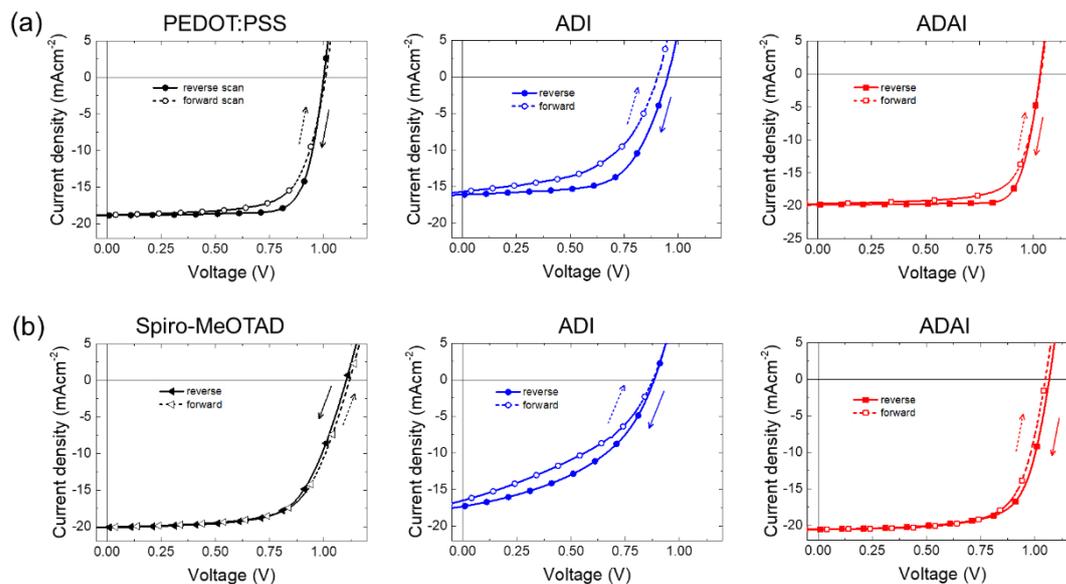
Figure S3. Forward and reverse and *J-V* scans of the optimized devices with (a) p-i-n and (b) n-i-p architectures.

Thin film UV-vis spectra
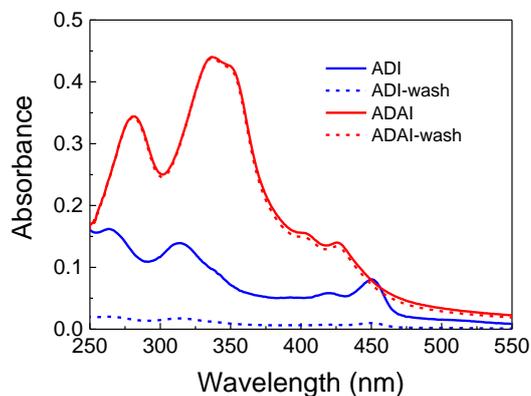
Figure S4. UV–vis absorption spectra of **ADI** and **ADAI** thin films before and after DMF treatment.

Time Correlated Single Photon Counting
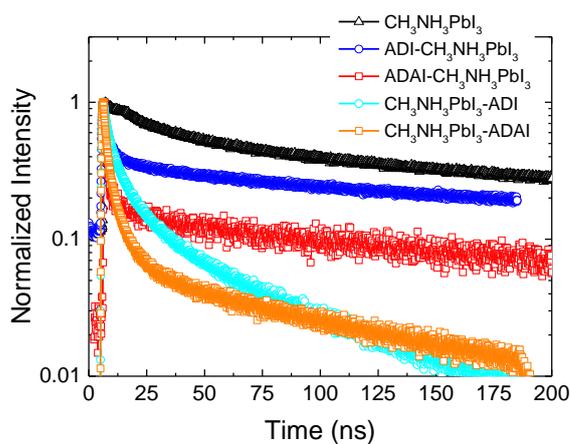
Figure S5. Time-resolved photoluminescence decay profiles registered at PL maximum.

Table S1. Time Correlated Single Photon Counting fitting parameters.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	$\tau_{avg.}$ (ns)
glass / MAPI	0.58	21.8	0.42	162	140
glass / ADI / MAPI	9.2	2.24	0.22	79	37
glass / ADAI / MAPI	12.7	2.20	0.36	51	21
glass / MAPI / ADI	4.3	3.20	0.36	26	12
glass / MAPI / ADAI	20.8	1.91	0.18	21	3.5

[a] $\tau_{avg.} = \sum A_i \tau_i^2 / \sum A_i \tau_i$

References

[1]   M. Más-Montoya, P. Gómez, D. Curiel, I. da Silva, J. Wang, R. A. J. Janssen, *Chem. Eur. J.* **2020**, *26*, 10276-10282.
[2]   P. N. Murgatroyd, *J. Phys. D: Appl. Phys.* **1970**, *3*, 151-156.