Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2016

Supporting Information

Efficient Perovskite Solar Cell with Symmetrical Zn(II) Phthalocyanine Infiltrated Buffering Porous Al_2O_3 as Hybrid Interfacial Hole-Transporting Layer

Peng Gao,[1] Kyung Taek Cho,[1] Antonio Abate,[2] Giulia Grancini,[1] Paidi Yella Reddy,[3] Marredu Srivasu,[3] Mitsuhiro Adachi,[4] Akira Suzuki[4], Katsuya Tsuchimoto,[4] Michael Grätzel[2] and Mohammad Khaja Nazeeruddin*[1]

[1]Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland

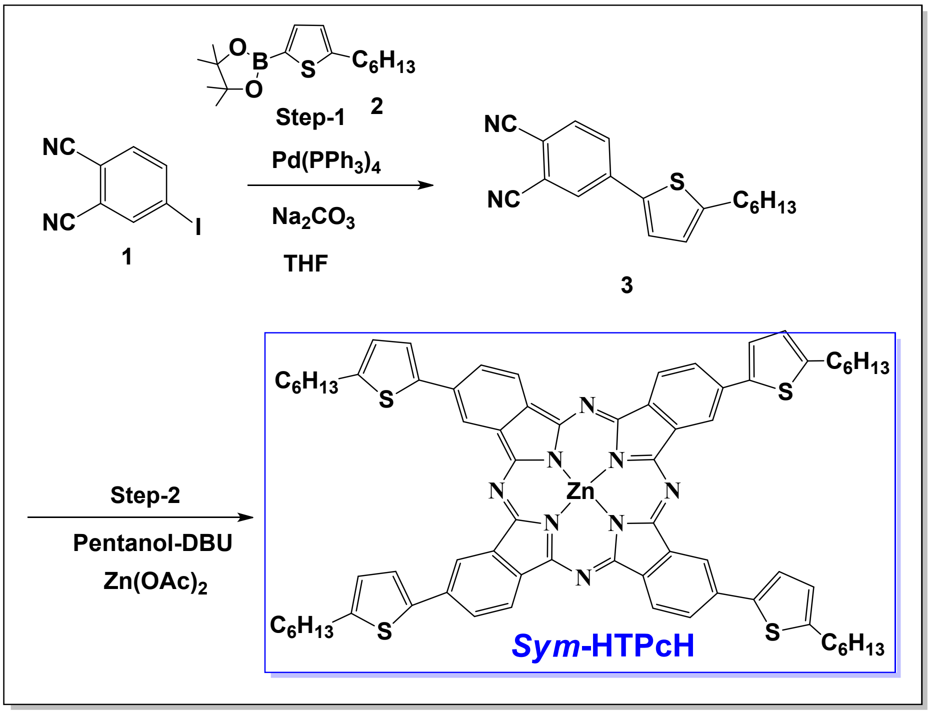
[2]Laboratory of Photomolecular Science, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015-Lausanne, Switzerland.

[3]Aisin Cosmos R&D Co LTD, Show room No 8, Block-D, HUDA Complex, Tarnaka,
Hyderabad, India

[4]Aisin Cosmos R&D Co LTD, 2-36, Hachiken-cho, Kariya City, Japan

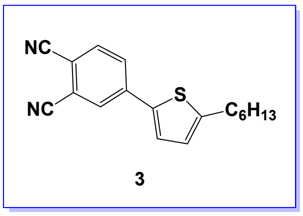
* Corresponding authors: MKN mdkhaja.nazzeruddin@epfl.ch.

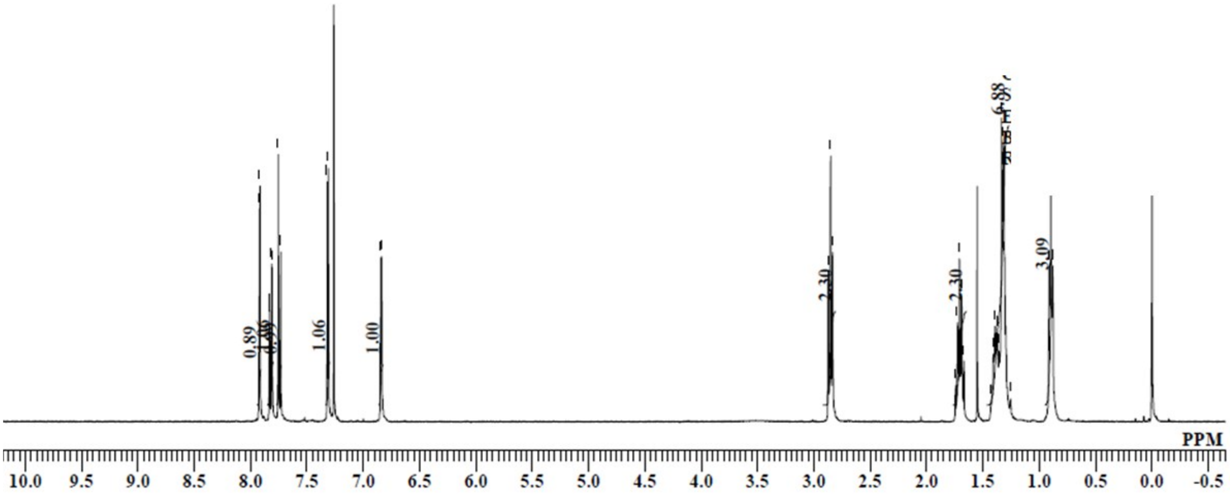
Synthetic scheme of *Sym*-HTPcH:



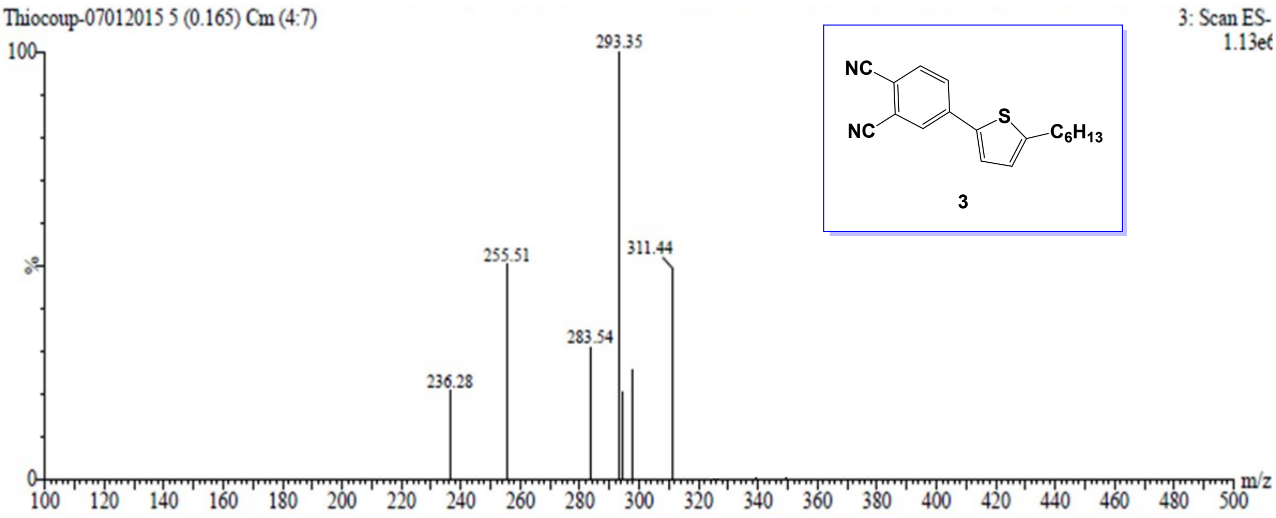
Synthesis of 4-(5-hexylthiophen-2-yl) phthalonitrile (3):

To a stirred solution of 4-iodophthalonitrile **1** (2.5 g 9.84 mmol), 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2** (3.183 g, 10.82 mmol) , water (20 mL) and Sodium bi carbonate (17.36 g, 206.6 mmol) in THF(100 mL). The reaction mixture was degassed with argon for 30 min, after $Pd(PPh_3)_4$ (1.13 g, 0.984 mmol) was added to the reaction mixture. Then, the reaction mixture was heated at reflux for 12 h under an argon atmosphere. The solvent was removed under vacuum; the crude residue was purified on a silica gel column chromatography by using Hexane/EtOAC (9:1) as an eluent to give the white solid compound **3** (2.3 g, 79.5% yield). ^1H NMR ($CDCl_3$, 400MHz): δ, ppm 7.92 (d, 1H, J = 1.8 Hz), 7.81 (dd, 1H, J = 1.8, 6.7 Hz), 7.73 (d, 1H, J = 8.5 Hz), 7.31(d, 1H, J = 3.6 Hz), 6.83 (d, 1H, J = 3.6 Hz), 2.8 (t, 2H, J = 7.6 Hz), 1.74 – 1.66 (m, 2H), 1.42-1.25 (m, 6H), 0.89 (t, 3H, J = 7.0 Hz). ESI-MS: *m/z* Calcd. For $C_{18}H_{18}N_2S$: 294.1, Found: 293.35 $[M]^-$.





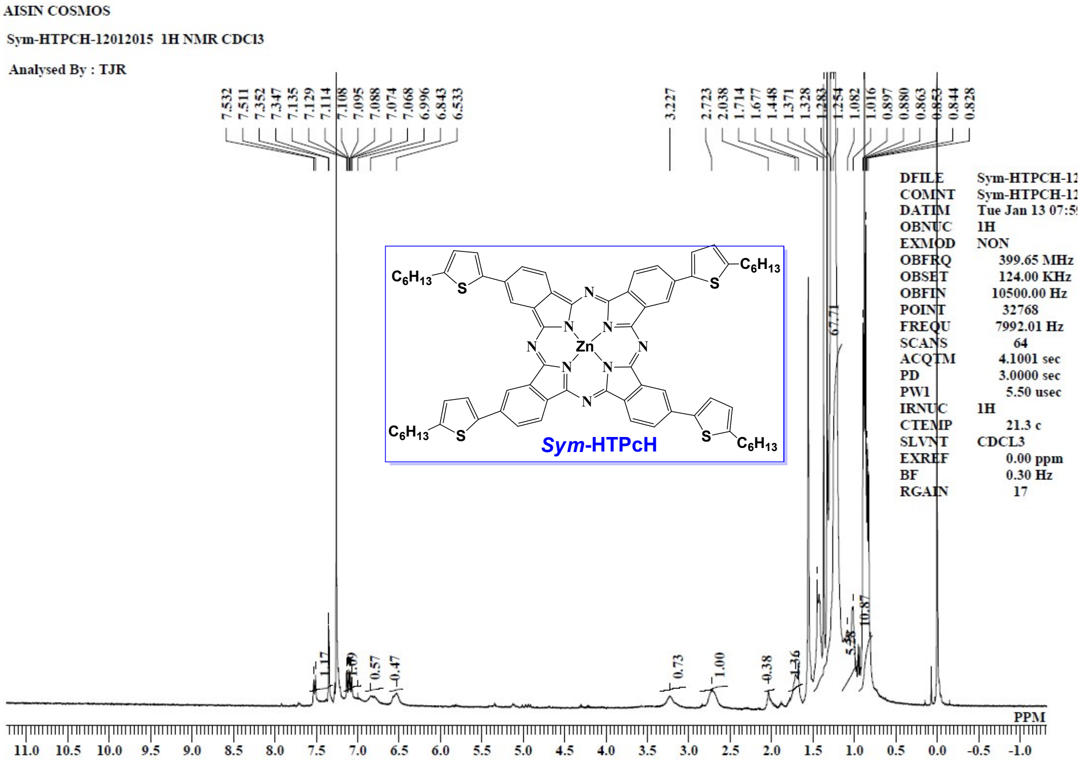
^{1}H NMR spectrum of Compound **3** in $CDCl_3$



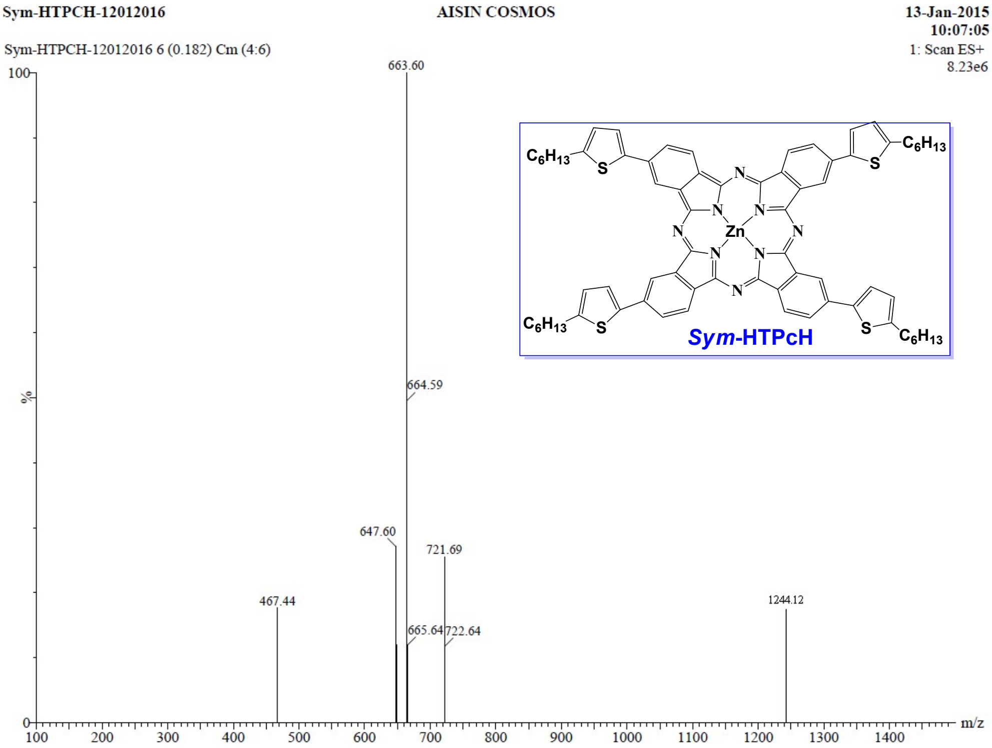
Mass spectrum of Compound **3**

Synthesis of *Sym*-HTPcH:

To a mixture of 4-(5-hexylthiophen-2-yl)phthalonitrile **3** (2.00 g, 6.80 mmol) and zinc acetate (0.596 g, 2.72 mmol) in Pentanol (20 mL). The reaction mixture was warmed to 100 ˚C at this temp the DBU (1.24 mL, 8.13mmol) was added drop wise to the reaction mixture, then the reaction mixture refluxed for 24 h, after completion of the reaction, the solvent was removed under reduced pressure; the crude residue was purified on a silica gel column chromatography by using DCM / MeOH (99:1) as an eluent to give the green solid and recrystallised from MeOH to afford ***sym*-HTPcH** (1.0 g, 11.8 % yield). ^{1}H NMR (CDCl$_3$, 400MHz): δ, ppm 7.52 (d, 1H, J = 8.5 Hz), 7.35 (d, 1H, J = 2.0 Hz), 7.09 (ddd, 1H, J = 2.4, 5.3, 6.1 Hz), 6.84 (br. S, 1H), 6.53 (br. S, 1H), 2.72 (br. S, 2H), 1.71 – 1.67 (m, 2H), 1.44-1.25 (m, 6H), 0.89-0.82 (m, 3H) [Not properly integrated]. ESI-MS: m/z Calcd. For $C_{72}H_{72}N_8S_4Zn$:1243.0, Found: 1244.12[M] $^+$.UV-vis:(0.01mM) in THF: λ_{max}= 630 (ε = 53, 951), & 700 nm (ε = 2, 92, 309) cm^{-1}.



^{1}H NMR spectrum of ***Sym*-HTPcH** in CDCl$_3$.



MASS spectrum of ***Sym*-HTPcH**

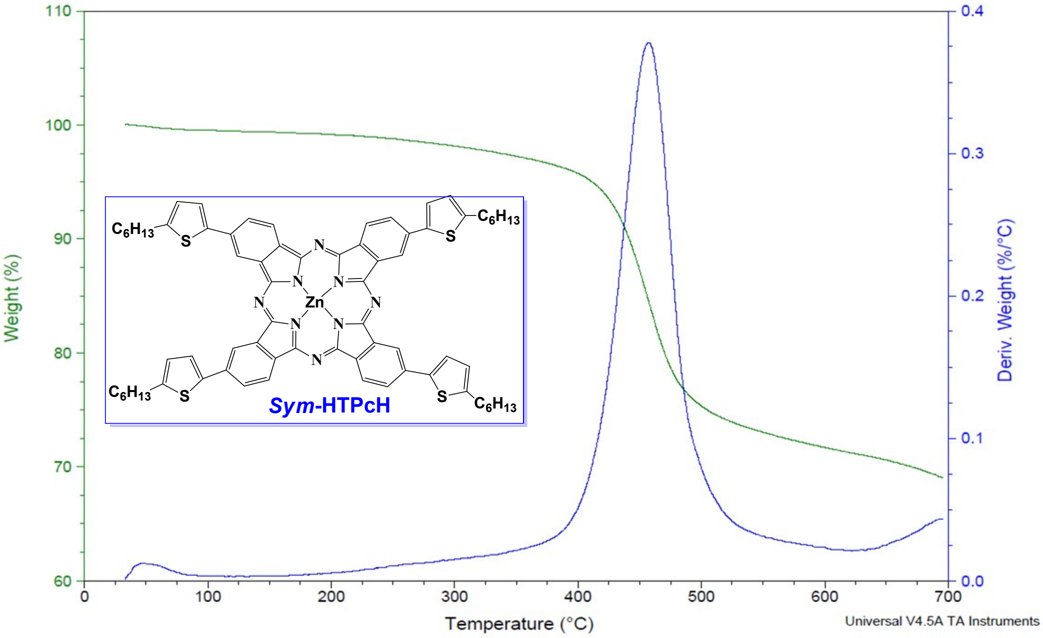


Figure S1. **TG/DTG** curves of ***Sym*-HTPcH**.

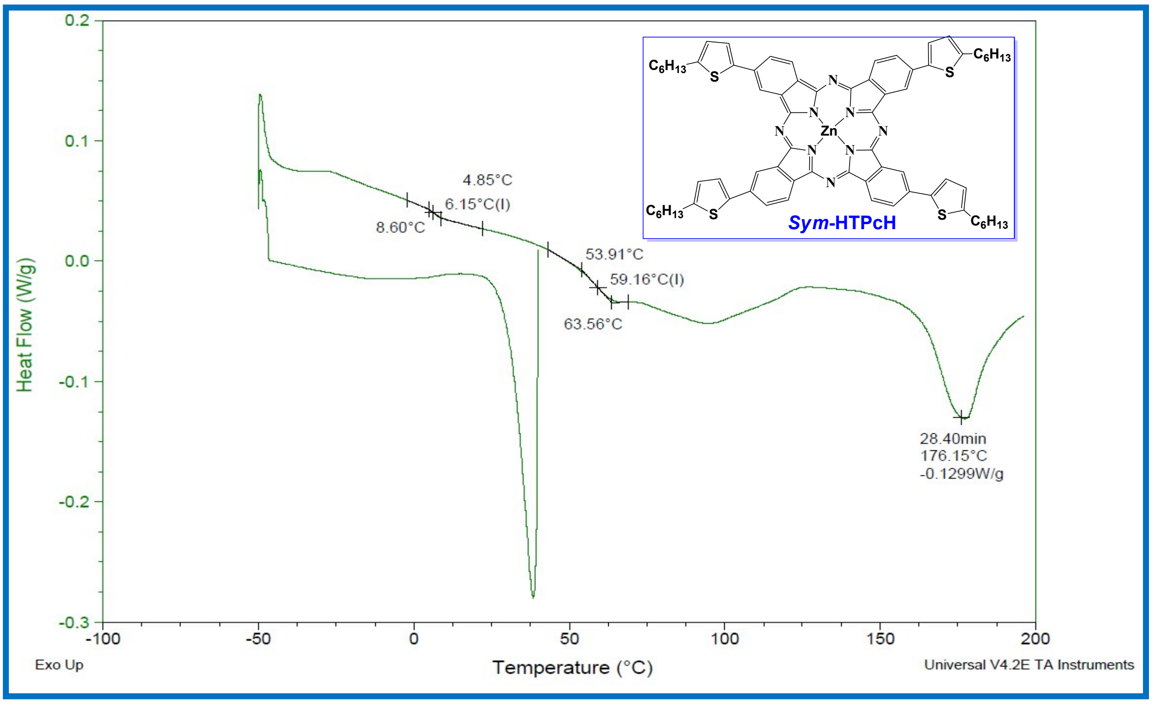


Figure S2. **DSC** curves of ***Sym*-HTPcH**.

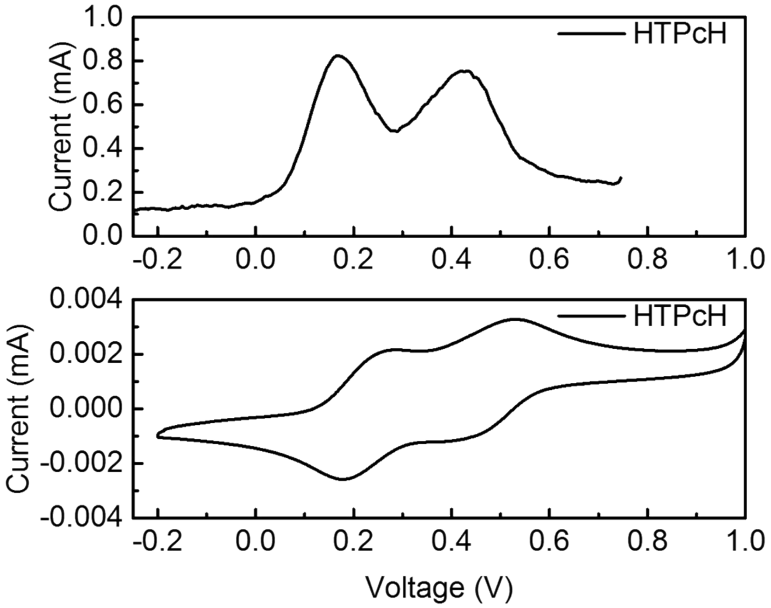


Figure S3. CV and DPV measurement of ***Sym*-HTPcH** with ferrocene as an internal standard and platinum wire as reference electrode.

Solar cells fabrication. Devices were fabricated on fluorine doped tin oxide (FTO) coated glass substrates. The substrates were cleaned sequentially with Hellmanex and isopropano in ultrasonic bath for 30 min, then washed with acetone and finally with UV/ ozone surface cleaning for 15 min. A 30 nm TiO_2 compact layer was deposited on FTO via spray pyrolysis at 450°C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. After the spraying, the substrates were left at 450°C for 5 min, then they were left to cool down to room temperature. Mesoporous TiO_2 layer was deposited by spin coating for 20 s at 4000 rpm with a ramp of 2000 rpm s^{-1}, using 30 nm particle paste (Dyesol) diluted in ethanol to achieve 150 nm thick layer. After the spin coating, the substrate was immediately dried at 100°C for 10 min and then sintered again at 500°C for 30 min, under dry air flow. Upon cooling to room temperature, the perovskite layer was deposited in a nitrogen-filled glovebox by spin coating the perovskite precursor solution. The latter was prepared dissolving a stoichiometric amount (1:1 molar ratio) of lead iodide and methyl ammonium iodide in dimethylsulfoxide at a concentration of 1.1 M of each component. The spin coating program includes two steps, first 1000 rpm for 10 s with a ramp of 200 rpm s^{-1}, then 6000 rpm for 30 s with a ramp of 2000 rpm s^{-1}. 10 s before the end of the spin-coating program, chlorobenzene was gently dropped on the spinning substrate for 2 s using an automatic dispenser. The substrate was then heated at 100°C for 1 h on a hotplate in the nitrogen-filled glovebox.

For the spiro-OMeTAD, the HTM solution was prepared dissolving the molecule in chlorobenzene at concentration of 70 mM, with the addition of 50 mol% of bis(trifluoromethanesulfonyl)imide (Aldrich) from a stock solution of 1.8 M in acetonitrile), 330 mol% of tert-butylpyridine (Aldrich) and 2 mol% of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)- cobalt(III) Tris(bis(trifluoromethylsulfonyl)imide) (Dyesol) from a stock solution 0.25 M in acetonitrile. The HTM layer was deposited on the top of the perovskite layer by spin coating from solution at 4000 rpm for 20 s with a ramp of 2000 rpm s^{-1}.

For device prepared using **HTPcH**, we deposited a thin alumina mesoporous layer directly on the top of the perovskite layer. This layer was prepared by spincoating a colloidal dispersion of

< 50 nm Al_2O_3 nanoparticles at 2 wt% in isopropanol at 2000 rpm. The **HTPcH** solution was prepared dissolving the molecule in chlorobenzene at concentration of used 30 mM, with the same doping composition we used for the spiro-OMeTAD solution. The HTM layer was finally deposited by spin coating from solution at 4000 rpm for 20 s with a ramp of 2000 rpm s^{-1}. Finally, 80 nm of gold was deposited by thermal evaporation under high vacuum, using a shadow masking to pattern the electrodes.

Solar cells characterisation. A ZEISS Merlin HR-SEM was used to characterize the morphology of the device cross-section. Current-voltage characteristics were measured in air under AM 1.5 simulated sunlight with a potentiostat (Keithley). The light intensity was measured for calibration with an NREL certified KG5 filtered Si reference diode. The solar cells were masked with a metal aperture of 0.16 cm^2 to define the active area. The current-voltage curves were recorded scanning at 0.01 V s^{-1}.