Electronic Supplementary Information (ESI) for

Synthesis of a side-chain hole transporting polymer through Mitsunobu post-functionalization for efficient inverted perovskite solar cells

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Experimental section

Measurement and characterization

^1H and ^{13}C NMR spectra were measured on Bruker-400 spectrometer. Chemical shifts were reported as *d* value (ppm) relative to an internal tetramethylsilane (TMS) standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on PerkinElmer STA6000 in nitrogen, with a heating rate of 20 °C/min. Atomic force microscopy (AFM) measurements were carried out using a Nanoscope NS3A system (Digital Instrument) in taping mode. The scanning electron microscopy (SEM) images were acquired by using an electron microscopy, scanning (QUATTRO S). UV-vis absorption spectra were recorded on a Shimadzu 1700 spectrophotometer. Steady state photoluminescence (PL) and time resolved photoluminescence (TRPL) decay were measured by using a spectrofluorometer system (Edinburgh FLS980). Cyclic voltammograms measurements (CV) were recorded on a CH 1750A electrochemical workstation using a three-electrode setup with Ag/Ag^+ reference electrode, platinum wire auxiliary electrode, and platinum disk working electrode. Measurements were performed in an anhydrous and nitrogen-saturated solution of tetrabutylammonium hexafluorophospate (Bu_4NPF_6) (0.1 M) in dichloromethane at a scan rate of 100 mV/s at room temperature. Ferrocene was used as an external standard, with the oxidation onset relative to ferrocene/ferrocenium taken as E_{HOMO}.

Water contact angle was carried out using a homemade contact angle measurement apparatus.

Device fabrication and characterization

Patterned indium tin oxide (ITO)-glass substrates were cleaned by sequentially sonication with detergent, deionized water, acetone, and isopropyl alcohol for 15 min, and then dried in oven at 100 °C, followed by an O_3 plasma for 10 min. The cleaned glass was transferred to glove box for following film preparation. The solution of PVP-CZ in cyclopentanone (2 mg/mL) were spin-coated on the ITO at 6000 rpm for 30 s, which was annealed on the hotplate at 150 °C for 10 min. While the PTAA film was prepared from spin coating the solution of PTAA in toluene (2 mg/mL) on the ITO at 6000 rpm for 30 s, which was then annealed on the hotplate at 100 °C for 10 min. Perovskite precursor was prepared by mixing 171.9 mg of FAI, 507.1 mg of PbI_2, 22.4 mg of MABr and 73.4 mg of $PbBr_2$ in 1 mL blend solution of DMF/DMSO (v/v = 5/1). Afterwards, 89 uL CsI solution (1.5 M in DMSO) was added to obtain a composition of $Cs_{0.05}FA_{0.83}MA_{0.17})_{0.95}Pb(Br_{0.17}I_{0.83})_3$ and 1% in volume of NH_4BF_4 solution (1M in mix solution of DMF:DMSO = 5:1) was then added. The perovskite solution was spin-coated on the film of PVP-CZ at 1000 rpm and 6000 rpm for 5 s and 30 s. 110 uL of anti-solvent (chlorobenzene, CB) was quickly dropped on the film for 5 s, followed by annealing at 100 °C for 30 min. PCBM solution (20 mg/mL in CB) was spin-coated on perovskite layer at 1500 rpm for 40 s. Finally 6 nm BCP and 100 nm Ag were thermally evaporated under vacuum. The active layer area of the device was defined and characterized as 0.16 cm^2 by metal shadow mask.

The power conversion efficiencies of perovskite solar cells (PVSCs) were measured under 1 sun, AM 1.5 G (air mass 1.5 global) spectrum from a solar simulator (Enlitech SS-F5) (100 mW cm^{-2}). The current density–voltage (*J–V*) characteristics were recorded with a Keithley 2400 source meter. The scanning direction is from 1.3V to -0.2V and the sweep speed is 2000 mV/s. The external quantum efficiency (EQE) was measured with a commercial Enlitech EQE measurement system.

Space charge limited current (SCLC) measurement

Hole-only device was fabricated to measure the hole mobility by using the space charge limited current (SCLC) method. The device configuration was ITO/PEDOT:PSS/PVP-CZ/MoO_3/Ag. The PEDOT:PSS layer was spin-cast onto the pre-cleaned ITO glass at 4000 rpm for 30 s, and the film was thermally annealed on the hotplate at 150 °C for 30 min under ambient conditions. The substrate was then quickly transferred into an N_2-filled glovebox. Subsequently, the solution of PVP-CZ (10 mg/ml in CB) was spin-coated on ITO/PEDOT:PSS substrate at 4000 rpm for 30 s followed by annealing at 150 °C for 10 min.. Finally, MoO_3 (~6nm) and Ag (~100 nm) were sequentially thermally deposited on the top of PVP-CZ film in a vacuum system.

Materials

All the starting materials were purchased from Aldrich or Alfa Aesar and used without further purification unless stated otherwise. The average M_w for poly(4-vinylphenol) (PVP) is ~25000, and the T_d *and* T_g are at 300 °C and 130-185 °C as provided, respectively. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) was purchased from Xi'an Polymer Light Technology Corp. (PLT), MW. 6000~15000. All the reactions were carried out under argon at 1 atm unless mentioned otherwise.

Synthesis of compound ***2***

In a two-necked round-bottomed flask, 2,7-dibromocarbazole (0.5g, 1.54mmol), 2-bromoethanol (0.23g, 1.85mmol), K_2CO_3 (0.43g, 3.08mmol) and KI (0.26g, 1.54mmol) were added in 20 ml of dimethylformamide, and the reaction mixture was stirred and heated at 120 °C with nitrogen protection overnight. After reaction, the mixture was cooled and extracted with ethyl acetate and purified by silica column chromatography to give the pure product as white solid (0.52g, 91% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.61 (s, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 4.39 (s, 2H), 4.06 (s, 2H), 1.60 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.66, 122.99, 121.50, 121.42, 119.89, 112.28, 61.25, 45.66.

Synthesis of compound ***3***

In a two-necked round-bottomed flask, compound 2 (3.7g, 10 mmol), p-toluenesulfonyl chloride (3.82g, 20 mmol) and triethylamine (5.06g, 50 mmol) were added in 120 ml of dichloromethane, and the reaction mixture was stirred at room temperature with nitrogen protection overnight. After reaction, the mixture was extracted with dichloromethane and purified by silica column chromatography to give the pure product as white solid (4.79g, 92% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, $J = 6.5$ Hz, 2H), 7.38 (s, 2H), 7.31 (d, $J = 6.5$ Hz, 4H), 6.93 (d, $J = 7.2$ Hz, 2H), 4.43 (s, 4H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

144.76, 140.94, 131.66, 129.53, 127.23, 123.22, 121.47, 121.30, 119.92, 111.85, 66.61, 42.15, 21.67.

Synthesis of compound ***4***

In a two-necked round-bottomed flask, compound 3 (4g, 7.64 mmol), bis(4-methoxyphenyl)amine (3.85g, 16.8 mmol), t-BuONa (1.69g, 17.6 mmol), palladium acetate (0.17g, 0.76 mmol) and tri-tert-butylphosphine tetrafluoroborate (0.46 g, 1.6 mmol) were added in 110 ml of anhydrous toluene, and the reaction mixture was stirred and heated at 110 ^{o}C with nitrogen protection overnight. After reaction, the mixture was cooled and roto-evaporated to remove toluene. Then the crude product was extracted with ethyl acetate and purified by silica column chromatography to give the pure product as yellow solid (4.1g, 65% yield). ^{1}H NMR (400 MHz, DMSO) δ 7.78 (d, *J* = 7.8 Hz, 2H), 6.92 (dd, *J* = 32.8, 15.1 Hz, 24H), 6.64 (s, 2H), 4.25 (s, 2H), 4.08 (s, 2H), 3.73 (s, 12H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 155.34, 146.20, 144.77, 141.72, 141.62, 131.39, 130.10, 127.07, 125.58, 120.39, 118.08, 115.68, 115.20, 103.03, 69.00, 55.67, 31.43, 21.53.

Synthesis of compound ***5***

In a two-necked round-bottomed flask, compound 4 (0.21g, 0.26 mmol) and magnesium (0.19g, 7.8 mmol) were added in 20 ml of methanol, and the reaction mixture was stirred and heated at 50 °C for 6 hours. After reaction, the mixture was extracted with ethyl acetate and purified by silica column chromatography to give the pure product as pale yellow solid (0.15g, 88% yield). ^{1}H NMR (400 MHz, DMSO) δ 7.79 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 10H), 6.88 (d, *J* = 8.3 Hz, 8H), 6.66 (d, *J* = 8.3 Hz, 2H), 4.81 (d, *J* = 3.5 Hz, 1H), 3.98 (s, 2H), 3.73 (s, 12H), 3.51 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 155.44, 146.37, 142.21, 141.70, 125.87, 120.35, 117.59, 115.22, 115.07, 102.67, 59.37, 55.66, 45.36.

Synthesis of compound ***PVP-CZ***

In a two-necked round-bottomed flask, compound 5 (0.35g, 0.53 mmol), poly(4-vinylphenol) (0.05g, 0.42 mmol) and triphenylphosphine (0.26 g, 0.99 mmol) were added in 6 ml of tetrahydrofuran, then diisopropyl azodicarboxylate (0.44 g, 2.17 mmol) was slowly added. The reaction mixture was stirred and heated at 40 °C with nitrogen protection overnight. After reaction, the mixture was concentrated to 2~3ml solution and precipitated from methanol twice to get polymer PVP-CZ as slightly yellow solid (230mg, 71% yield). ^{1}H

NMR (400 MHz, DMSO) δ 7.79 (d, *J* = 7.7 Hz, 2H), 6.96 (s, 10H), 6.87 (d, *J* = 7.5 Hz, 10H), 6.66 (d, *J* = 7.5 Hz, 4H), 3.73 (s, 12H), 3.61 (s, 2H), 3.51 (s, 2H), 1.15 (s, 2H), 0.76 (s, 1H).

Additional figures

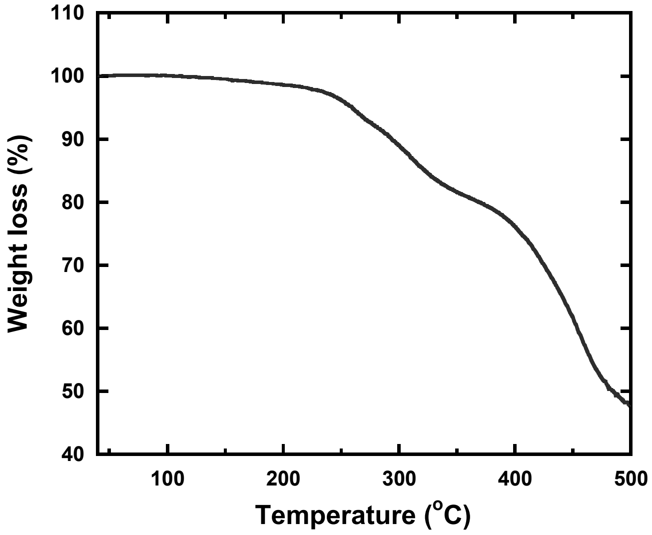

Fig. S1. TGA curve for PVP-CZ.

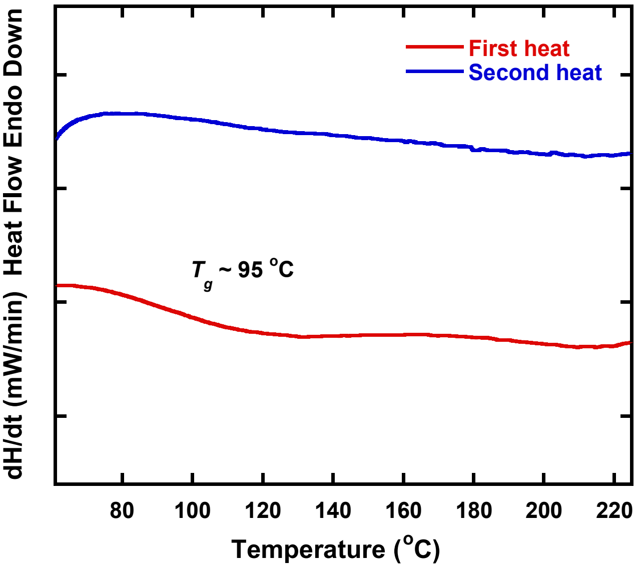

Fig. S2. DSC curve for PVP-CZ.

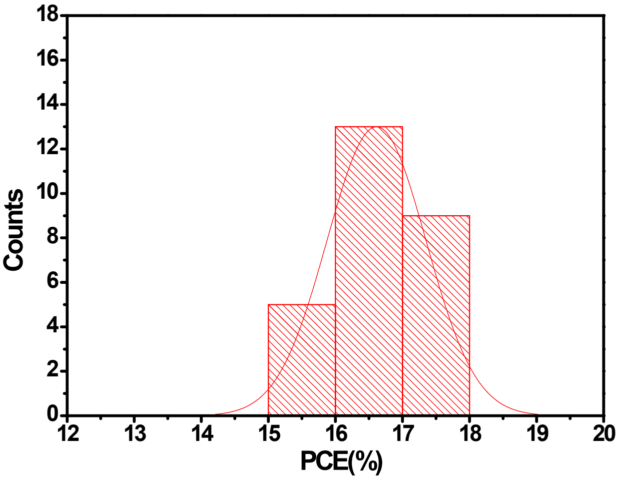

Fig. S3. Histogram of PCEs for 27 devices using PVP-CZ as HTM.

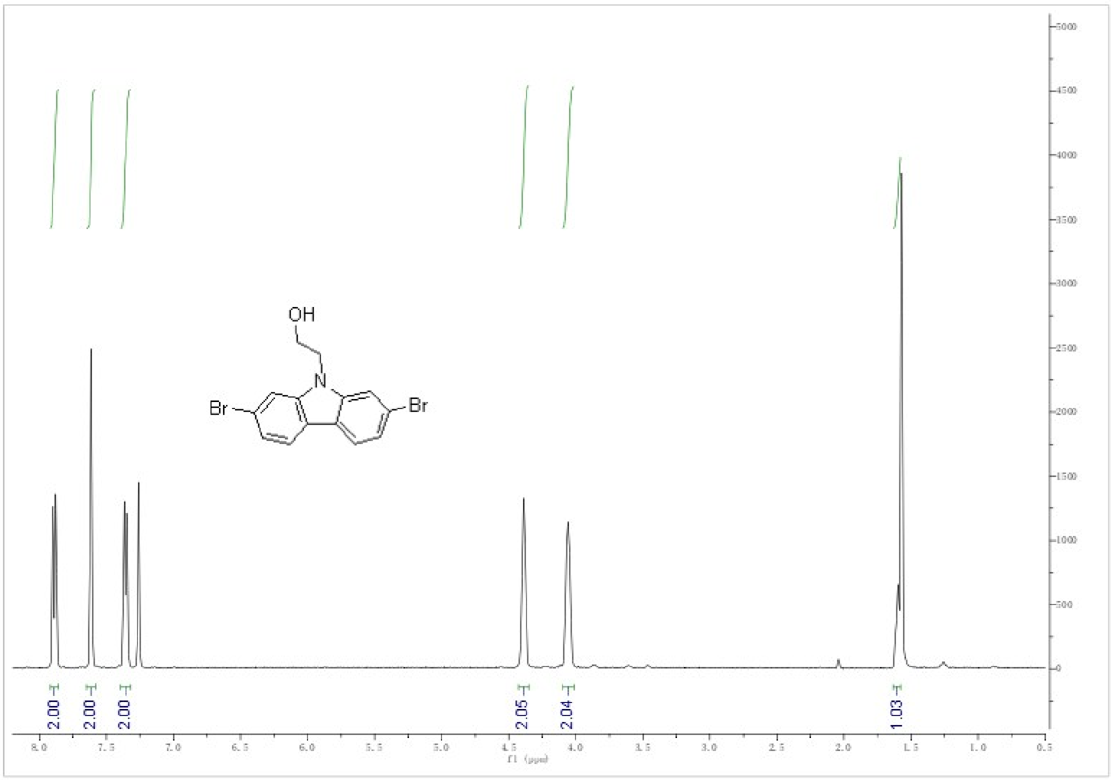

Fig. S4. ^{1}H NMR ($CDCl_3$) of compound **2**.

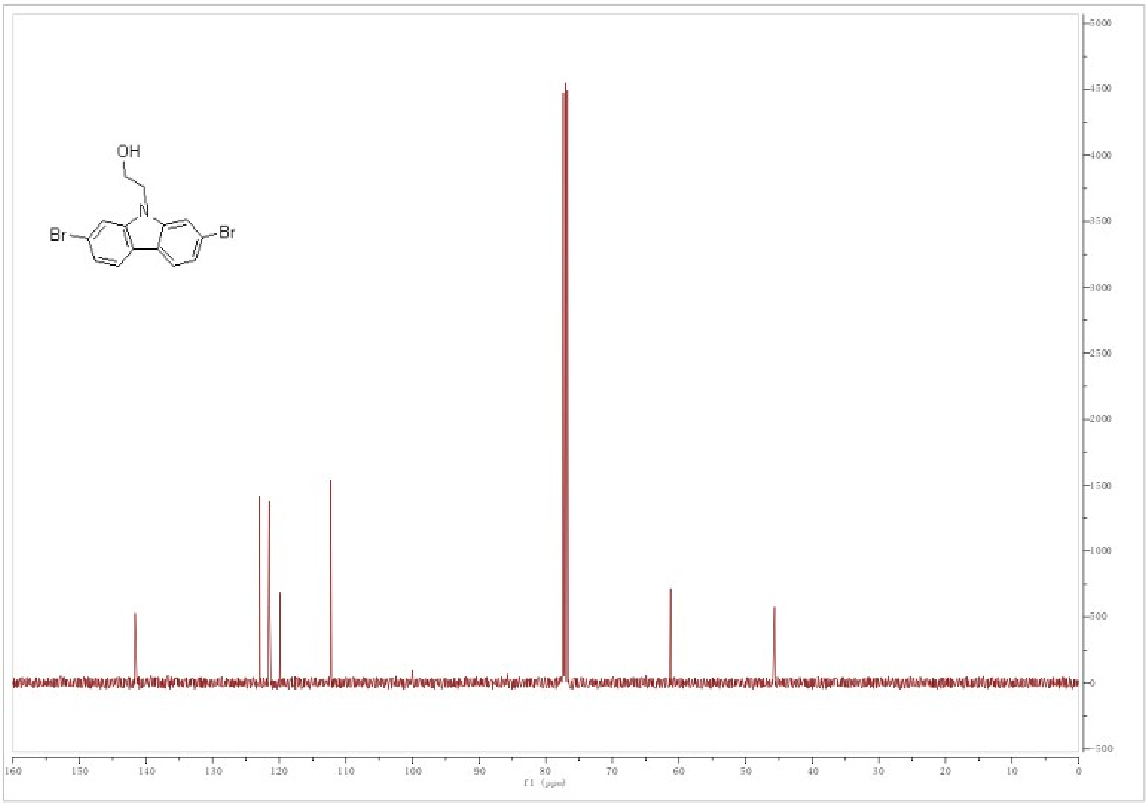

Fig. S5. ^{13}C NMR (CDCl$_3$) of compound **2**.

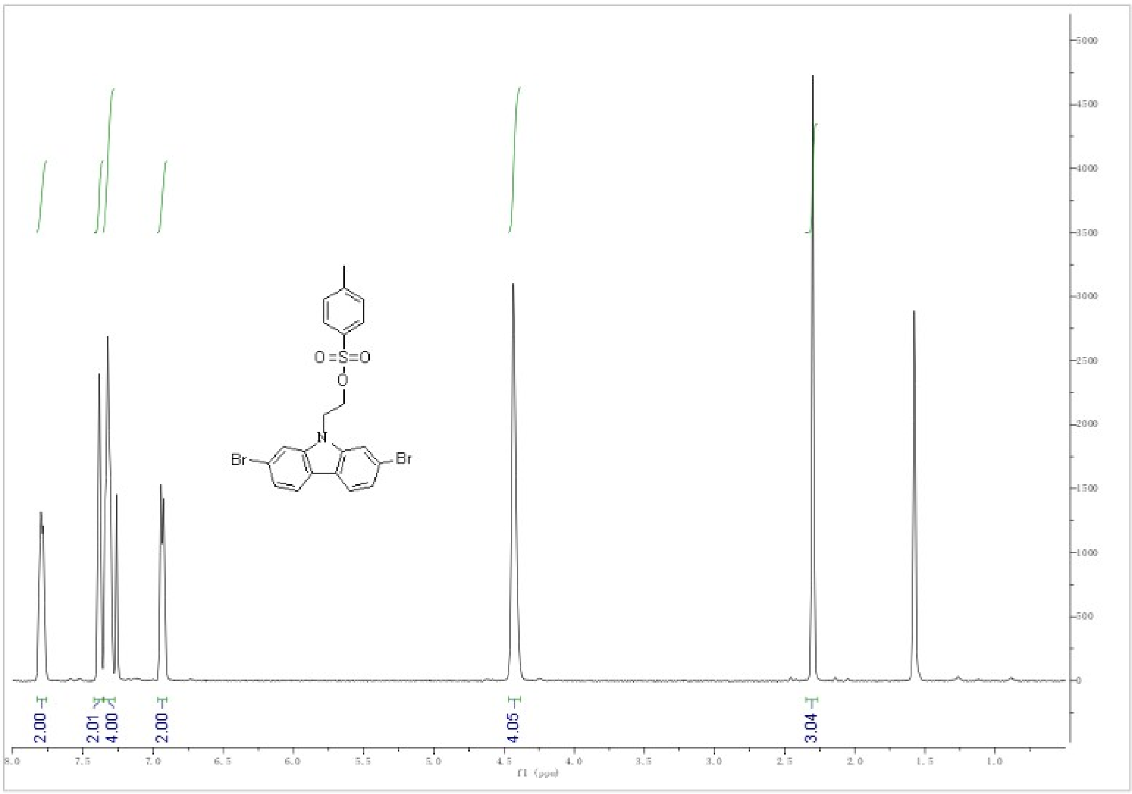

Fig. S6. ^{1}H NMR (CDCl$_3$) of compound **3**.

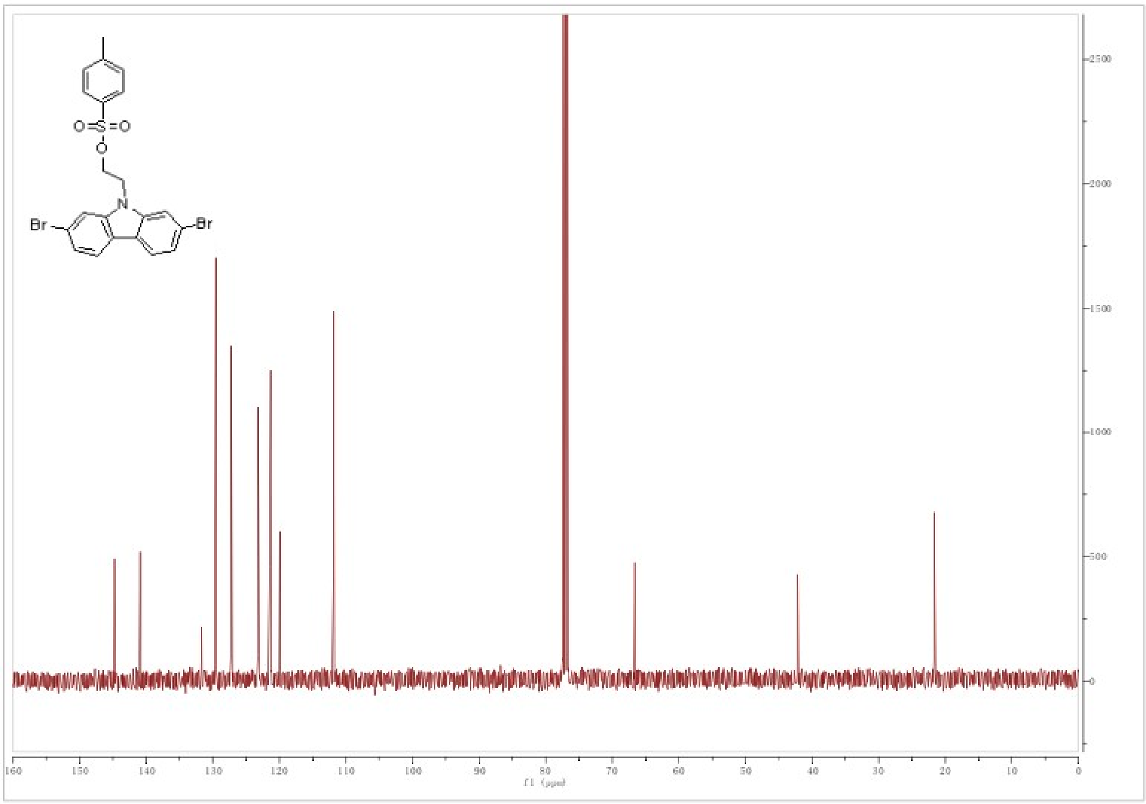

Fig. S7. ^{13}C NMR ($CDCl_3$) of compound **3**.

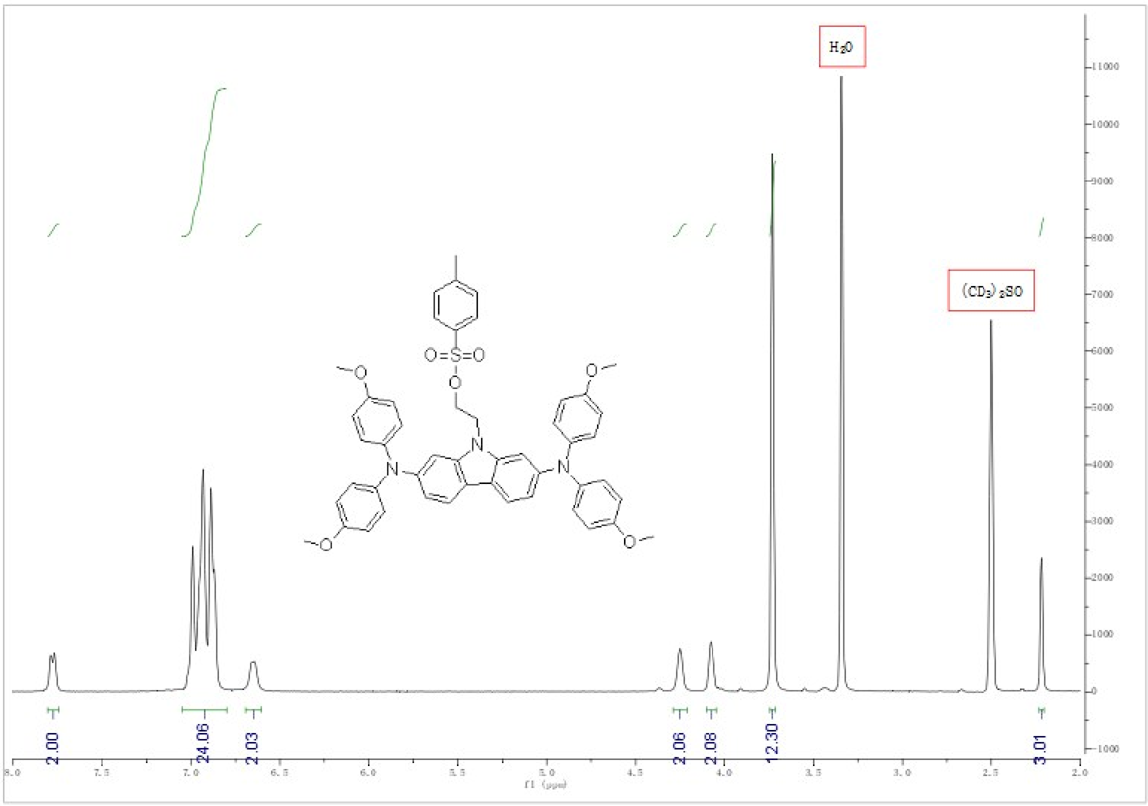

Fig. S8. ^{1}H NMR (DMSO-d6) of compound **4**.

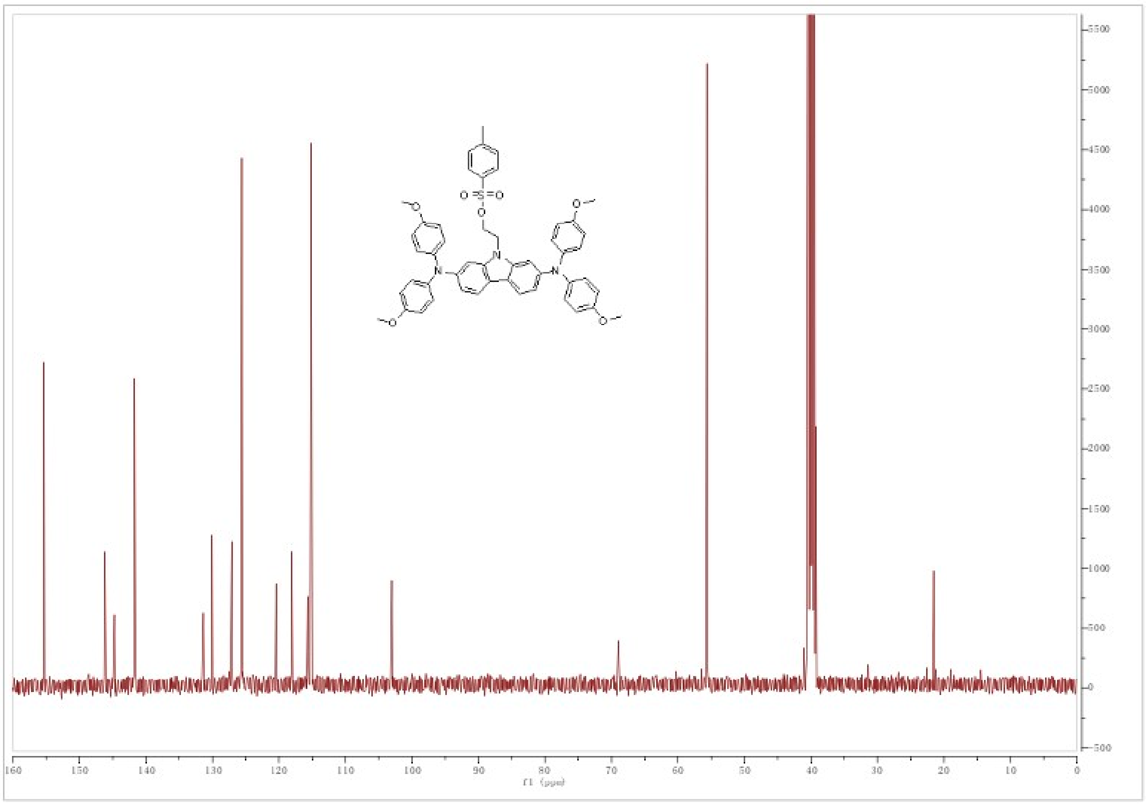

Fig. S9. ^{13}C NMR (DMSO-d6) of compound **4**.

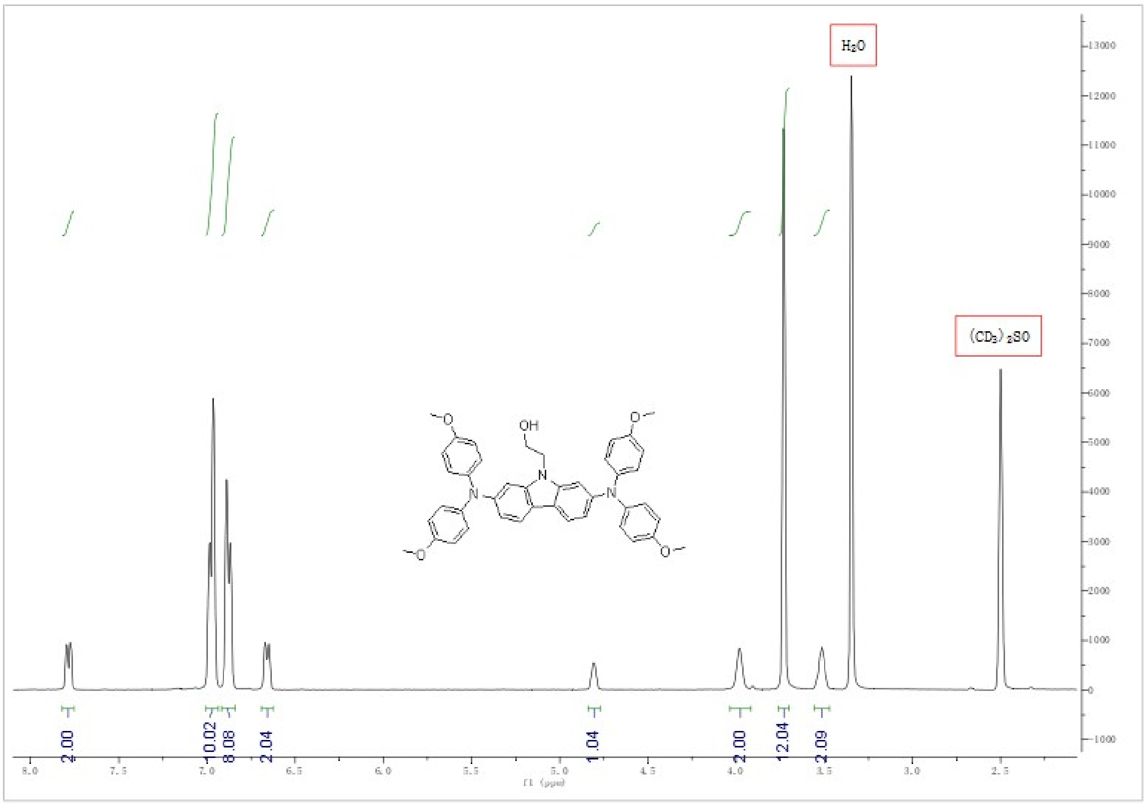

Fig. S10. ^{1}H NMR (DMSO-d6) of compound **5**.

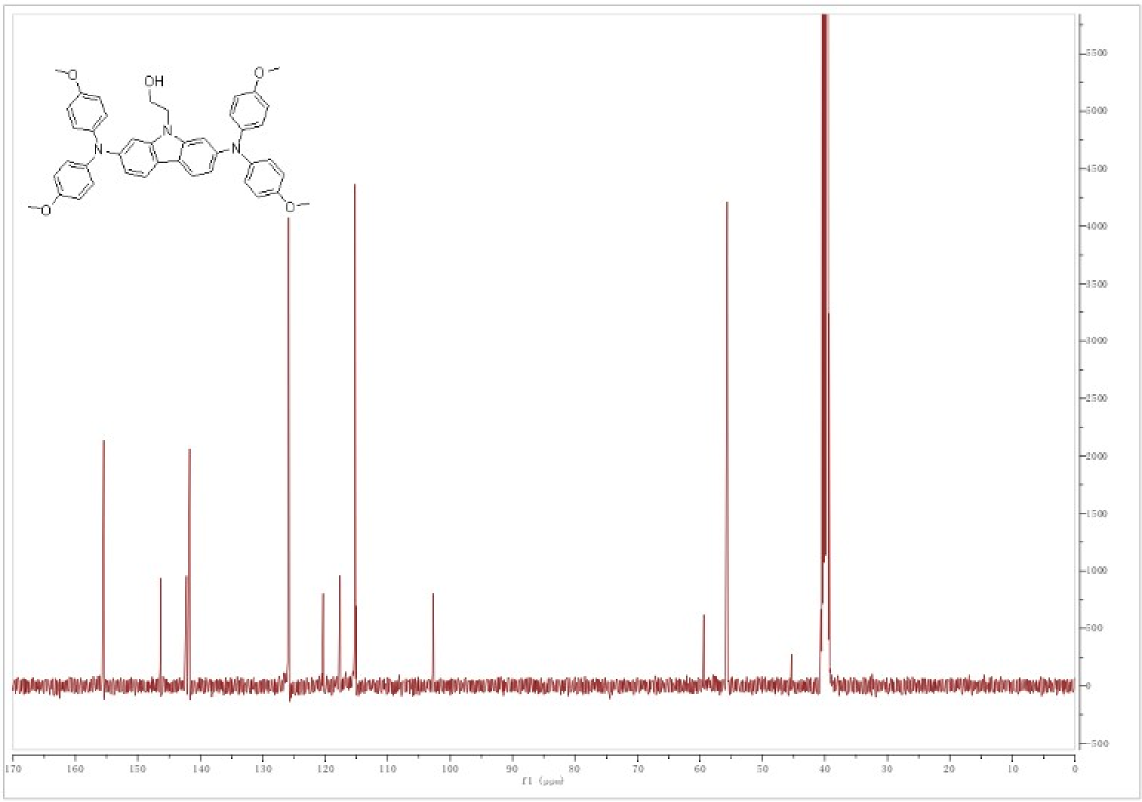

Fig. S11. ^{13}C NMR (DMSO-d6) of compound **5**.

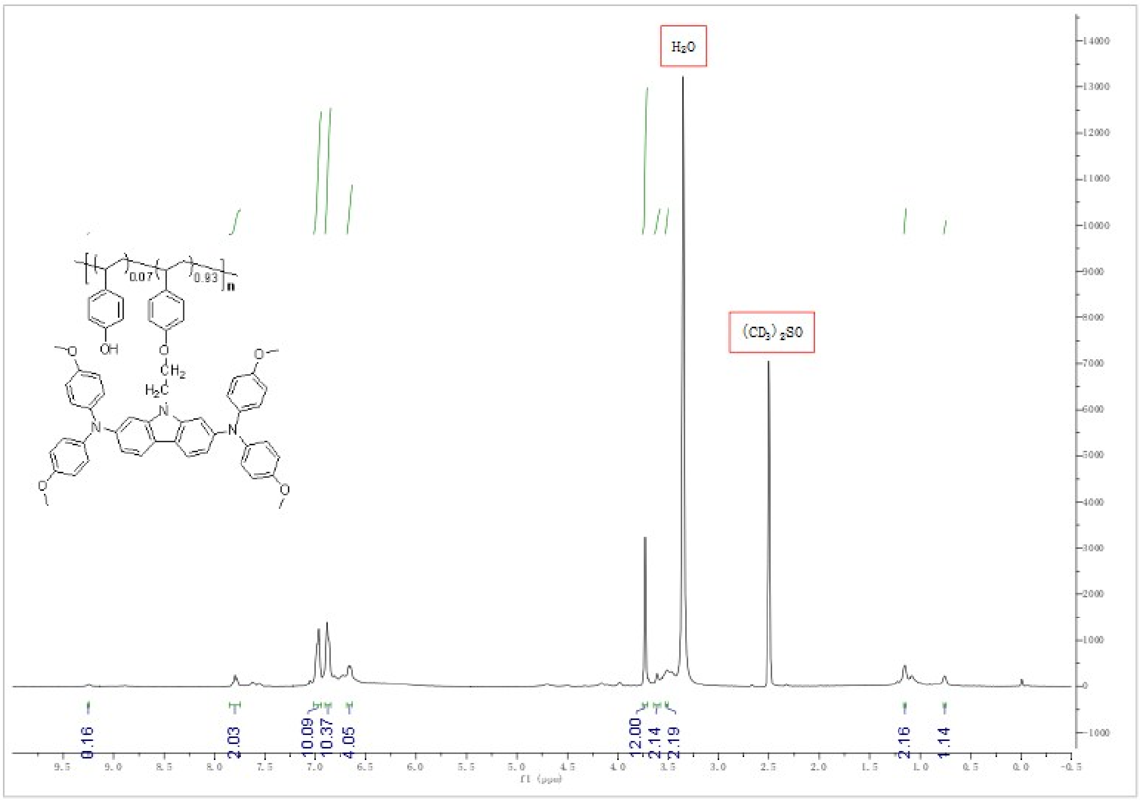

Fig. S12. ^{1}H NMR (DMSO-d6) of **PVP-CZ**.

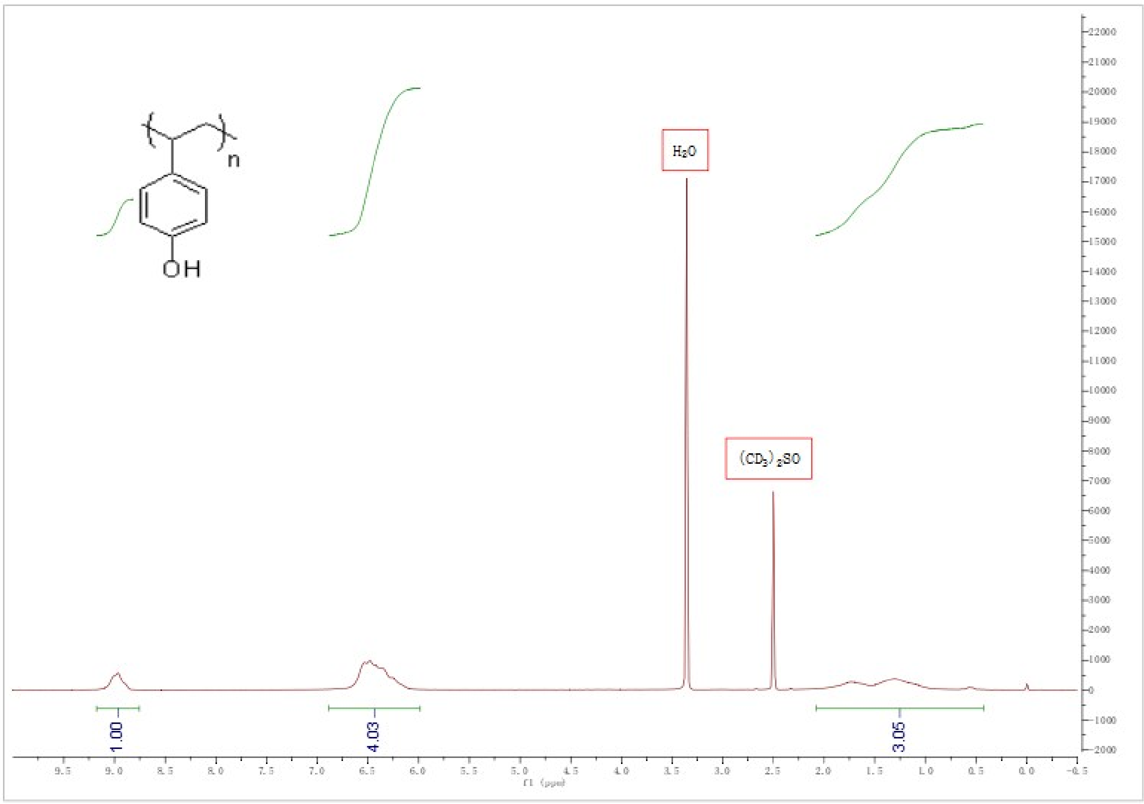

Fig. S13. ^{1}H NMR (DMSO-d6) of poly(4-vinylphenol).

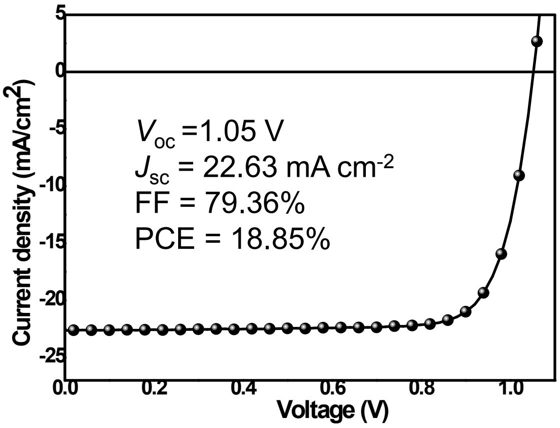

Fig. S14. *J–V* curve of the PVSC with PTAA as HTM measured under AM 1.5 G illumination (100 mW cm^{-2}).

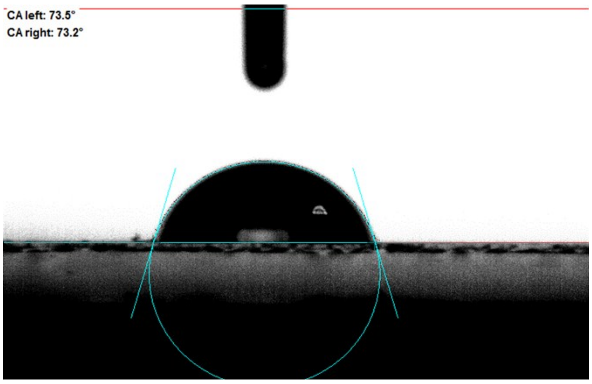

Fig. S15. Contact angle of water on PVP-CZ film.

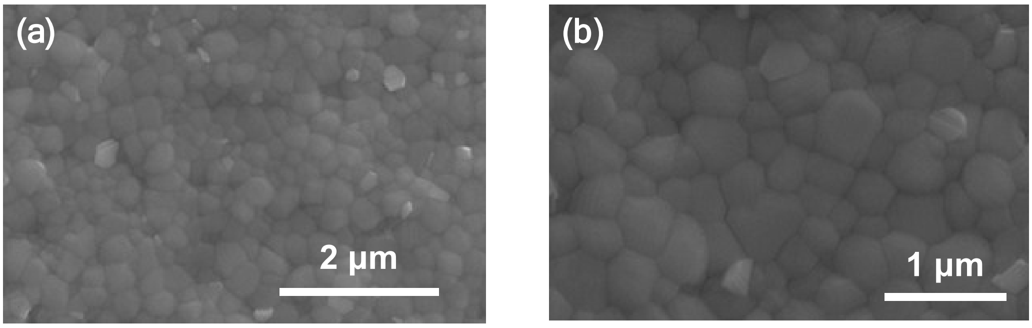

Fig. S16. Top-view SEM images of perovskite film on PVP-CZ. Scale bars: 2 μm for (a) and 1 μm for (b).