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SUPPORTING INFORMATION

A Partially-planarised Hole-transporting Quart-*p*-phenylene for Perovskite Solar Cells

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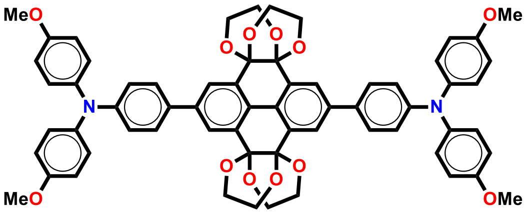
1. Experimental procedures

Commercial chemicals and solvents were used as received. Toluene was dried using an Innovative Pure Solve solvent purification system. Analytical thin layer chromatography (TLC) was carried out using aluminum sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck. Column chromatography was carried out using Silica gel 60 (40-60 µm) from Scharlab. NMR spectra in solution were recorded on a Bruker Avance 400 MHz spectrometer at 298 K using partially deuterated solvents as internal standards. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments MALDI-TOF) were recorded on Bruker REFLEX spectrometer in POLYMAT by Dr. Antonio Veloso. Absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 950 spectrometer, and a LS55 Perkin-Elmer Fluorescence spectrometer, respectively. Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with glassy carbon disc working electrode, a platinum wire counter electrode and a silver wire pseudoreference electrode. All the potential values are reported versus the redox potential of the ferrocene/ferrocenium couple. TGA/SDTA 851 Mettler Toledo was used to perform the thermogravimetric analysis (TGA) using a 10 °C min^{-1} heating rate under a nitrogen flow. The ATR-FTIR spectrum was recorded on a Bruker ALPHA ATR-IR spectrometer.The sample was sealed in an aluminium pan, and measured at a scanning rate of 10 °C min^{-1} under a nitrogen flow. X-ray single crystal diffraction experiments were performed by the X-ray diffraction unit of General Services SG-Iker (UPV/EHU) by Dr. Leire San Felices. Intensity data were collected on an Agilent Technologies Super-Nova diffractometer, which was equipped with monochromated Cu kα radiation (λ= 1.54184 Å) and Atlas CCD detector. Measurement was carried out at 150.00(10) K with the help of an Oxford Cryostream 700 PLUS temperature device. Data frames were processed (united cell determination, analytical absorption correction with face indexing, intensity data integration and correction for Lorentz and polarization effects) using the Crysalis software package. The structure was solved using Olex2 and refined by full-matrix least-squares with SHELXL-97. Final geometrical calculations were carried out with Mercury and PLATON as integrated in WinGX. The atomic force microscopy AFM were recorded with a AFM Dimension ICON (Bruker). The measurements were recorded using tesp-v2 probes in tapping mode. The specification of the equipment: tip radius (nom): 7 nm, cantilever frequency 320 kHz and a stiffness of 37 N/m.

2. Synthesis and characterisation

Synthesis of (4,4'-(5,6,12,13-tetrahydro-3b,7a:10b,14a-bis(epoxyethanooxy)pyreno[4,5-b:9,10-b']bis([1,4]dioxine)-2,9-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline)) (1)



Compound **2** (300 mg, 0.43 mmol), 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline **3** (565 mg, 1.30 mmol) and Pd(PPh_3)$_4$ (6 mg) were dissolved in dry toluene (20 mL) in a Schlenk-flask. K_2CO_3 (5 mL, 2.0 M aq.) was added to the previous solution and the reaction was stirred at 90 °C for 72 h under nitrogen. The product was extracted with chloroform (3 x 100 mL), dried over sodium sulfate and the organic phase was removed by rotary evaporation. The resulting solids were loaded onto a chromatographic column (eluent mixture hexane: ethyl acetate 4:1). The product was isolated as a yellow solid after precipitation in chloroform/methanol (287 mg, 63%). ^{1}H NMR (400 MHz; CD_2Cl_2): δ 7.98 (4H, s), 7.58 (4 H, d, *J* = 8.7 Hz), 7.14 (8 H, d, *J* = 9.0 Hz), 7.02 (4 H, d, *J* = 8.5 Hz), 6.91 (8 H, d, *J* = 8.9 Hz), 4.27 (8 H, br s), 3.90 – 3.50 (20 H, m). ^{13}C NMR (100 MHz; CD_2Cl_2) ^{13}C NMR δ 156.66, 149.16, 142.05, 140.97, 133.60, 131.97, 127.84, 127.25, 125.04, 120.43, 115.09, 93.08, 61.82, 55.82. EM (MALDI-TOF) (m/z): Calcd for $C_{64}H_{56}N_2O_{12}$: 1044.383 [M]$^+$, Found: 1044.376.

3. NMR spectra

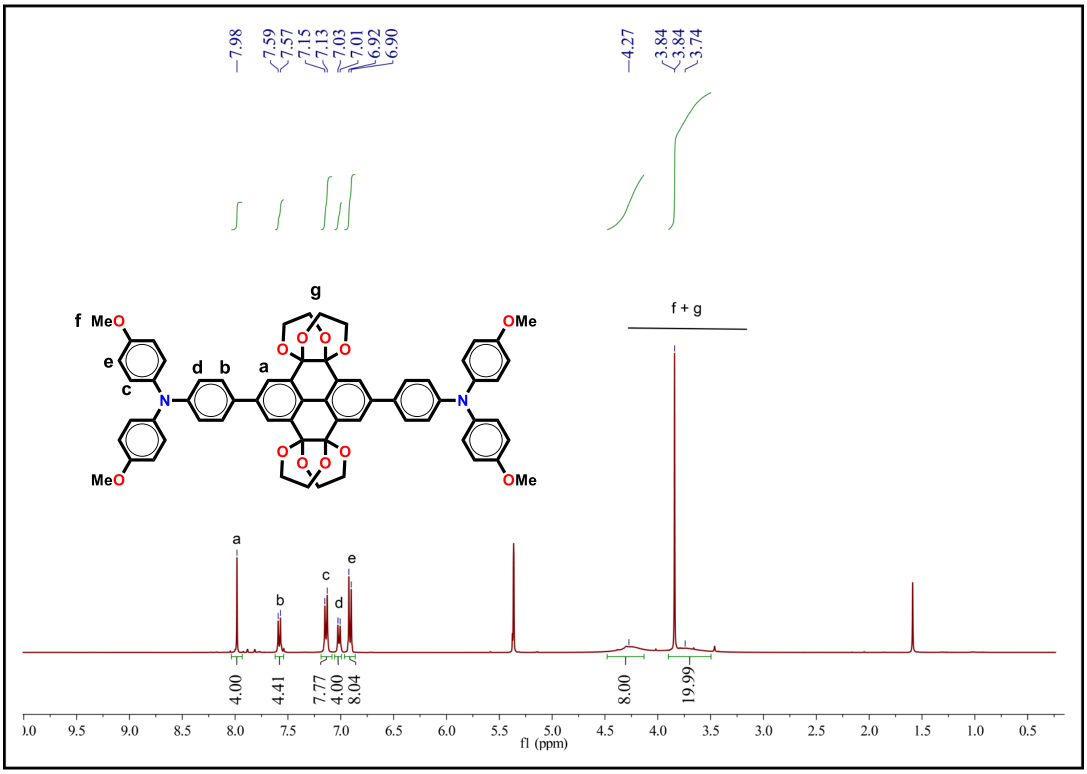


Figure S1. ^{1}H NMR of compound **1** (400 MHz, CD_2Cl_2).

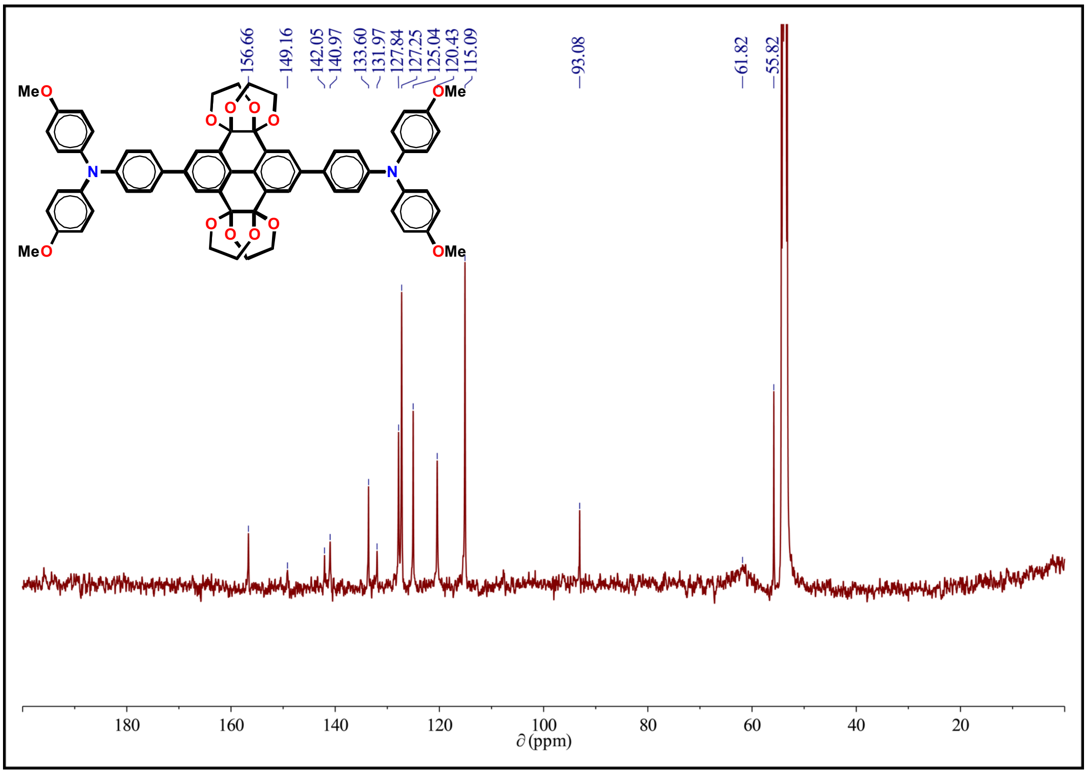


Figure S2. ^{13}C NMR of compound **1** (100 MHz, CD_2Cl_2).

4. IR Spectroscopy

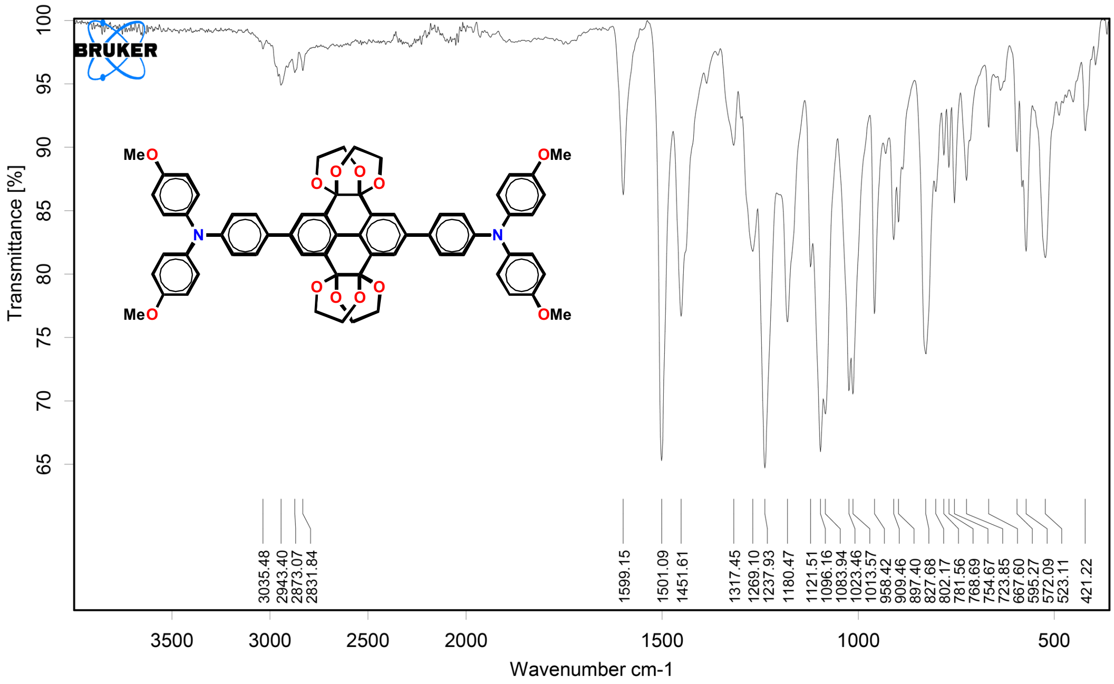


Figure S3. IR spectrum of compound **1**.

5. Thermogravimetric analysis

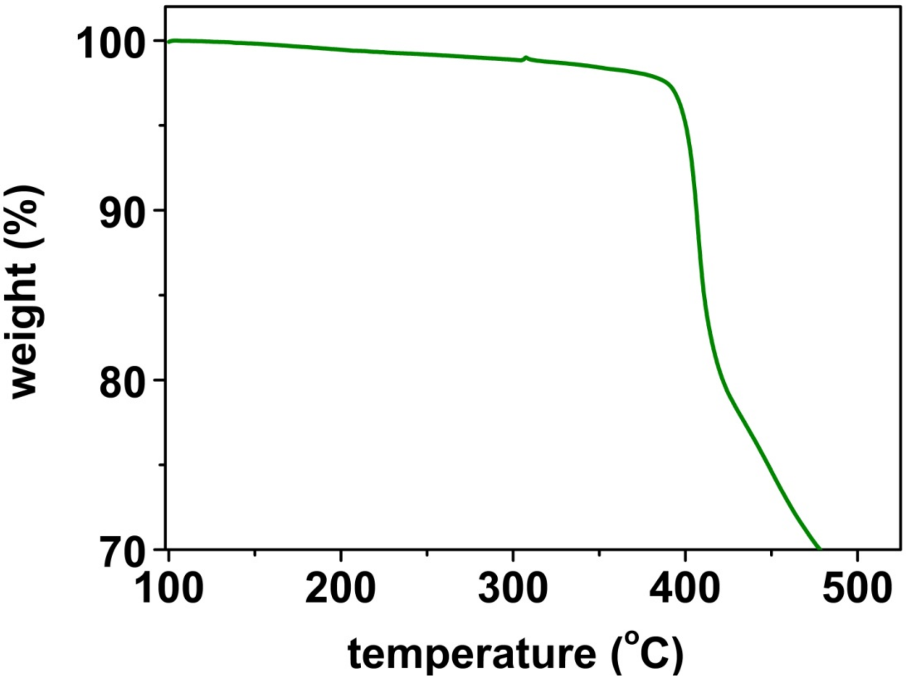


Figure S4. Thermogravimetric analysis of **1**.

6. Computational Studies

Transition #	eV	nm	Osc. Strength	Major contribs
TD-DFT 1	2.68	462	1.482	HOMO->LUMO (97%)
TD-DFT 8	3.69	336	0.8574	H-2->LUMO (31%) H-1->L+4 (53%)
EXP 1	3.24	383		
EXP 2	4.23	293		

Table S1. TD-DFT more intense transitions at the B3LYP-CH_2Cl_2-6311+g(2d,p)/B3LYP-CH_2Cl_2-6-31(d,p) level.

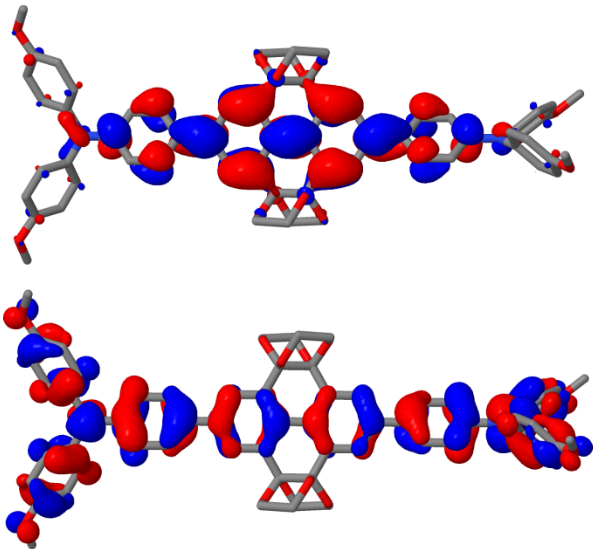


Figure S5. B3LYP-CH_2CL_2-6311+g(2d,p)/B3LYP-CH_2CL_2-6-31(d,p) transition natural orbitals accounting for 98% of for the first, most intense, transition, S0 (bottom) -> S1(top) from TD-DFT.

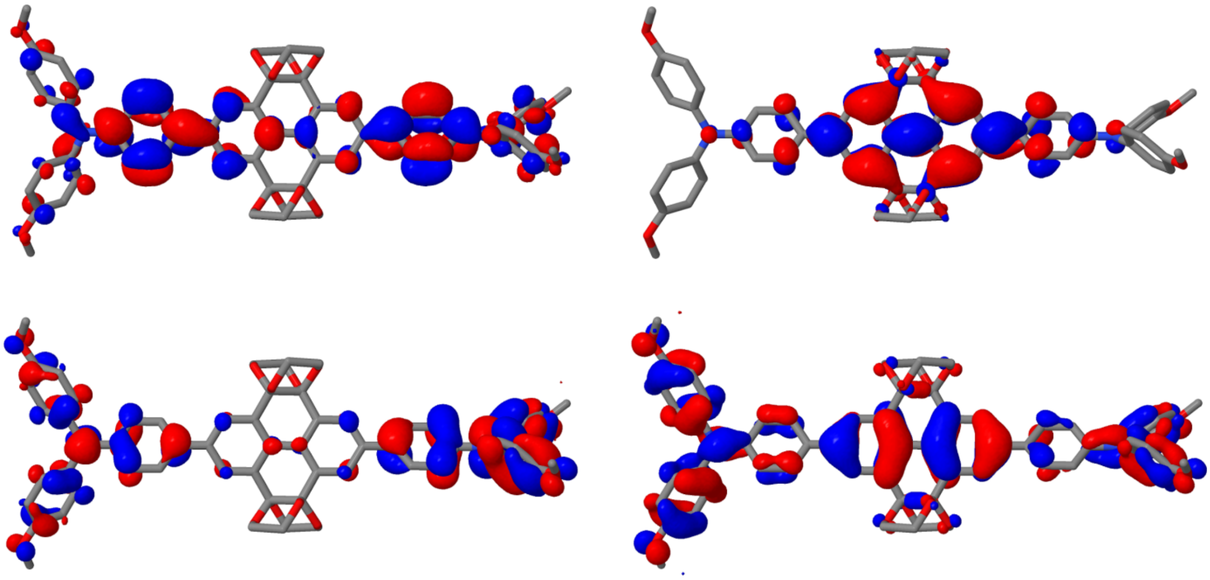


Figure S6. B3LYP-CH_2CL_2-6311+g(2d,p)/B3LYP-CH_2CL_2-6-31(d,p) four transition natural orbitals accounting for 57% (left) and 36% (right) for the second most intense transition S0 (bottom) -> S8 (top) from TD-DFT.

7. Atomic Force Microscopy

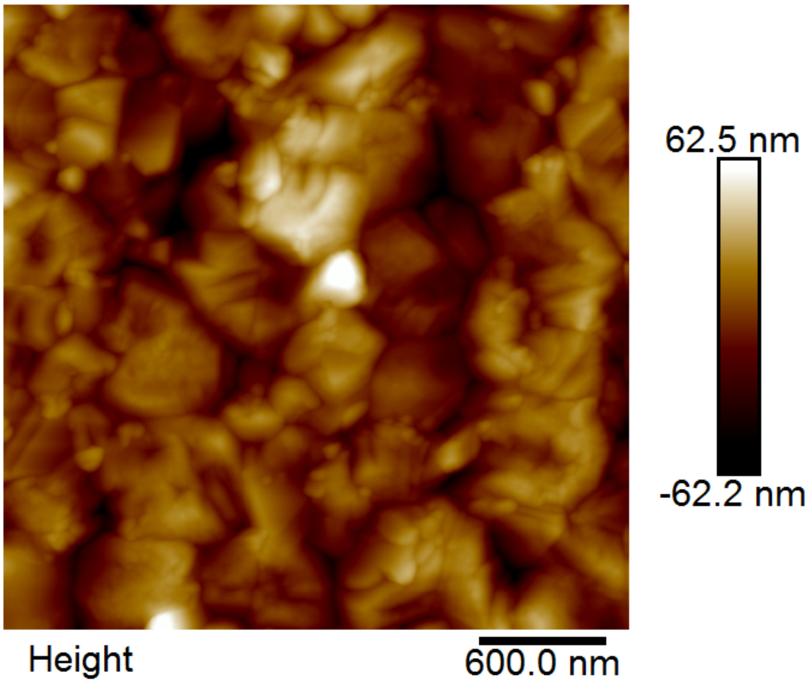


Figure S7. AFM image of **PVSK/TiO$_{2\,M}$/TiO$_{2\,C}$/FTO/Glass.** R$_A$ (nm): 13

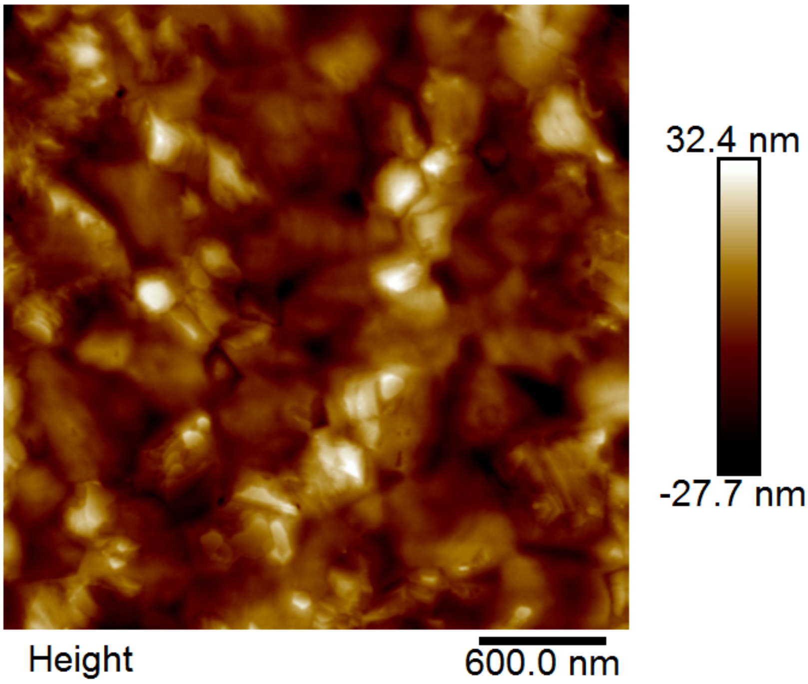


Figure S8. AFM image of **Compound 1/PVSK/TiO$_{2\,M}$/TiO$_{2\,C}$/FTO/Glass.** R$_A$ (nm): 6.4

8. Solar cell fabrication

The materials used in the photovoltaic study were obtained from commercial suppliers in high purity and used without further purification: glass/FTO (Nippon Sheet Glass), methylammonium bromide (MABr, DYESOL), formamidinium iodide (FAI, DYESOL), PbI_2 (99.99%, TCI chemicals), $PbBr_2$ (99.99%, TCI chemicals), *spiro*-OMeTAD (Solarpur), lithium bis(trifluoromethane) sulfonimidate (LiTFSI, 99.9%, Sigma-Aldrich), *tert*–butylpyridine (96%, Sigma–Aldrich), *tris*(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) tri[*bis*(trifluoromethane)sulfonimide] (FK 209, Dyenamo), DMSO (extra dry, Acros Organics), acetone (technical grade, Scharlab), chlorobenzene (extra dry, Acros Organics) and acetonitrile (extra dry, Acros Organics). The complete procedure for the preparation of the cells can be found in the SI. The morphologies and structural properties of the films were analyzed recurring to an ULTRA plus ZEISS field-emission scanning electron microscope (FESEM) and a Bruker AXS-D8 Advance X-ray diffractometer with CuKa radiation. The solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott) and it was recorded during each measurement. Current-voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate was 20 mV s^{-1} and no device preconditioning was applied before starting the measurement, such as light soaking or forward voltage bias applied for long time. The starting voltage was determined as the potential at which the cells produce 1 mA in forward bias. The cells were masked with a black metal mask (0.16 cm^2) to estimate the active area and reduce the influence of the scattered light.

Construction and testing of perovskite solar cells

Substrate preparation

FTO/Glass 10 Ω/sq was cleaned by sonication in 2% Hellmanex water solution for 15 min. After rinsing with deionised water, the substrates were further sonicated in ethanol for 15 min, and finally in acetone for the same amount of time. After a 15 min UV-ozone treatment, a TiO_2 compact layer was sprayed on FTO/Glass at 450 °C from a precursor solution of 600 µl titanium diisopropoxide bis(acetylacetonate) and 400 µl acetylacetone in 9 ml ethanol. After the deposition, the substrates were sintered at 450 °C for 30 min and left to cool down to room temperature. Then, mesoporous TiO_2 layer was deposited by spin coating for 10 s at 4000 rpm, using 30 nm particle paste (Dyesol 30 NR-D) diluted in ethanol (150 mg ml^{-1}). After the spin coating, the substrates were sintered with a heating ramp up to 450°C, at which they were left for 30 min under dry air flow. Right before perovskite deposition, mesoporous TiO_2 underwent Li-doping treatment, by spin coating a 10 mg ml^{-1} solution of Li-TFSI in acetonitrile at 3000 rpm for 10 s. The substrate was sintered again, the same way as before. After cooling down to 150°C the substrates were immediately transferred in a nitrogen atmosphere glove box to deposit the perovskite films.

Perovskite precursor solution and film preparation

The perovskite films were deposited from a precursor solution containing FAI (1 M), PbI_2 (1.1 M), CsI (0.05 M), MABr (0.2 M) and $PbBr_2$ (0.22 M) in anhydrous DMF:DMSO 4:1 (v:v). The perovskite solution was spin coated in a two-step program at 1000 and 5000 rpm for 10 and 20 s, respectively. During the second step, 150 *µ*l of chlorobenzene were poured on the spinning substrate 5 s prior the end of the program. The substrates were then annealed at 100°C for 45 min in the glove box.

Hole transporting layer and top electrode

After perovskite annealing, the substrates were cooled down for few minutes, and *spiro*-OMeTAD (Solarpur, 70 mmol in chlorobenzene) or **1** (15, 20 or 30 mmol in chlorobenzene) were spun at 4000 rpm for 20 s. Both molecules were doped with bis(trifluoromethylsulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich), tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK209, Dynamo) and 4-*tert*-butylpyridine (TBP, Sigma-Aldrich). The molar ratio of additives concerning the HTM were 0.5, 0.05, and 3.3 for Li-TFSI, FK209, and TBP respectively. The device was completed by a gold top electrode.

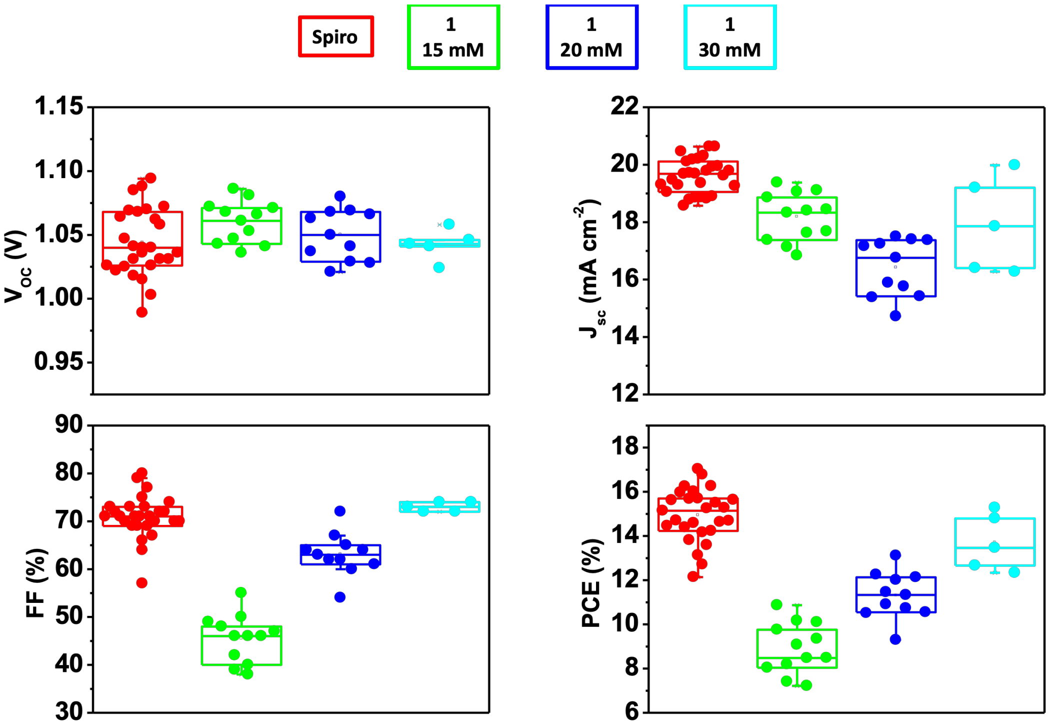


Figure S9. Statistics of the photovoltaic parameters of *spiro*-OMeTAD (red) and **1** containing devices (15 mM: green, 20 mM: blue, 30 mM: cyan).

References

(1) R. García, S. More, M.Melle-Franco, A. Mateo-Alonso, *Org. Lett.* 2014, **16**, 6096-6099

(2) K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* 2015, **137**, 16172-16178