Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

[2,2]Paracyclophane Triarylamine based Hole-Transporting Material for High Performance Perovskite Solar Cells

General: Unless stated otherwise, all of the chemicals and solvents for the reactions and device fabrications were purchased from Sigma-Aldrich, TCI CO., Ltd. and used without further purification. Spiro-OMeTAD was purchased from Dyesol Co., Ltd. and used directly to hole transporting layer (HTM) on reference devices. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*N,N*-bis(4-methoxyphenyl)aniline were synthesized following the procedures reported in the literatures.[1] All the synthesized products were confirmed by a nuclear magnetic resonance (NMR) spectroscopy, ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker Ascend 400 spectrometer using $CDCl_3$ or CD_2Cl_2 as a solvents at room temperature. The chemical shifts (δ) of the NMR data were relative to tetramethylsilane (TMS, ^{1}H NMR), $CDCl_3$ or CD_2Cl_2 (^{13}C NMR) and expressed as parts per million (ppm).[2] The splitting pattern of the NMR data were reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m). The final product (PCP-TPA) was double-checked by matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF MS, Bruker autoflex Ⅲ) using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix. Photo electron spectroscopy in air (PESA) measurements were recorded with RikenKeiki AC-2 surface analyzer with a 10 nW of UV source. The samples for PESA were prepared on a glass substrate with the same condition to that used for HTM fabrication in solar cell devices.

Optical properties measurements

The ultraviolet-visible (UV/vis) absorption spectra of PCP-TPA and spiro-OMeTAD were obtained by a PerkinElmer Lambada 35 UV/vis spectrometer at room temperature. The photoluminescence (PL) spectra of the PCP-TPA and spiro-OMeTAD were obtained by a Fluorolog3 spectrofluorometer system of HORIBA scientific. The solution samples were prepared by dissolving the compounds in toluene and the films were prepared by spin coating on a pre-cleaned glass substrate.

Thermal properties measurements

The thermal decomposition temperature (T_d) was confirmed by a thermogravimetric analysis (TGA) from Q50 thermal analysis system of TA instruments at a heating rate of 25 ℃/min. The differential scanning calorimetry (DSC) performed on Q20 system of TA instrument and the DSC data were recorded in the temperature range from 25 ℃ to 270 ℃ at a heating rate of 10 ℃/min.

Electrochemical properties

Cyclic voltammetry (CV) was measured to study the electrochemical properties of hole transporting materials using CH instruments electrochemical analyzer. The sample solutions were prepared by dissolving the compound in deoxygenated 1,2-dichloroethane (DCE) (2.5×10^{-3} M) containing tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) (0.1 M) as the supporting electrolyte. A three-electrode cell was used which was equipped with a glassy carbon electrode as a working electrode, a platinum (Pt) wire as a counter electrode and

Ag/AgCl in 3 M KCl as a reference electrode. All of the measurements were carried out after nitrogen (N_2) bubbling and under N_2 condition at a scan rate of 50 mV/sec. The redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured under the same condition for calibration before and after sample measurements, and $E^{1/2}$ was located at 0.52 V vs. Ag/AgCl electrode. The energy levels of the highest occupied molecular orbital (HOMO) was then calculated by the following equation.[3]

$$E_{HOMO} = - (E_{[onset,\ ox.\ vs.\ Fc/Fc+]} + 5.1)\ (eV)$$

Synthesis of PCP-TPA

4,7,12,15-Tetrabromo[2,2]paracyclophane (2) Iodine (78.7 mg, 0.31 mmol) and bromine (48.15 g, 301 mmol) were added into the reaction flask and cooled down to 0 ℃ using an ice bath. [2,2]Paracyclophane **(1)** (5.23 g, 25.11 mmol) was added into the reaction flask with small portions at 0 ℃. After addition, the reaction flask was kept with stirring at R.T. for 8 days. And then, the reaction was quenched and neutralized by addition of sodium bisulfide and a sodium hydroxide aqueous solution. Crude product was extracted by chloroform (200 mL) three times and the solution was dried over anhydrous magnesium sulfate. The pure product **(2)** was obtained by column chromatography (eluent: hexane) (2.23 g, 17.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 4H), 3.18-3.30 (m, 4H), 2.92-3.05 (m, 4H). ^{13}C NMR (100 MHz) δ 140.31, 134.41, 125.28, 32.67.

4,7,12,15-tetrakis-[4-amino-[*N,N*-di-(4-methoxyphenyl)]-phenyl]-[2,2]paracyclophane (PCP-TPA) 4,7,12,15-Tetrabromo[2,2]paracyclophane **(2)** (806 mg, 1.54 mmol), 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*N,N*-bis(4-methoxyphenyl)aniline **(3)** (3.185 g, 7.39

mmol), and tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$) (355.6 mg, 0.31 mmol) were added into a 50 mL flask. After equipped with a condenser, the reaction flask purged with argon. Deoxygenated toluene (24 mL), sodium hydroxide solution (2 M in deionized water, 8 mL), and aliquat 336 (a few drops) were added into the reaction flask. The reaction flask stirred at 110 ℃ for 36h under argon condition. After the reaction, the resulting crude product was diluted with chloroform (200 mL) and washed with water and brine. The solution was dried with magnesium sulfate and rotary evaporator. Combine the chloroform part and dry over anhydrous magnesium sulfate. Filter the solution from the drying agent and remove the solvent under reduced pressure. The pure product (PCP-TPA) was obtained by column chromatography (eluent: ethyl acetate:hexane=1:2) (626 mg, 28.6%) ^1H NMR (400 MHz, CD_2Cl_2) δ 7.18 (d, 8H), 7.06 (d, 16H), 6.90 (d, 8H), 6.83 (d, 16H), 6.73 (s, 4H), 3.79 (s, 24H), 3.35-3.60 (m, 4H), 2.65-2.90 (m, 4H). ^{13}C NMR (100MHz) δ 156.42, 147.83, 141.28, 139.58, 137.07, 133.32, 132.47, 130.08, 127.11, 120.65, 115.07, 55.93, 33.78. MADLI-TOF MS m/z (%) calcd. for $C_{96}H_{84}N_4O_8$= 1420.629 (96.3) $[M]^+$, 1421.632 (100), 1422.636 (41.2), 1423.639 (11.3), 1424.642 (4.0); found 1420.409 (97.9) $[M]^+$, 1421.334 (100), 1422.375 (66.2), 1423.416 (30.8), 1424.226 (11.6).

Syntheis of $CH_3NH_3PbI_3$ ($MAPbI_3$) perovskite solution

We used all chemicals as received. MAI was synthesized by reacting 50 mL hydroiodic acid (HI, 57% in water, 50 mL, Lot:MKBS1107V, Aldrich) and 50 mL methylamine (40 % in methanol, 500 mL, Lot:5VT7EQH, Junsei Chemical Co. Ltd.) in a 250-mL flask at 0 °C for 2h with stirring. The precipitated product was recovered by evaporation of the solvents at 50 °C for 1h using rotary evaporator. The resulting product was dissolved in ethanol, recrystallized from diethyl ether, and finally dried at room temperature under reduced pressure oven for 24h. 40 wt% of $MAPbI_3$ solution was then prepared by mixing equimolar MAI and PbI_2 (50g Lot:BCBP521V, Aldrich) (1:1 mole ratio) in *N,N*-dimethylformamide (DMF, 1L, Lot:SHBF6963V, Aldrich) at 60 °C for 30 min and then, hydriodic acid (HI, 57 % in water, 50 mL, Lot:MKBS1107V, Aldrich) was added into the $MAPbI_3$ perovskite solution.

Hole Mobility Measurement

Hole-only devices with a structure of ITO/PEDOT:PSS/HTM layer/Au were fabricated. The HTM layers were prepared by the same conditions to those used for solar cell device fabrications. The hole mobilities of the devices were determined with the space-charge-limited current (SCLC) method by using the following equation:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_o\mu_h\frac{V^2}{L^3}$$

In the equation, ε_0 is the permittivity of a free space, ε_r is the dielectric constant of the HTM, μ is the hole mobility, V is the voltage drop across the device, and L is the HTM thickness; the thickness of the HTM layers were averaged from 5 point measurements using Alpha-step and the values are 140 nm and 149 nm for PCP-TPA and spiro-OMeTAD, respectively. In $V = V_{appl} - V_r - V_{bi}$, V_{appl} is the applied voltage to the device, V_r is the voltage drop due to constant resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes.[4,5] The dielectric constant is assumed to be 3 in our analysis, which is a typical value for organic molecules. The current density versus voltage characteristics were recorded on a Keithley model 2400 source measuring unit. The calculated mobilities are 6.32×10^{-4} cm^2/V·s and 5.22×10^{-4} cm^2/V·s for PCP-TPA and spiro-OMeTAD, respectively. We fabricated 10 more hole-only devices and measured hole mobilities using the same method. The thickness of the HTM layer was varied in the range of 140~190 nm for both of the HTMs. The averaged mobility values are 6.28×10^{-4} cm^2/V·s (standard deviation: 1.11×10^{-4} cm^2/V·s) and 5.17×10^{-4} cm^2/V·s (standard deviation: 1.09×10^{-4} cm^2/V·s) for PCP-TPA and spiro-OMeTAD, respectively and overall, PCP-TPA showed a 20% enhanced hole mobility compared with spiro-OMeTAD.

Fabrication of perovskite solar cell devices

For $MAPbI_3$ planar hybrid solar cells, a ~50 nm-thick dense TiO_2 electron conductor was deposited on a cleaned F-doped SnO_2 (FTO, Pilkington, TEC8) glass substrate by spray pyrolysis deposition (SPD) method with 40 mL of 20 mM of titanium diisopropoxide bis(acetylacetonate) (Aldrich)/iso-propanol solution at 450 °C. We repeated the spraying process about 40 times to spray 40 mL solution manually by using glass type atomizer. A 0.1 mL of 40 wt% $MAPbI_3$/DMF solution with a HI solution (40 wt% $MAPbI_3$ solution in DMF/HI = 1 mL/0.1 mL) was then spin coated on the TiO_2/FTO substrate at 3000 rpm for 200 s and the resulting film was dried on a hot plate at 100 °C for 2 min in air under 35 % relative humidity. An HTM layer was formed by spin-coating 0.1 mL of a spiro-OMeTAD (Dyesol; no further purification) or PCP-TPA solution in toluene (1 L, Lot:SHBG0205V, anhydrous, 99.8 %, Aldrich : 60 mg HTM in 1 mL toluene) containing 25 μL of a Li-TFSI (170 mg Li-TFSI in 1 mL acetonitrile) and 40 μL of *t*-BP (1 mL 4-*tert*-butyl pyridine in 1 mL acetonitrile) additive solutions at 2000 rpm for 30 s. Finally, ~60 nm-thick Au counter electrode was deposited by thermal evaporation. We used all chemicals as received. The active area was fixed to 0.16 cm^2. All precursor preparation and device fabrication were performed under air condition and humidity of about 35%.

Device characterization

For the characterization of photovoltaic properties, the current density-voltage (*J*-*V*) curves were measured by a solar simulator (Peccell, PEC-L01) with a potentiostat (IVIUM, IviumStat) under illumination of 1 sun (100 mW/cm^2 AM 1.5G) which is calibrated by Si-reference cell certificated by JIS (Japanese Industrial Standards). We fixed the scan rate was fixed to 200 ms/10 mV irrespective of the scan direction. The *J*-*V* curves of all devices were measured by masking the active area with a metal mask of 0.096 cm^2. The external quantum efficiency (EQE) was measured by a power source (ABET 150W Xenon lamp, 13014) with a monochromator (DONGWOO OPTORN Co., Ltd., MonoRa-500i) and a potentiostat (IVIUM, IviumStat).

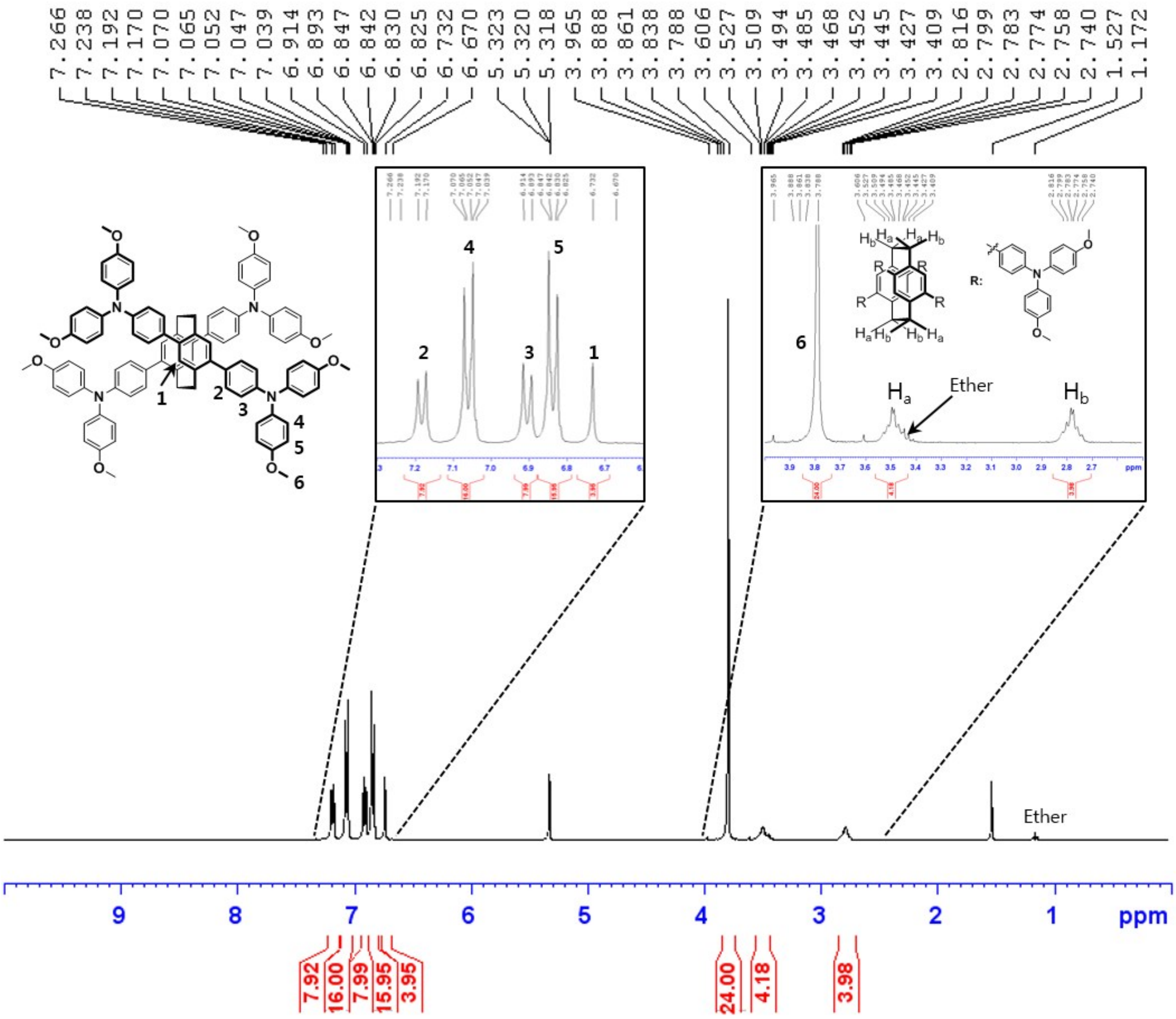


Fig. S1 ^{1}H NMR spectrum of PCP-TPA in CD_2Cl_2

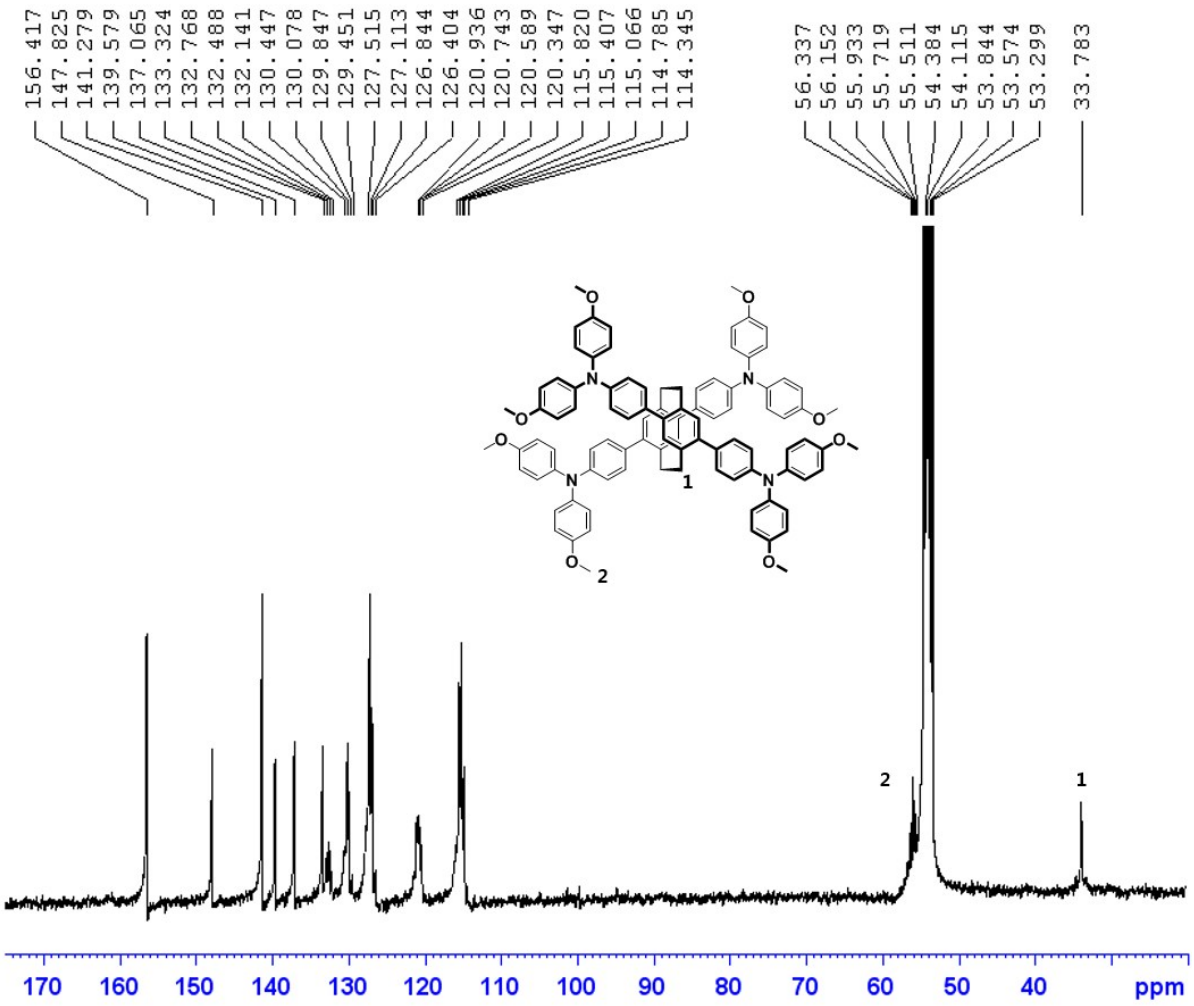


Fig. S2 ^{13}C NMR spectrum of PCP-TPA in CD_2Cl_2

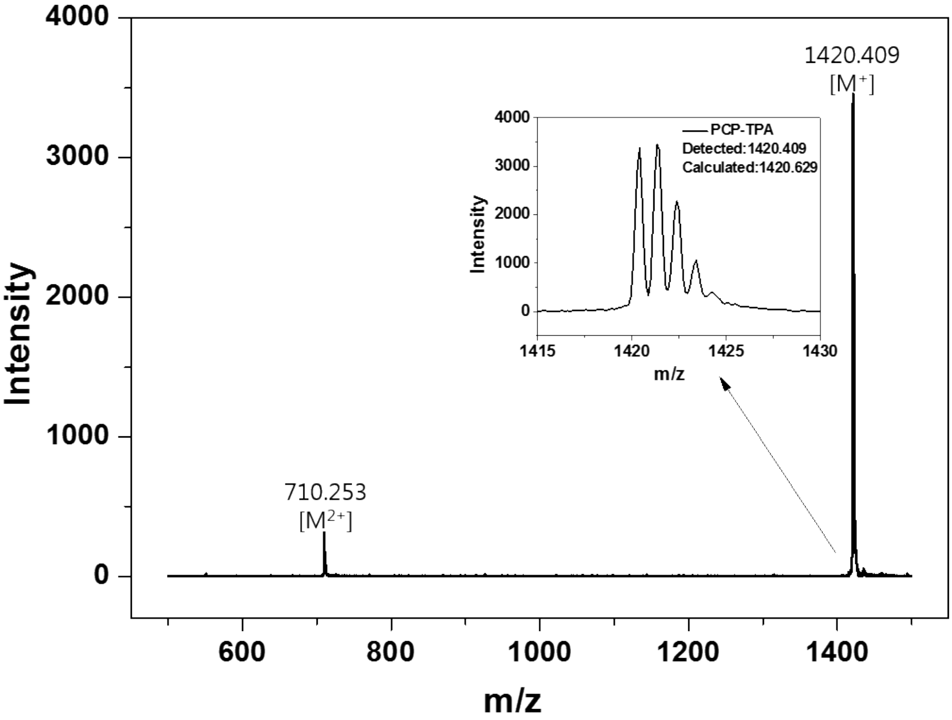


Fig. S3 MALDI-TOF mass spectrum of PCP-TPA: MALDI-TOF MS m/z (%). calcd. for $C_{96}H_{84}N_4O_8$=1420.629 (96.3) [M]$^+$, 1421.632 (100), 1422.636 (41.2), 1423.639 (11.3), 1424.642 (4.0); found 1420.409 (97.9) [M]$^+$, 1421.334 (100), 1422.375 (66.2), 1423.416 (30.8), 1424.226 (11.6).

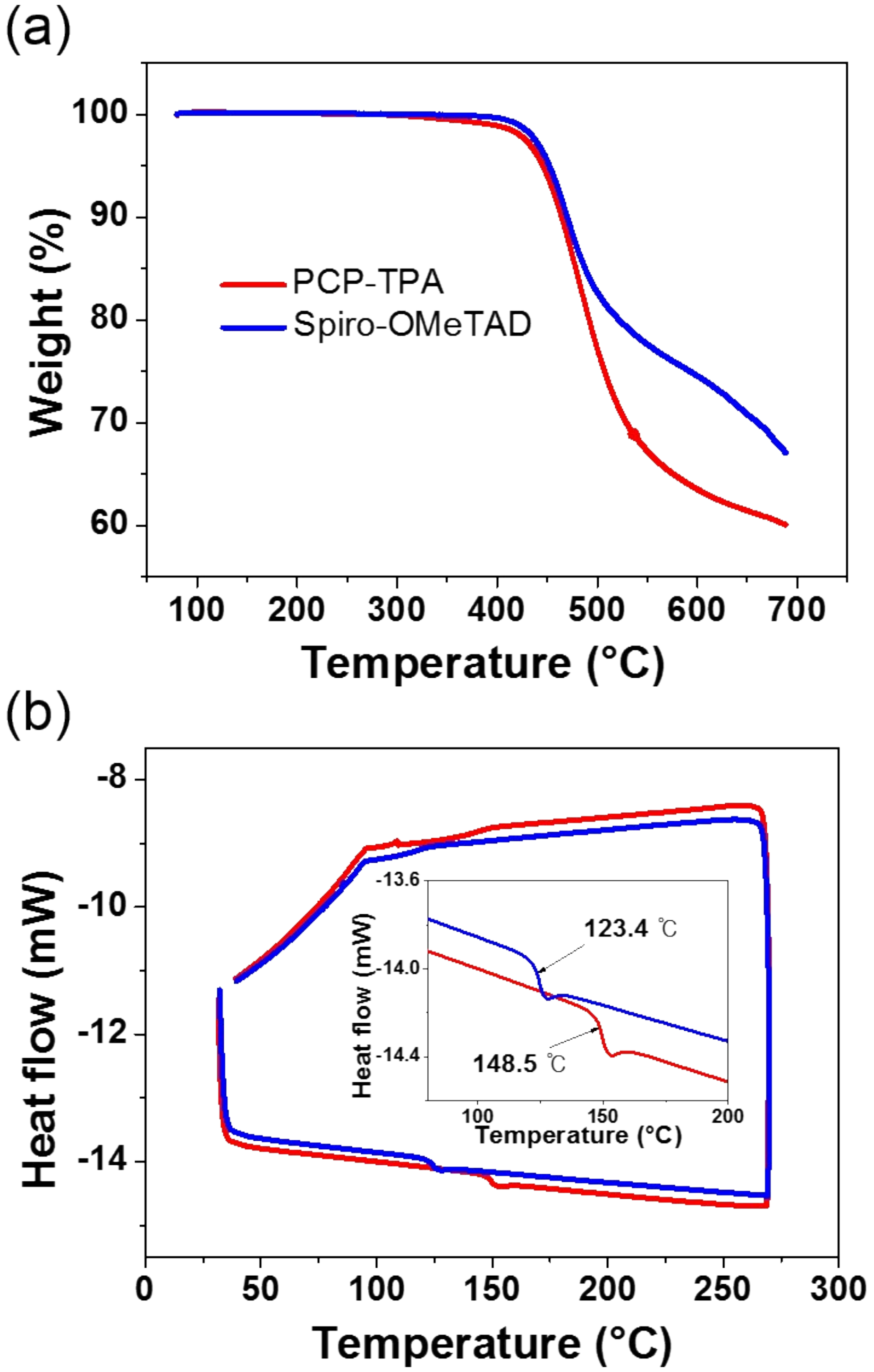


Fig. S4 TGA (a) and DSC (b) results of PCP-TPA and spiro-OMeTAD

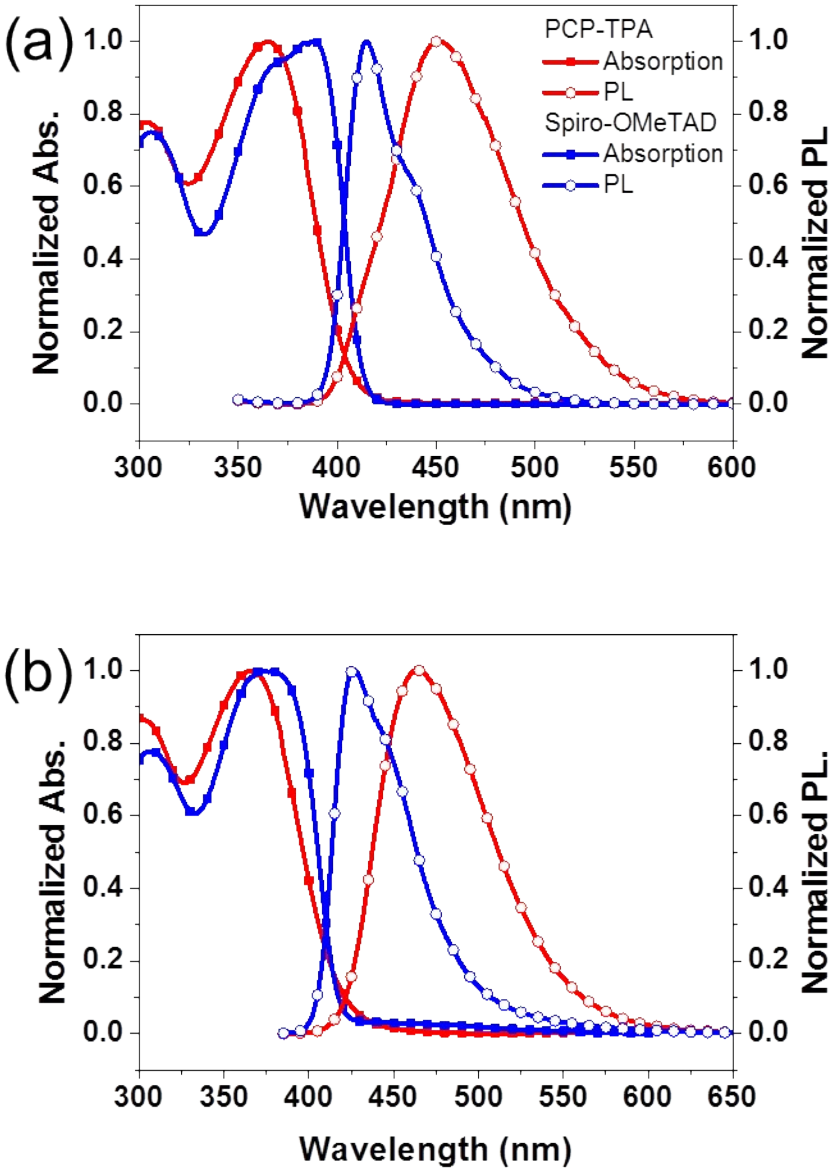
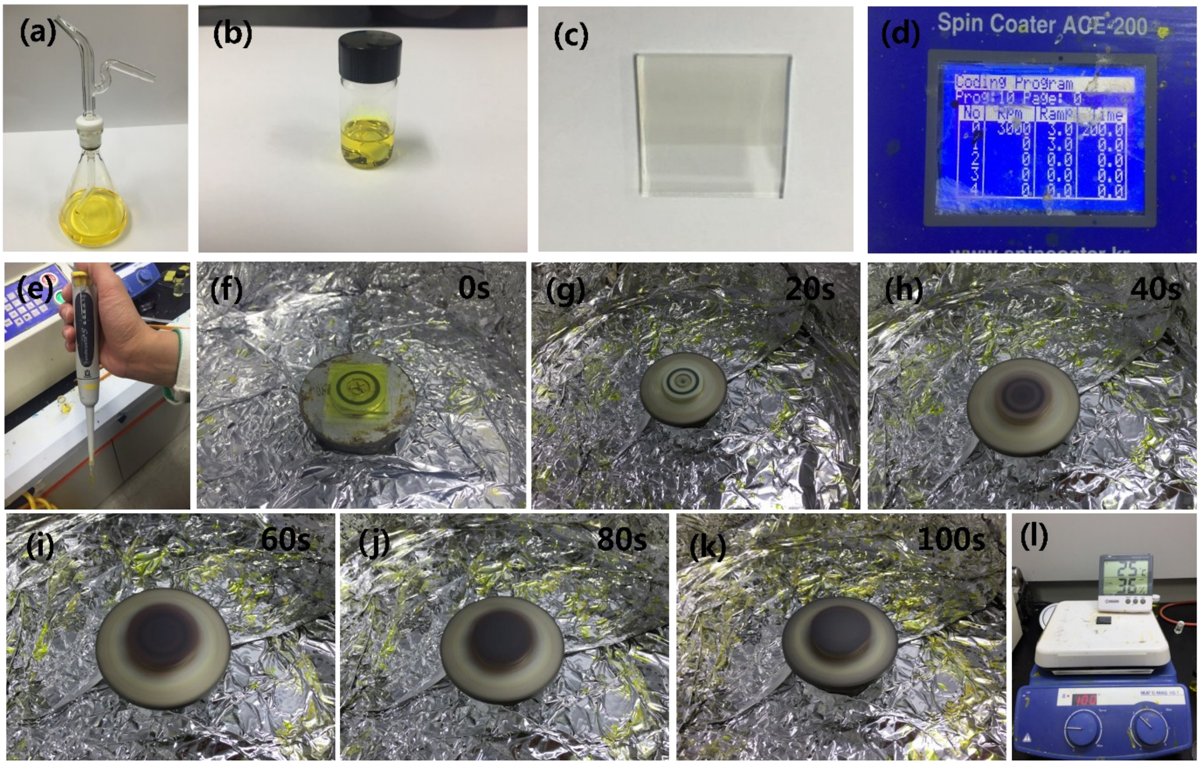


Fig. S5 UV-vis absorption and PL spectra of PCP-TPA and spiro-OMeTAD in a solution (a) and a film (b).



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4	0	0.0	0.0

Fig. S6 (a) glass atomizer charged 40 mL of 20 mM titanium diisopropoxide bis(acetylacetonate) (Aldrich)/iso-propanol solution, (b) 40 wt% $MAPbI_3$ solution in DMF/HI = 1 mL/0.1 mL, (c) the TiO_2/FTO substrate, (d) spin-coating condition, (e) 0.1 mL of solution (b), (f)-(k) representative image for the deposition of perovskite film by single step spin-coating process with time (f = 0 s, g = 20 s, h = 40 s, I = 60 s, j = 80 s, k = 100 s), and (l) drying step for 2 min at 100 ℃: the surrounding temperature = 25 ℃, relative humidity = 35 %.

Reference

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