Herein, we describe the synthesis of a hole transporting material based on a partially planarised quart-p-phenylene core incorporating tetra-ketal and diphenylamine substituents that show optimal energy levels and solubility for perovskite solar cell applications. Triple-cation perovskite devices incorporating such quart-p-phenylene derivative show power-conversion efficiencies, short circuit currents, open circuit voltages, and fill factors that are comparable to those of spiro-OMeTAD.
A Partially-planarised Hole-transporting Quart-p-phenylene for Perovskite Solar Cells

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Abstract

Herein, we describe the synthesis of a hole transporting material based on a partially planarised quart-p-phenylene core incorporating tetraketal and diphenylamine substituents that show optimal energy levels and solubility for perovskite solar cell applications. Triple-cation perovskite devices incorporating such quart-p-phenylene derivative show power-conversion efficiencies, short circuit currents, open circuit voltages, and fill factors that are comparable to those of spiro-OMeTAD.
In recent years, perovskite solar cells (PSCs) have rapidly emerged as a promising technology in photovoltaics. Current state-of-the-art PSCs have surpassed the power-conversion efficiencies (PCEs) of organic solar cells and dye-sensitized solar cells and recently surpassed those reached with the current market leader polycrystalline silicon. In PSCs, light is harvested by organic-inorganic metal halide perovskites, which show strong absorption in the UV-visible-near infrared range, large free charges diffusion lengths, small exciton binding energy, and low-cost fabrication. The free charges formed in the perovskite after the absorption of light are separated in electrons and holes, which are respectively transported to the electrodes by an electron transporting material (ETM) and a hole transporting material (HTM) to close the circuit.

Currently, the most commonly used small molecule as HTM is 2,2′,7,7′-tetrakis(N,N-bis(p-methoxyphenyl)amino)-9,9′-spirobifluorene (spiro-OMeTAD) (Figure 1). However, the long synthetic route of spiro-OMeTAD limits its suitability for large-scale industrial applications. Furthermore, the exploration of other HTM provides key and valuable information for the design of new materials with improved processability and performance for PSCs. Spiro-OMeTAD is constituted by two fluorene units in a spiro configuration with two triphenylamines at the 2 and 7 positions. Its electronic structure is analogous to that of a planarised p-biphenylene. Oligo- and poly-p-phenylenes are a class of conjugated materials that have received much interest as hole transporting materials, since the HOMO level can be controlled with the number of rings in the p-phenylene chain. Nevertheless, the phenylene rings adopt a non-planar conformation with a dihedral angle that (i) partially interrupts the longitudinal conjugation resulting in a lower effective conjugation, and also (ii)
Figure 1. Structure of spiro-OMeTAD and of quart-p-phenylene 1
interferes with the co-facial packing optimal for charge transport. Therefore, planarised $p$-phenylenes with a higher effective conjugation are attractive candidates for the design of efficient HTM.

Herein, we report the synthesis and characterisation of a novel HTM based on a partially planarised quart-$p$-phenylene structure (1), in which the two central rings are embedded on a planar tetrahydropyrene core with four lateral tetraketals (Figure 1) that enhance the stability of the tetrahydropyrene core against oxidation and also that can potentially passivate the perovskite surface by coordination$^{32-36}$. Furthermore, electron donating diphenylamine substitutents have been introduced in order to obtain optimal energy levels and solubility for solution-processable HTMs. Quart-$p$-phenylene 1 was investigated as a HTM in PSCs with a fluorine-doped tin oxide (FTO)/compact TiO$_2$/mesoporous TiO$_2$/Cs$_x$(MA$_{0.17}$FA$_{0.83}$)$_{(100-x)}$Pb$(I_{0.83}Br_{0.17})_3$/1/Au configuration that show PCE, short circuit current ($J_{SC}$) open circuit voltage ($V_{OC}$) and fill factor ($FF$) values that are comparable to those of spiro-OMeTAD.
Scheme 1. Synthesis of 1. Reaction conditions: i) K$_2$CO$_3$, Pd(PPh$_3$)$_4$, toluene, water, 90°C, 72 hours, 63%.
Quart-p-phenylene 1 is easily obtained in a gram-scale via Suzuki cross-coupling reaction between tetrahydropyrene 2 and triarylamine 3 in a good yield (63%). Precursors 2\textsuperscript{37-40} and 3\textsuperscript{41} were prepared from commercially available compounds in three and one steps, respectively. Quart-p-phenylene 1 showed a high stability under ambient conditions without any sign of decomposition after several months. Also, thermogravimetric analysis of 1 reveals a thermal stability up to \textit{circa} 280 °C (Figure S4). Moreover, quart-p-phenylene 1 was soluble in common organic solvents (toluene, chlorobenzene, CH\textsubscript{2}Cl\textsubscript{2}, and CHCl\textsubscript{3}).

The structure of quart-p-phenylene 1 was determined by \textsuperscript{1}H-NMR, \textsuperscript{13}C-NMR, HRMS and single crystal X-ray diffraction. Single crystals of 1 were obtained by slow vapor diffusion of EtOH into a solution of 1 in CHCl\textsubscript{3}. The X-ray structures show that the two central rings on the tetrahydopyrene core are almost co-planar with a small torsion angle of 8° as an effect of the ketal substituents (Figure 2a). On the other hand, the torsion angle of the more external phenyl rings of the quart-p-phenylene core with the tetrahydropyrene reside is substantially higher (24°) as an effect of the free rotation. The distance of the central C-C bond between the phenyl rings of the tetrahydropyrene core was 1.468 Å, in agreement with the bond distance observed in tetrahydropyrene (1.470 Å)\textsuperscript{42} for the same bond, which is slightly larger than that in pyrene (1.422 Å).

The optical properties of 1 were investigated in solution. Figure 2b shows the UV-Vis absorption and the normalized photoluminescence spectra of 1 in CH\textsubscript{2}Cl\textsubscript{2}. Quart-p-phenylene 1 absorbs light preferentially in the UV region of the electromagnetic spectrum, thus avoiding overlapping with the absorption of triple cation perovskite (\textit{vide infra}). It shows two main absorption bands centered at 293 and 398 nm with large absorption coefficients, 47,716 and 68,695 L mol\textsuperscript{-1} cm\textsuperscript{-1}, respectively. The photoluminescence spectrum of 1 in CH\textsubscript{2}Cl\textsubscript{2} ($\lambda_{\text{ex}} = 370$
nm) exhibited a single featureless emission band centered at 515 nm with a large Stokes shift of 117 nm.

To understand the nature of the main electronic transitions in 1, time-dependent density functional theory (TD-DFT) was carried out in CH$_2$Cl$_2$ with the B3LYP Hamiltonian with a 6-311+g(2d,p) basis set on minimized geometries at the B3LYP-CH$_2$Cl$_2$-6-31(d,p) level (Supporting Information, Table S1). In addition, the natural transition orbitals were also computed to aid the visualization of the transitions (Figures S5 and S6). The calculations reproduced the difference in energy between both transitions (~ 1 eV). The experimental band at 383 nm is computed predominantly as the HOMO→LUMO transition (97%) with an oscillator strength of 1.482, whereas the experimental band at 293 nm is computed as the sum of two electronic transitions HOMO→2→LUMO (31%) and HOMO→1→LUMO+4 (53%), with an oscillator strength of 0.857.

The electrochemical properties of 1 were investigated by cyclic voltammetry in a CH$_2$Cl$_2$ solution using nBu$_4$NPF$_6$ (0.1 M) as the electrolyte (Figure 2c) in a three-electrode cell with a glassy carbon disk electrode as the working electrode, a Ag wire reference electrode and a Pt counter-electrode. The potential values are given versus the redox potential of the ferrocene/ferrocenium couple, which was used as an internal standard. Quat-$p$-phenylene 1 showed a reversible peak at $E_{1/2} = +0.23$ V. No reduction processes were observed within the solvent-supported electrolyte window.

The optical energy gap ($E_g = 2.78$ eV) was estimated from the onset of the longest absorption band, and the HOMO level (or ionization potential) of 1 ($E_{\text{HOMO}} = -4.97$ eV) was estimated from the onset of the first oxidation process. The LUMO level ($E_{\text{LUMO}} = -2.19$ eV) was then estimated from the difference
between $E_g$ and $E_{\text{HOMO}}$. Density Functional Theory calculations also provided information about the geometry, the energy levels and the electronic distribution of 1. The experimental energy levels are in good agreement with the theoretical values ($E_{\text{HOMO}} = -4.83$ eV; $E_{\text{LUMO}} = -1.74$ eV) calculated at 6-311+g(2d,p) basis set with the B3LYP Hamiltonian. The electron density of the HOMO level of 1 is delocalized from the two external triphenylamine moieties across the biphenyl core (Figure 2d). The molecule shows large delocalization along the whole molecule due to its planarity and it is worth noting that the four methoxy groups also participate in the delocalization of the electron density. The experimental and calculated $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ values indicate that 1 is a very promising candidate to behave as a hole-transporting and electron-blocking material (Figure 2e).
**Figure 2.** a) Two views for the X-ray crystal structure of 1. b) UV–vis absorption (black) and photoluminescence (blue) spectra of 1 in CH$_2$Cl$_2$. c) Cyclic voltammogram of 1 in nBu$_4$NPF$_6$ in CH$_2$Cl$_2$ (0.1 mM). Potential versus the ferrocene/ferrocenium couple. d) Electronic density of the frontier orbitals of 1. e) Energy levels (eV) of the different device components. f) FESEM cross section of a glass/FTO/c-TiO$_2$/mp-TiO$_2$/Cs$_x$(MA$_{0.17}$FA$_{0.83}$)$_{(100-x)}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$/1/Au device. g) J–V curves of the best performing devices. h) Statistics of series resistance of working devices.
To test the behavior of quart-p-phenylene 1 as a HTM, we prepared regular mesoporous PSCs with the triple-cation perovskite\textsuperscript{7} \((\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{(100-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3)\). The devices were fabricated using a configuration comprising layers of fluorine-doped tin oxide (FTO) glass/compact TiO\textsubscript{2}/mesoporous TiO\textsubscript{2}/perovskite/1/Au configuration. We also fabricated a set with spiro-OMeTAD instead of quart-p-phenylene 1, as a reference. Both HTMs were doped with small amounts of (bis(trifluoromethylsulfonyl)imide lithium salt (LiTFSI) and 4-tert-butylpyridine (TBP).\textsuperscript{43} A cross sectional FESEM micrograph of one of the devices shows clearly the heterostructure constituted by the different layers (Figure 2f). The observed thickness of the quart-p-phenylene 1 slab was around 70-90 nm. Notably, the HTM layer is compact and its thickness is uniform across the cell surface, which confirmed the high processability and suitability of this molecule for perovskite solar cells. The arithmetic roughness measured by AFM of a layer of quart-p-phenylene 1 directly on the \((\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{(100-x)}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3)\) layer shows that 1 contributes to the smoothness of the cells (Figure S7 and S8).

We investigated quart-p-phenylene 1 deposited from chlorobenzene solutions with three different concentrations (15, 20 and 30 mM). The photovoltaic parameters of such solar devices were compared to those containing spiro-OMeTAD, illustrating the best performance for the ones fabricated from 30 mM solutions of quart-p-phenylene 1 (Figure S9). The \(J-V\) curves and the extracted cell parameters obtained for the best-performing cells using quart-p-phenylene 1 (30 mM in chlorobenzene) as HTMs (Figure 2g and Table 1) show PCE, \(J_{SC}\), \(V_{OC}\) and \(FF\) values that are comparable to those of obtained for the spiro-OMeTAD reference cells. In particular, the average PCE (PCE\textsubscript{av} = 12.8\%) and the maximum PCE (PCE\textsubscript{max} = 15.3\%) observed for quart-p-phenylene 1 are
comparable to those values observed for spiro-OMeTAD ($\text{PCE}_{\text{ave}} = 14.4\%$ and $\text{PCE}_{\text{max}} = 17.0\%$).

| HTM           | $V_{\text{OC}}$ | $J_{\text{SC}}$ | FF  | $\text{PCE}_{\text{ave}}$ | $\text{PCE}_{\text{max}}$ |
|---------------|-----------------|-----------------|-----|---------------------------|---------------------------|
| spiro-OMeTAD  | 1.009           | 20.6            | 78  | 14.4                      | 17.0                      |
| 1             | 1.042           | 17.9            | 73  | 12.8                      | 15.3                      |

Table 1. $V_{\text{OC}}$ (V), $J_{\text{SC}}$ (mA cm$^{-2}$), FF (%) and PCE (%) of the devices.

The $V_{\text{OC}}$ values of quart-p-phenylene 1 ($V_{\text{OC}} = 1.042$ V) are slightly higher than those measured for spiro-OMeTAD ($V_{\text{OC}} = 1.009$ V), while the $J_{\text{SC}}$ values of quart-p-phenylene 1 ($J_{\text{SC}} = 17.9$ mA cm$^{-2}$) are slightly lower than those of spiro-OMeTAD ($J_{\text{SC}} = 20.6$ mA cm$^{-2}$). The FF of devices with 1 is lower, which can be rationalised in terms of the series resistance ($R_s$) observed in the different sets of devices (Figure 2h), which are obtained from the $J$–$V$ curves measured under 1 sun irradiation in a backward scan. Both molecules showed satisfying $R_s$ values, but in the case of quart-p-phenylene 1 are slightly higher, which account for the slightly smaller PCE values.

To conclude, we have described the synthesis and full characterization of a novel molecular hole transporting material based on a partially planarised quart-p-phenylene core. The optoelectronic (UV-vis absorption and photoluminescence), electrochemical, thermal and theoretical properties confirm that quart-p-phenylene 1 possesses a well aligned energy level arrangement and also an optimal stability and solubility to be implemented as a hole transporting and electron blocking material in PSCs. As a matter of fact, the characterization of regular Cs$_x$(MA$_{0.17}$FA$_{0.83}$)$_{100-x}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ PSC incorporating quart-p-phenylene 1 as a hole transporting material shows PCE, $J_{\text{SC}}$, $V_{\text{OC}}$ and $FF$ values
that are comparable to those obtained for the *spiro*-OMeTAD without any device optimization. We foresee that by further improvement of the deposition process and by controlling the number of rings and their planarization, the performance of oligo- and poly-*p*-phenylenes as HTM in PSCs can be further enhanced to rival with *spiro*-OMeTAD.
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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 Crystals 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 \((4,4'-(5,6,12,13\text{-tetrahydro}-3b,7a:10b,14a\text{-bis(epoxyethanooxy)pyreno[4,5-b:9,10-b']bis([1,4]dioxine)}-2,9\text{-diyl)}bis(N,N\text{-bis(4\text{-methoxyphenyl)aniline})}\) (1)

![Diagram of compound 1](image)

Compound 2 (300 mg, 0.43 mmol), 4-methoxy-\(N\)-(4-methoxyphenyl)-\(N\)-(4-(4,4,5,5\text{-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\(_2\)CO\(_3\) (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\(_2\)Cl\(_2\)): \(\delta\) 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\(_2\)Cl\(_2\)) \(^{13}\)C NMR \(\delta\) 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\(_2\)O\(_{12}\): 1044.383 [M]\(^+\), Found: 1044.376.
3. NMR spectra

Figure S1. $^1$H NMR of compound 1 (400 MHz, CD$_2$Cl$_2$).

Figure S2. $^{13}$C NMR of compound 1 (100 MHz, CD$_2$Cl$_2$).
4. IR Spectroscopy

![Figure S3. IR spectrum of compound 1.](image)

5. Thermogravimetric analysis

![Figure S4. Thermogravimetric analysis of 1.](image)
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<sub>2</sub>Cl<sub>2</sub>-6311+g(2d,p)/B3LYP-CH<sub>2</sub>Cl<sub>2</sub>-6-31(d,p) level.
Figure S5. B3LYP-CH\textsubscript{2}CL\textsubscript{2}-6311+g(2d,p)/B3LYP-CH\textsubscript{2}CL\textsubscript{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\textsubscript{2}CL\textsubscript{2}-6311+g(2d,p)/B3LYP-CH\textsubscript{2}CL\textsubscript{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-((1H-pyrazol-1-yl)-4-tert-butyl)pyridine)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 disopropoxide 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 μl 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(trifluoromethyl)sulfonyl)imide lithium salt (Li-TFSI, Sigma-Aldrich), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tris(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

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