

## Electronic Supporting Information

### Simple carbazole-based hole transporting materials with fused benzene rings substituents for efficient perovskite solar cells

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### Synthesis and characterization

#### Materials and characterization

Materials: Copper (I) oxide (97 %, Acros organics), potassium carbonate anhydrous (99 %, Alfa Aesar), 1,4-diiodobenzene (98 %, Acros Organics), N,N-dimethylacetamide (>99.5 %, Sigma Aldrich), Sodium tert-butoxide (98%, Acros Organics), 2-bromonaphtalene (97 %, Aldrich), tri-tert-butylphosphine (98 %, Aldrich), titanium isopropoxide (Sigma-Aldrich), titania paste solution (Dyesol) TiCl<sub>4</sub> (Sigma-Aldrich), Spiro-OMeTAD (Sigma-Aldrich), tert-butylpyridine (Sigma-Aldrich), Bis(trifluoromethane)sulfonamide lithium (sigma Aldrich). The 3,6CzDMPA molecule was synthesized following a previously described procedure<sup>1</sup> and this molecule can be purchased from Ikamba Organics (France)<sup>2</sup>. All chemicals were used without purification. NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm). UV-Vis. absorption spectra of solutions were recorded at room temperature with a Jasco V-670 spectrometer, using a quartz cuvettes and a concentration of a few mM in THF. However, for films the absorption spectra were recorded using an Agilent Cary 300 UV-vis spectrometer. Differential scanning calorimetry (DSC) measurements were performed on Perkin-Elmer DSC-400 (heating/cooling rate 10 °C/min). Thermogravimetric analysis (TGA) was fulfilled using a Perkin Elmer STA 6000 at a heating rate of 10 C/min under N<sub>2</sub>. Cyclic voltammetry measurements were performed on a Biologic Applied Research MPG2 multi-channel potentiostat, using a concentration of 10<sup>-3</sup> mol.L<sup>-1</sup> in dichloromethane containing 10<sup>-1</sup> mol.L<sup>-1</sup> supporting electrolyte of tetrabutylammonium perchlorate (Bu<sub>4</sub>N<sup>+</sup>, ClO<sub>4</sub><sup>-</sup>) at a scan rate of 50 mV/s in a three-electrode cell, where platinum disk and wire were used,

respectively, as working and counter-electrode. A silver wire was used as a pseudo-reference electrode and ferrocene was used as reference.

### **Synthesis of 3,6-Bis[*N,N'*-di(4-methoxyphenyl)amino]-9-(2-naphthyl)-carbazole (Cz-N).**

2-Bromonaphthalene (364 mg, 1.7 mmol), sodium tert-butoxide (465 mg, 4.8 mmol), *N*<sup>3</sup>,*N*<sup>3</sup>,*N*<sup>6</sup>,*N*<sup>6</sup>-tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine (1.00 g, 1.6 mmol), Pd(OAc)<sub>2</sub> (18 mg, 0.08 mmol) and P(tBu)<sub>3</sub> (33 mg, 0.16 mmol) were dissolved in anhydrous toluene (30 mL) in a Schlenk flask. The reaction mixture was stirred and refluxed under Ar atmosphere for 7 h. At the end of the reaction, the mixture was filtered through celite and the filtrate was concentrated under reduced pressure to give a green-black solid. The solid was purified by column chromatography on silica gel, eluting with cyclohexane/ethyl acetate (8:2) to afford **Cz-N** as a yellow product (1.10 g, 92 %). <sup>1</sup>H NMR (acetone-D<sub>6</sub>, 300 MHz) δ : 8.20 (d, 1H, *J* = 8.7 Hz), 8.13 (d, 1H, *J* = 1.8 Hz), 8.04-8.07 (m, 2H), 7.71 (d, 1H, *J* = 1.7 Hz), 7.69 (d, 2H, *J* = 2.0 Hz), 7.63-7.60 (m, 2H), 7.39 (d, 2H, *J* = 8.8 Hz), 7.12 (dd, 2H, *J* = 2.2, 8.8 Hz), 6.95-6.90 (m, 8H), 6.83-6.77 (m, 8H), 3.73 (s, 12H). <sup>13</sup>C NMR (acetone-D<sub>6</sub>, 75 MHz) δ : 155.9, 143.3, 143.1, 138.5, 136.1, 135.1, 133.3, 130.9, 128.8, 128.7, 127.8, 127.4, 125.8, 125.7, 125.5, 124.9, 116.8, 115.4, 111.5, 55.6. MS (m/z) : calculated 747, found 747.3 [M]<sup>+</sup>.

### **Synthesis of 3,6-Bis[*N,N'*-di(4-methoxyphenyl)amino]-9-(1-pyrenyl)carbazole (Cz-Pyr).**

The synthesis was performed using the same procedure as for **Cz-N**, replacing 2-bromonaphthalene with 1-bromopyrene to afford **Cz-N** as a yellow product (0.74 g, 95 %). <sup>1</sup>H NMR (acetone-D<sub>6</sub>, 300 MHz) δ : 8.45 (d, *J* = 8.1 Hz, 1H), 8.40 (d, *J* = 7.5 Hz, 1H), 8.28 (s, 3H), 8.12-8.06 (m, 3H), 7.75 (s, 2H), 7.55 (d, *J* = 9.1 Hz, 1H), 7.03 (dd, *J* = 2.0, 8.7 Hz, 2H), 6.99-6.85 (m, 10H), 6.78 (d, *J* = 9.0 Hz, 8H), 3.72 (s, 12H). <sup>13</sup>C NMR (acetone-D<sub>6</sub>, 75 MHz) δ : 155.9, 143.3, 143.0, 140.2, 132.3, 132.1, 131.9, 129.6, 129.1, 128.2, 127.6, 127.5, 126.9, 126.8, 125.5, 125.0, 124.8, 123.1, 116.9, 115.3, 111.7, 55.6. MS (m/z) : calculated 821, found 821.3 [M]<sup>+</sup>.

### **Fabrication and testing of field-effect transistors.**

Field effect transistors were fabricated in a bottom-gate bottom-contact configuration by drop-casting of a dilute HTM solution in chlorobenzene (3 mg/mL) on pre-patterned OFET substrates with thermally evaporated gold electrodes on silicon/silicon oxide (Ossila). The channel length (L) and width (W) were 30

$\mu\text{m}$  and  $1\text{ mm}$ , respectively. The oxide capacitance  $C_{ox}$  was  $1.09 \cdot 10^{-8}\text{ F}\cdot\text{cm}^{-2}$ . The measurements were recorded immediately after fabrication under ambient atmosphere at room temperature using a Keithley 4200. The mobility was extracted from transfer characteristics in saturation regime according to the following equation:

$$\mu_{sat} = \frac{2L}{WC_{ox}} \left( \frac{\partial \sqrt{I_{DS}}}{\partial V_{GS}} \right)^2$$

where  $\mu_{sat}$  is the hole mobility in saturation regime,  $V_{GS}$  the gate voltage,  $I_{DS}$  the drain current.

## Photovoltaic device fabrication and characterization

The photovoltaic cells are fabricated as previously described. All the devices were fabricated using the mesoporous structure: FTO/TiO<sub>2</sub>-c/TiO<sub>2</sub>-m/perovskite/HTM/Au electrode. Fluorine doped tin oxide (FTO) coated glasses were etched, using zinc powder and hydrochloric acid, to obtain the desired design. The FTO substrates were cleaned by ultrasonication in acetone, isopropanol and ethanol, dried at high pure nitrogen flow and then treated by ultraviolet oxygen for 20 min. The TiO<sub>2</sub> compact layer (TiO<sub>2</sub>-c) is deposited by spin coating of 25  $\mu\text{L}$  from a solution of titanium isopropoxide in ethanol (15,4  $\mu\text{L}/\text{mL}$ ) at 4 Krpm for 10 s. Afterwards, the substrates were annealed at 450°C for 20 min and then 70 °C for 30 min. The mesoporous TiO<sub>2</sub> layer (TiO<sub>2</sub>-m) is produced with a diluted titania paste solution (210 mg in 700 mg of ethanol) spin coated directly on the compact TiO<sub>2</sub> layer and gradually annealed between 325 °C and 500 °C during 80 min. Both TiO<sub>2</sub> layer are immersed in titanium (IV) chloride TiCl<sub>4</sub> (220  $\mu\text{L}$  diluted in 100 mL of distilled water) at 70 °C for 30 min. On top of this electron transporting layer, an active layer is composed of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> perovskite is deposited using one-step deposition. The solution of perovskite is made with 40 wt% of PbCl<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I with a molar ratio of 1:3, 59 wt% of DMF and 1% of diiodooctane. The HTMs was deposited by spin-coating at 2,000 rpm for 20 s on top of the perovskite from a precursor solution of  $5.97 \cdot 10^{-2}$  mmol HTM in chlorobenzene (1 mL) with 4-tert-butylpyridine (28.8  $\mu\text{L}$ ) and bis(trifluoromethane)sulfonamide lithium salt solution (17.5  $\mu\text{L}$ , previously diluted at 530 mg/ml in acetonitrile). This step is followed by the thermal evaporation under high vacuum of a 100 nm thick gold top electrode.

The Current density-voltage characteristics were measured in ambient air (25-35°C, moisture level in the order of 50%) on un-encapsulated devices using a solar simulator (1600W NEWPORT) equipped with an AM 1.5G filter and a source meter (Keithley 2400). The active area of the devices was defined by an aperture of approximately 0.22 cm<sup>2</sup>. Spectral mismatch correction has been performed using conventional protocols.<sup>3</sup> Several devices (>3) presenting comparable features have been characterized in each case, both

in forward and backward scans (voltage scan in the order of 50 mV/s), in order to extract the dispersion of performance. The hysteresis index (HI) was calculated using a reported procedure.<sup>4</sup> The external quantum efficiency or IPCE was measured under steady-state conditions using a continuous monochromated Xenon lamp and a calibrated pico-amperemeter (Keithley 485).

**Table 1.** Summary of the properties of the investigated HTMs **Cz-N**, **Cz-Pyr** and **Spiro-OMeTAD**.

	Spiro-OMeTAD	Cz-N	Cz-Pyr
$T_d^a$		432	425
$T_g^b$	125 <sup>g</sup>	107	109
$\lambda_{max}$ (nm)	385	307	310, 324, 341
$\lambda_{onset}$ (nm)	415	407	434
$E_{gap}$ (eV) <sup>c</sup>	2.99	3.05	2.86
$E_{HOMO}$ (eV) <sup>d</sup>	-5.20	-5.19	-5.18
$E_{LUMO}$ (eV) <sup>e</sup>	-2.21	-2.14	-2.32
Hole mobility <sup>f</sup> ( $cm^2 \cdot V^{-1} s^{-1}$ )	$2.5 \times 10^{-5}$	$1.0 \times 10^{-5}$	$7.4 \times 10^{-6}$

<sup>a</sup> Determined by thermogravimetric analysis (TGA). <sup>b</sup>Determined by differential scanning calorimetry (DSC). <sup>c</sup> Determined at the UV absorption onset.;  $E_g = hc/\lambda_{onset} = 1240/\lambda_{onset}$   
<sup>d</sup>Determined by solution-based cyclic voltammetry (CV);  $E_{HOMO} = -(e(E_{1/2}) + 5.1 \text{ eV})$ . <sup>e</sup>  $E_{LUMO} = E_g + E_{HOMO}$  <sup>f</sup> Measured for pristine (dopant-free) HTM. <sup>g</sup> Data from ref. [5].

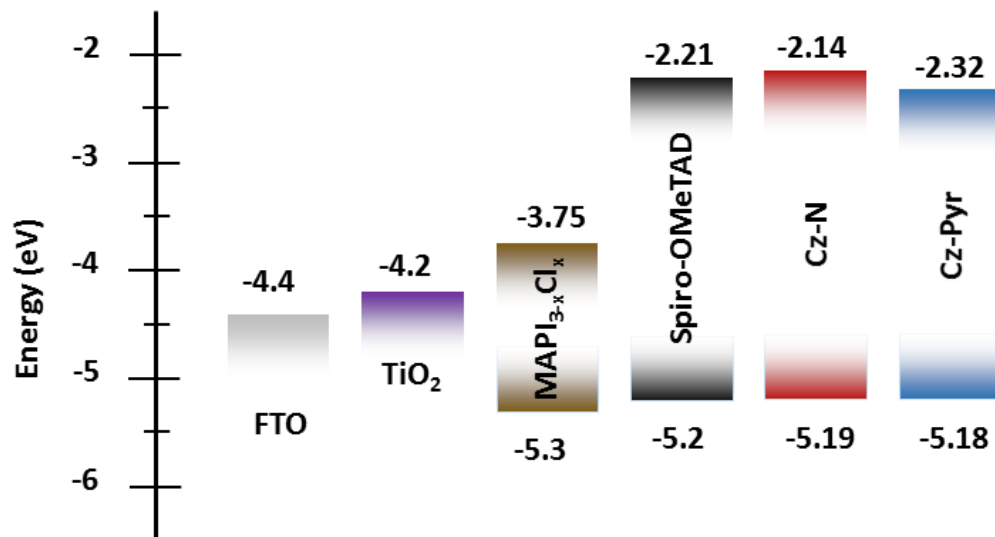


Figure S1: Energy levels of HTMs CzN, CzPyr and spiro-OMeTAD with respect to the perovskite and electrode.

## NMR spectra

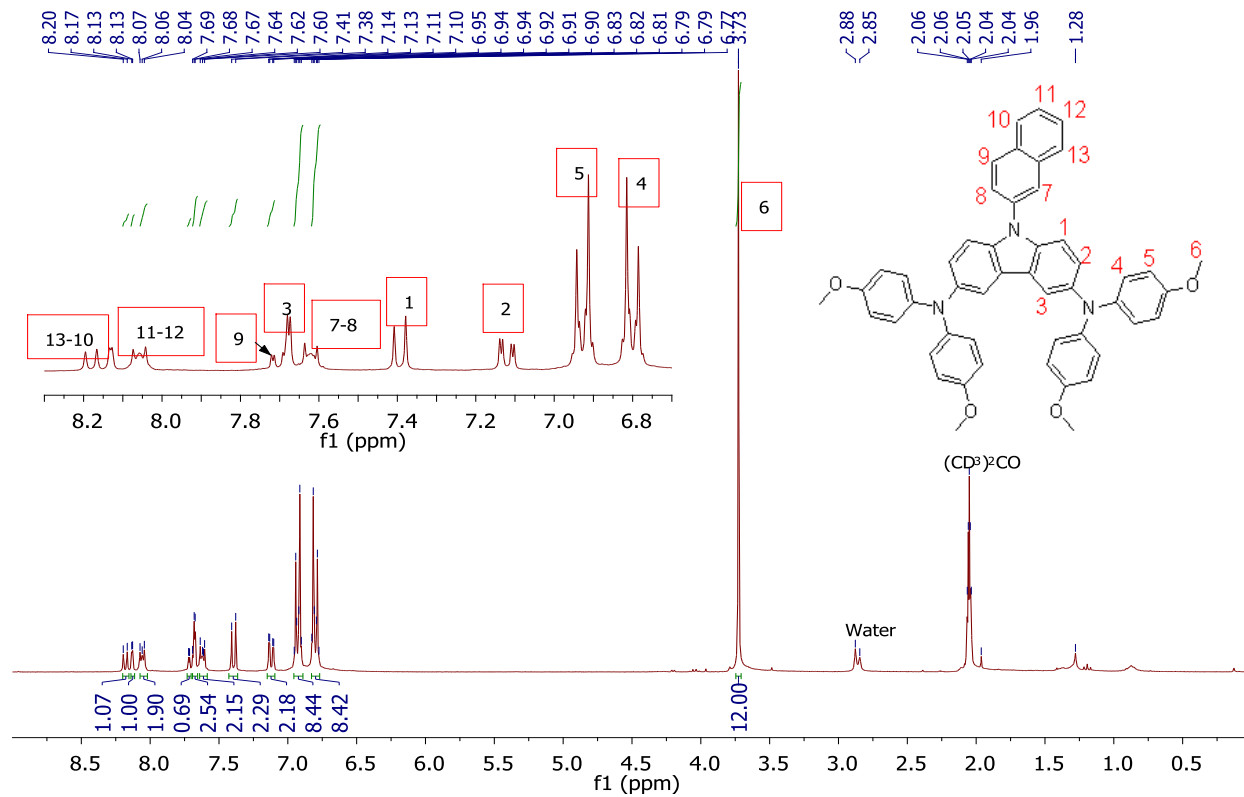


Figure S2:  $^1\text{H}$  NMR spectrum of **Cz-N** in  $(\text{CD}_3)_2\text{CO}$ .

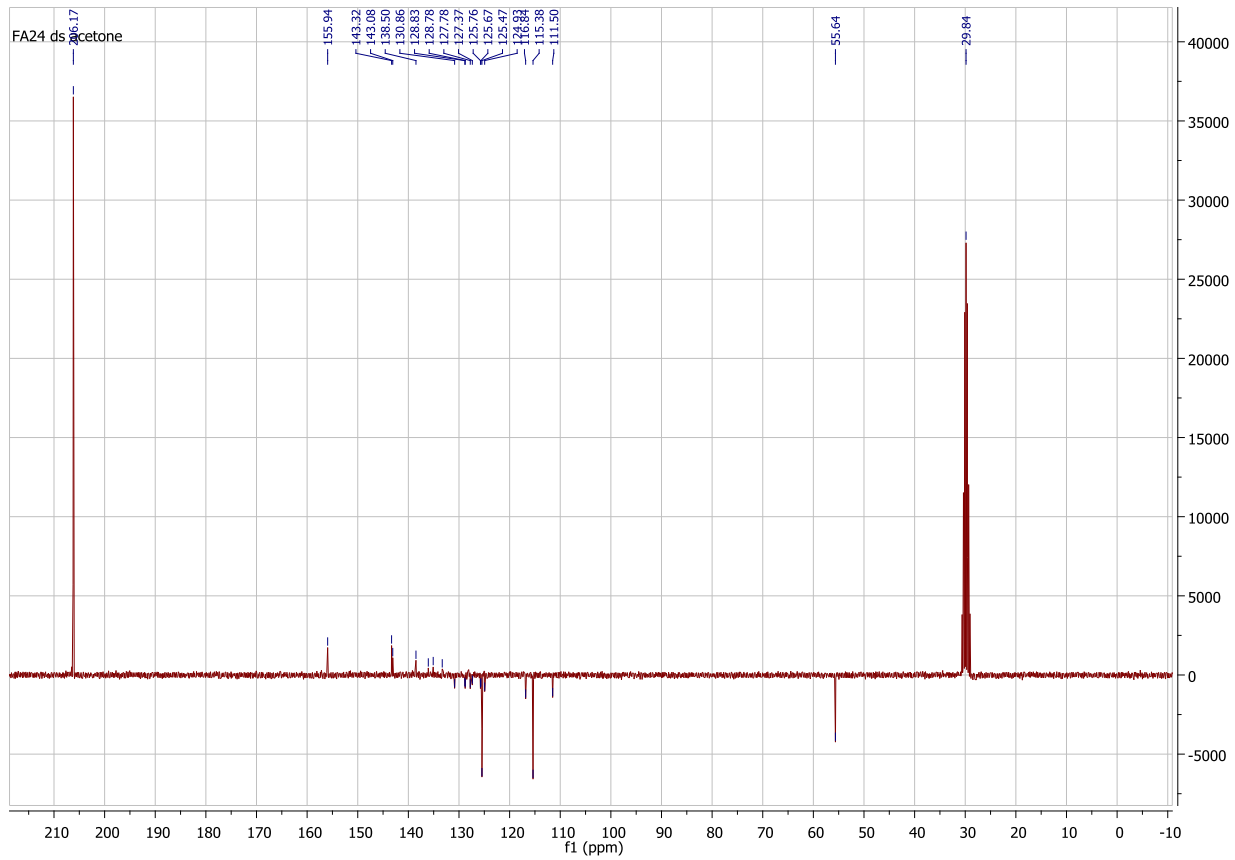


Figure S3:  $^{13}\text{C}$  NMR spectrum of **Cz-N** in  $(\text{CD}_3)_2\text{CO}$ .

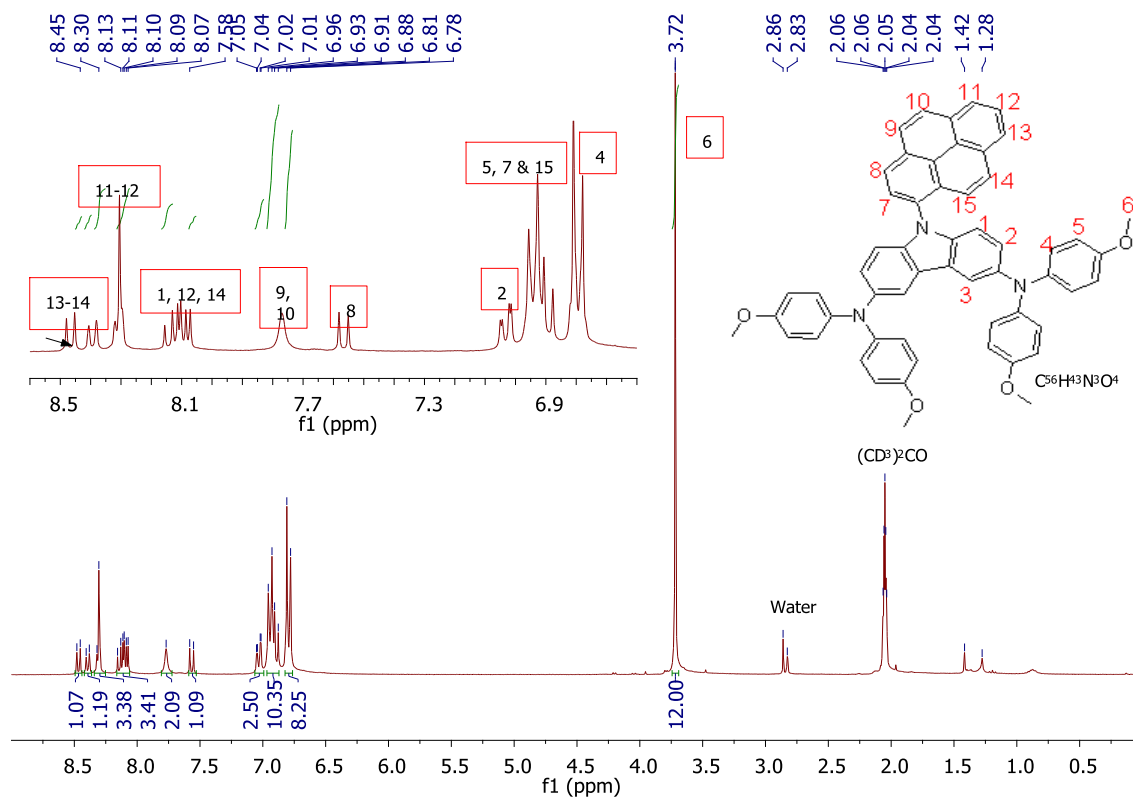


Figure S4:  $^1\text{H}$  NMR spectrum of **Cz-Pyr** in  $(\text{CD}_3)_2\text{CO}$ .



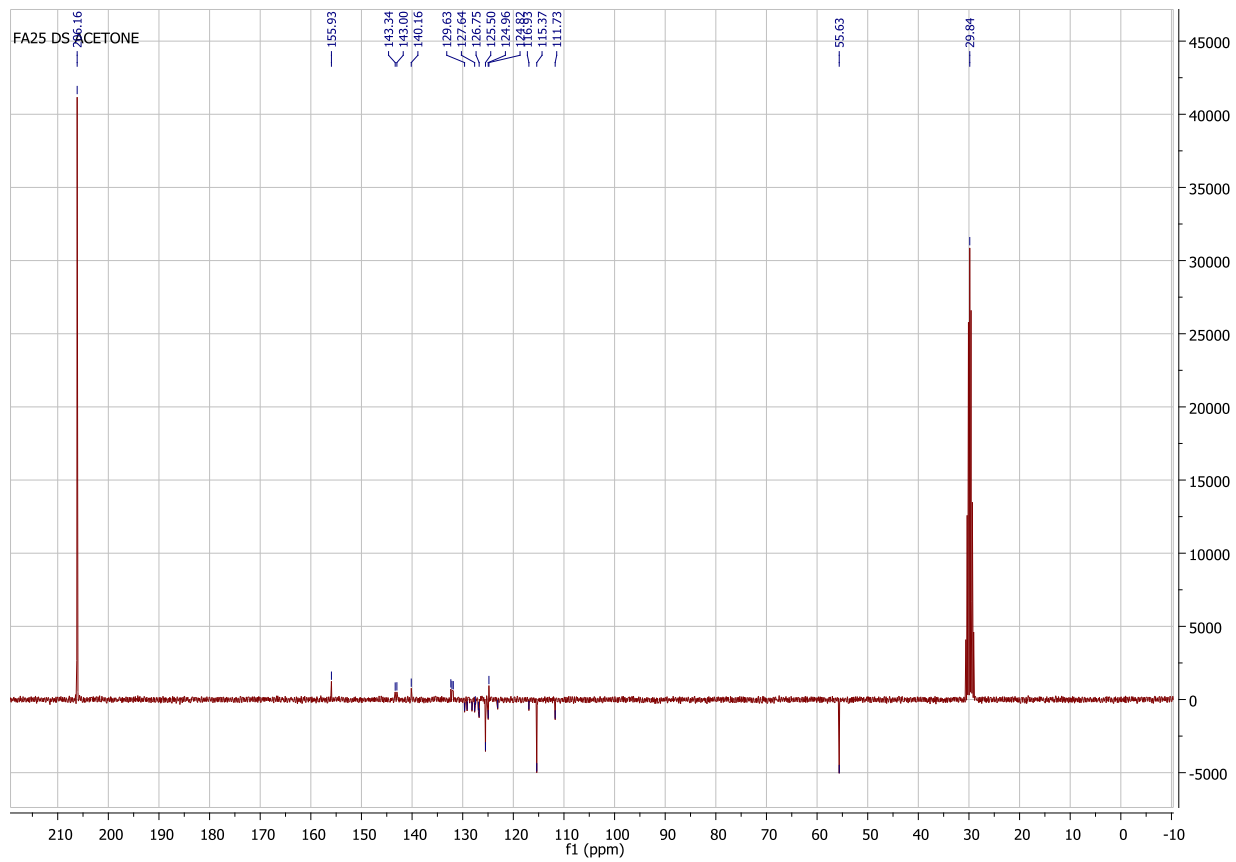


Figure S5:  $^{13}\text{C}$  NMR spectrum of **Cz-Pyr** in  $(\text{CD}_3)_2\text{CO}$ .

## Thermal properties

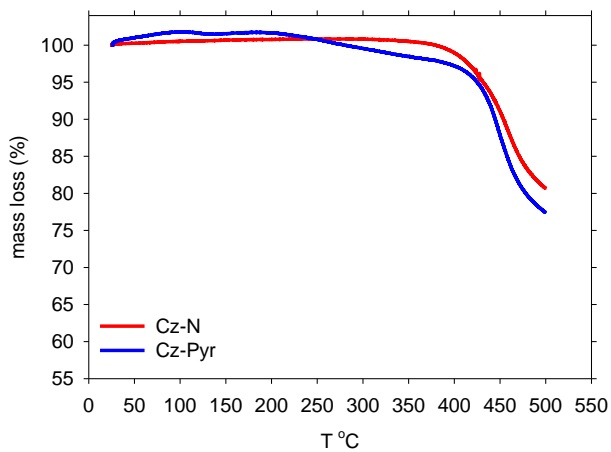


Figure S6: TGA thermograms of **Cz-N** and **Cz-Pyr**.

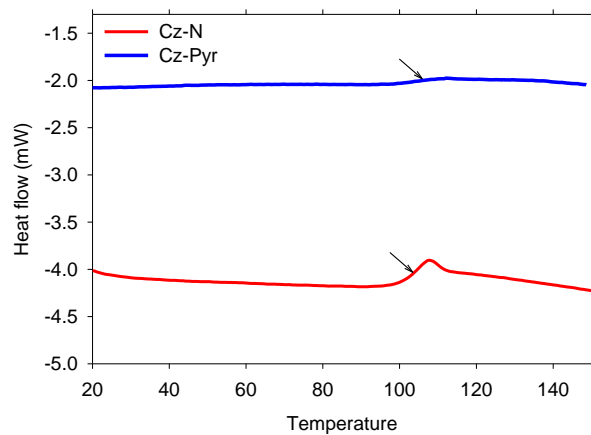


Figure S7: DSC curves of **Cz-N** and **Cz-Pyr**.

## Photovoltaic properties

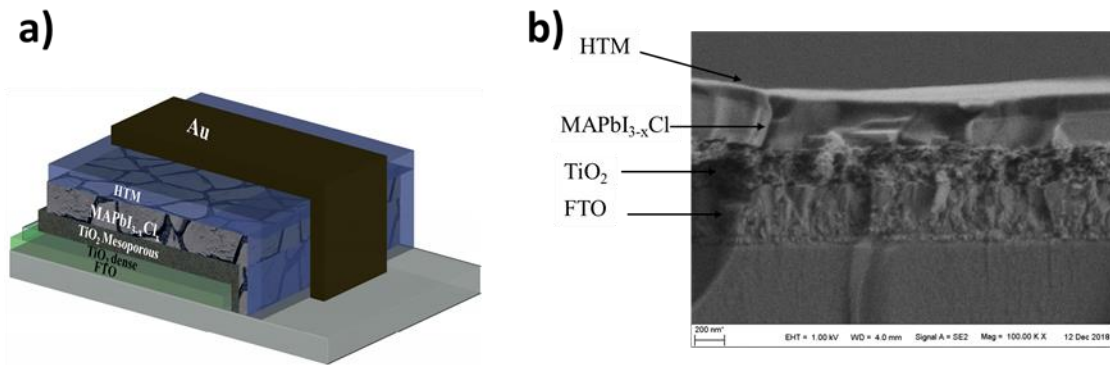


Figure S8: (a) Schematic of the device architecture FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub>/MAPbI<sub>3-x</sub>Cl<sub>x</sub>/HTM/Au and (b) cross-sectional SEM image of the complete device without gold top electrode.

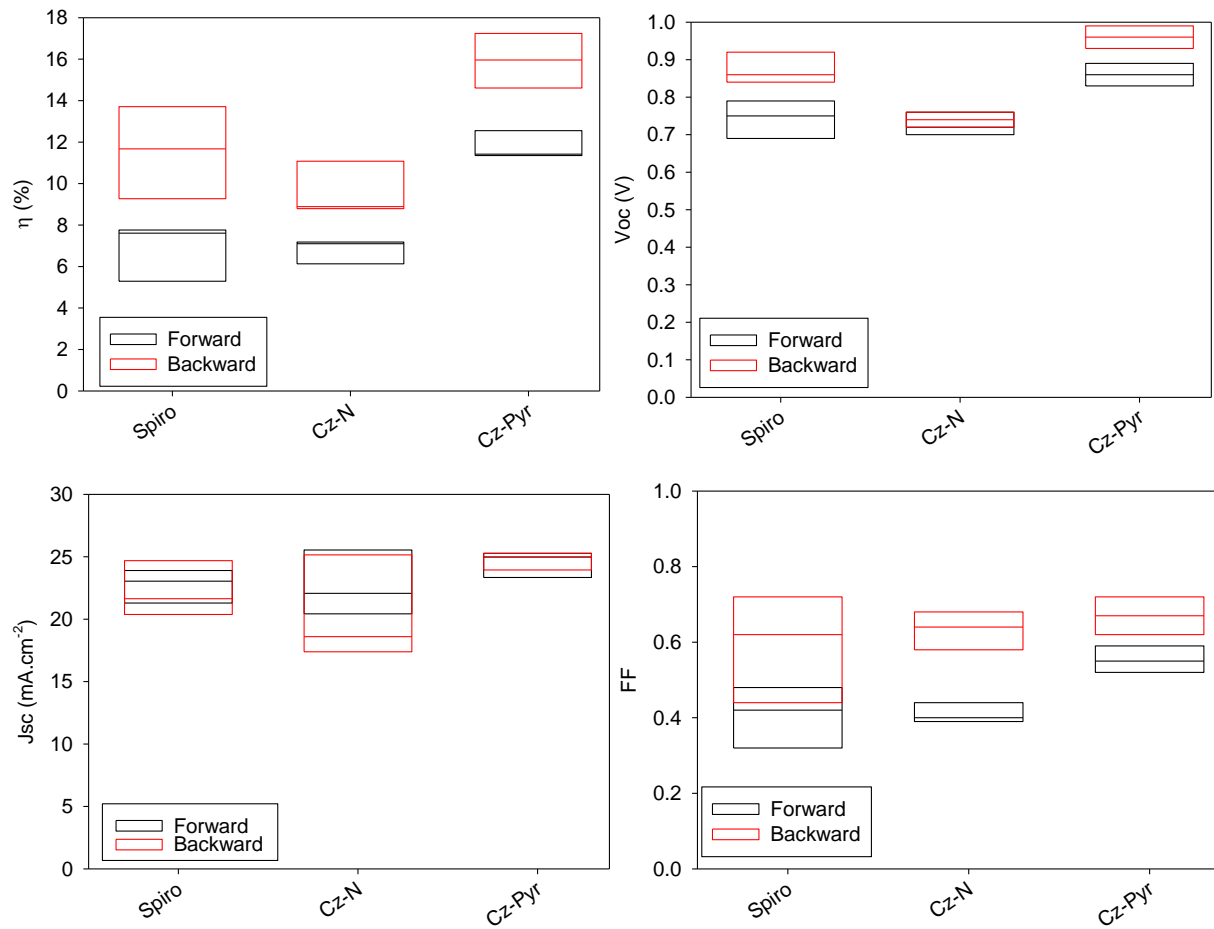


Figure S9: Statistical data of PCE, Voc, Jsc and FF for devices prepared with Spiro-OMeTAD, Cz-N and Cz-Pyr (in doped state)

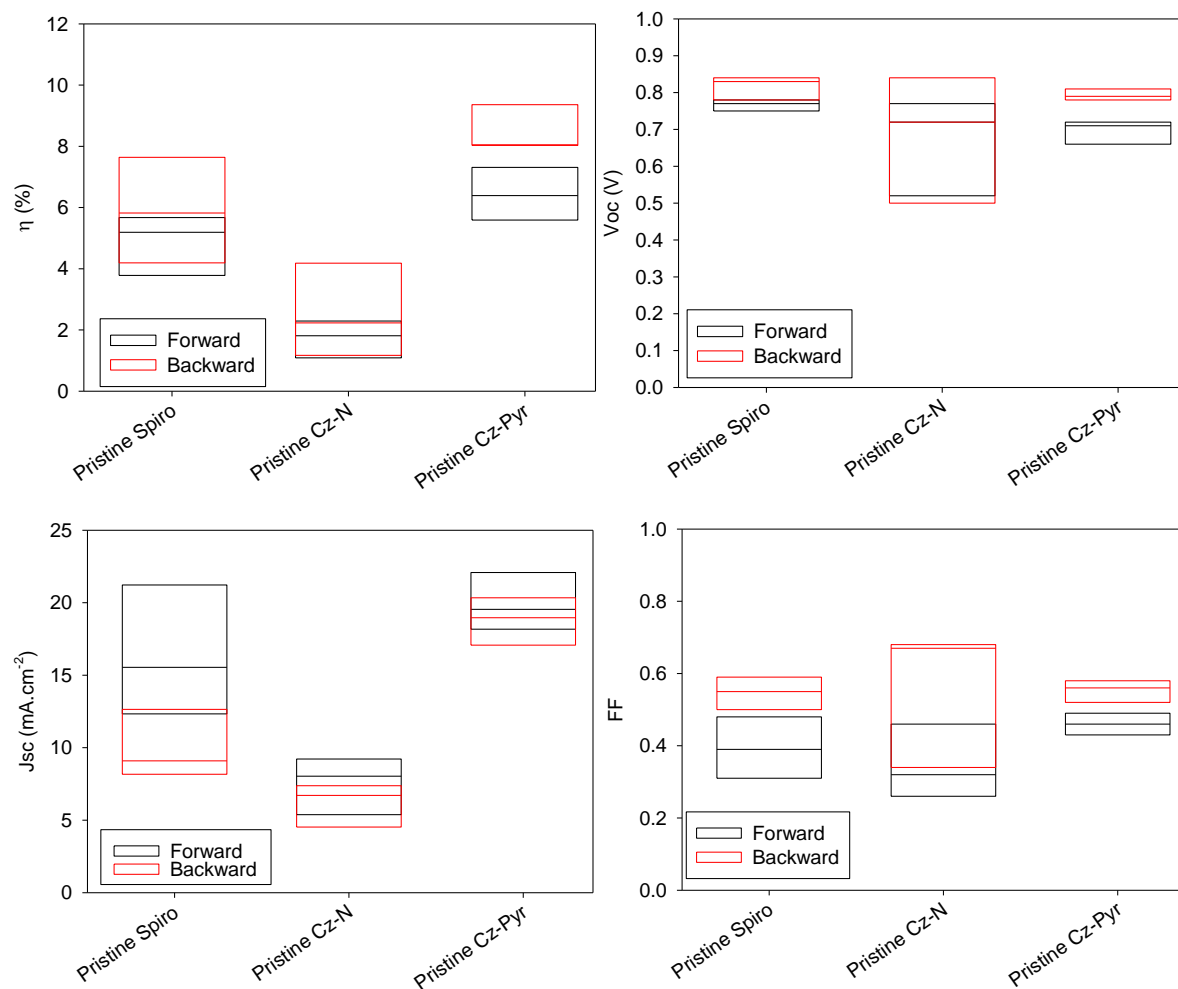


Figure S10: Statistical data of PCE, Voc, Jsc and FF for devices prepared with Spiro-OMeTAD, Cz-N and Cz-Pyr (in pristine state).

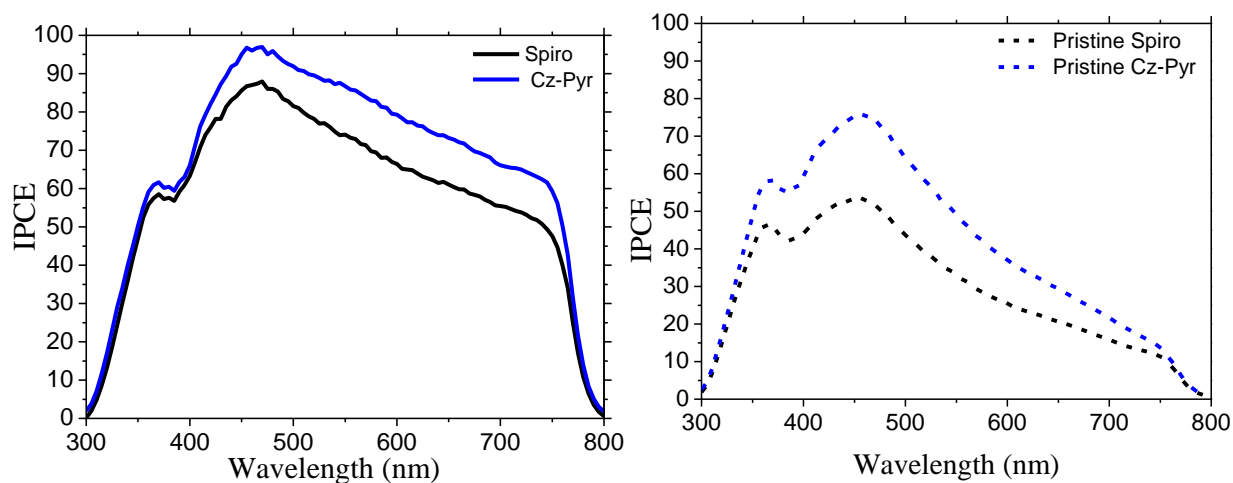


Figure S11: IPCE spectra for the champion solar cells with doped and pristine Cz-Pyr and Spiro-OMeTAD

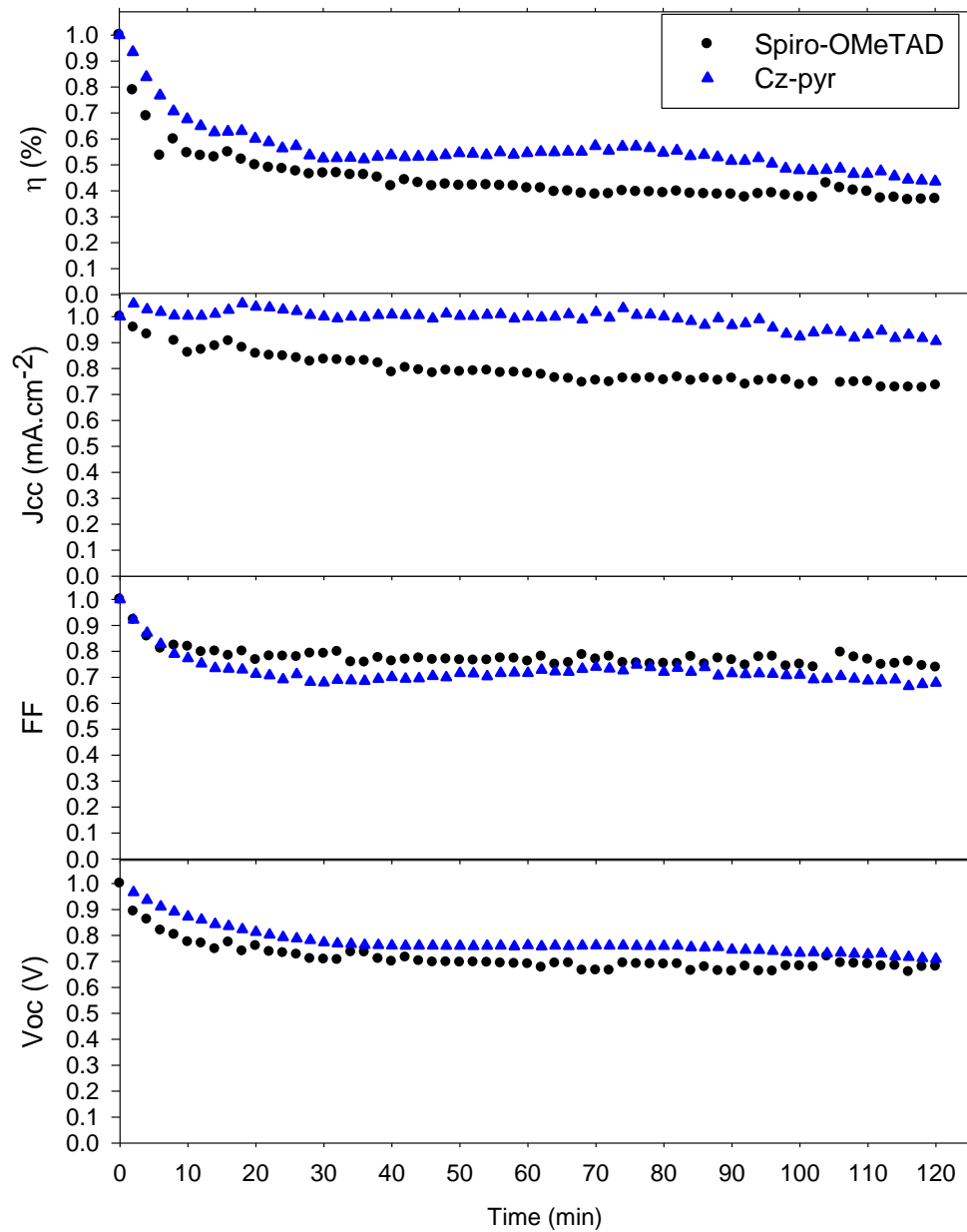


Figure S12: Normalized photovoltaic parameters as a function of aging time for the perovskite solar cells employing spiro-MeOTAD (black), Cz-Pyr (blue).

## References

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[4] R. S. Sanchez, V. Gonzalez-Pedro, J. W. Lee, N. G. Park, Y. S. Kang, I. Mora-Sero and J. Bisquert, *J. Phys. Chem. Lett.*, 2014, **5**, 2357.

[5] T. Leijtens, I.-K. Ding, T. Giovenzana, J.T. Bloking, M.D. McGehee and A. Sellinger, *ACS Nano*, 2012, **6**, 1455.