

Supporting Information

Efficient Asymmetric Structured Hole Transport Material for Perovskite Solar Cells

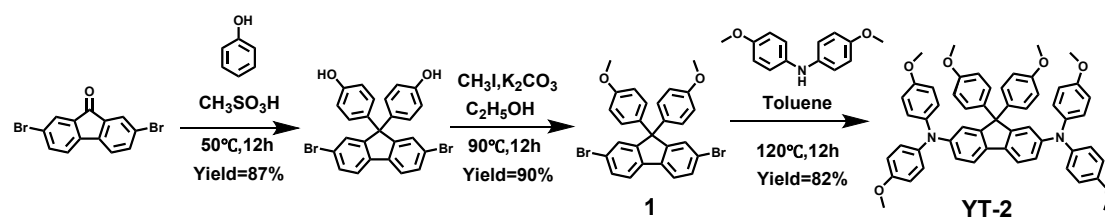
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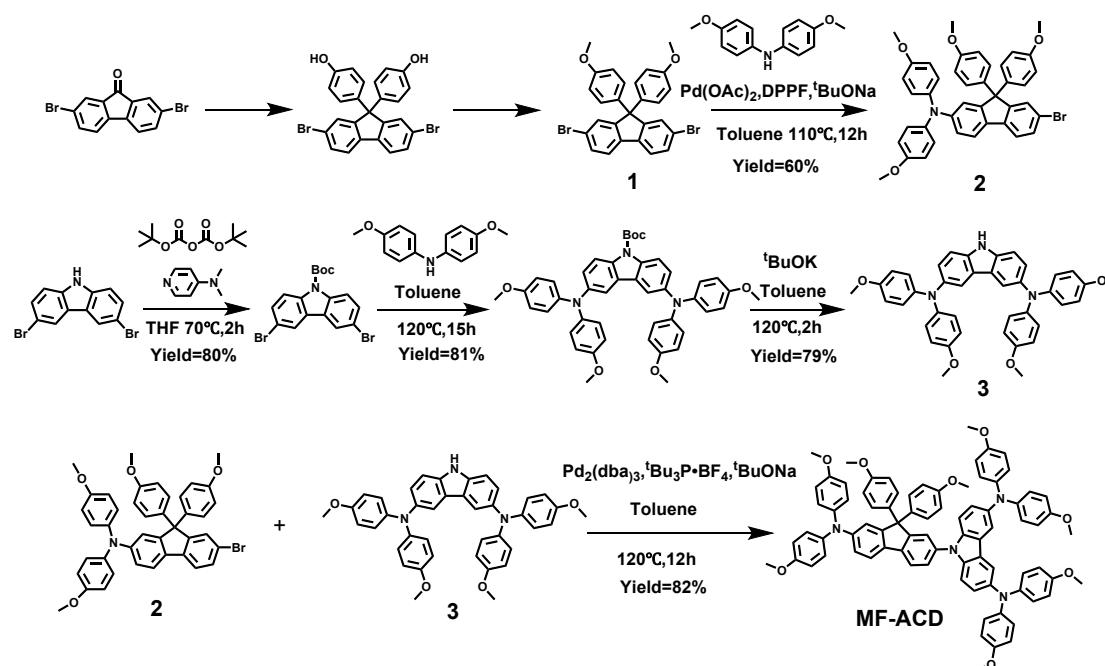
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1.Organic synthesis section

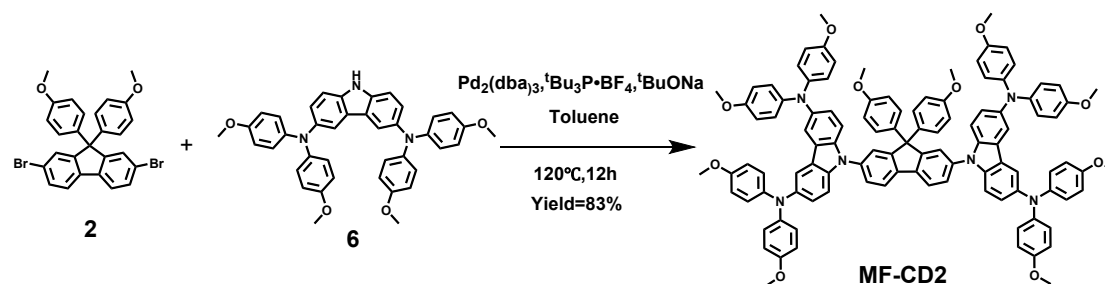
1.1The synthesis route of **YT-2** molecule:



1.2The synthesis route of **MF-ACD** molecule:



1.3The synthesis route of **MF-CD2** molecule:



Compounds **1**, **YT-2** and **3** were synthesized according to references^{1,2}.

7-bromo-*N,N*,9,9-tetrakis(4-methoxyphenyl)-9H-fluoren-2-amine (2): Add compound **1** (533 mg, 1 mmol), bis(4-methoxyphenyl)amine (92mg, 0.4mmol), $\text{Pd}(\text{OAc})_2$ (6.72 mg, 0.03mmol), 1,1'-bis(diphenylphosphino) ferrocene (DPPF)

(22mg, 0.04mmol), ^tBuONa (144mg, 1.5mmol) successively to the flask, add 30 mL toluene as solvent, run nitrogen into the flask for ten minutes to drain the air, The reaction was stirred at 110°C in nitrogen atmosphere for 12 hours³. After the reaction, it was cooled to room temperature, and the crude product was extracted with ethyl acetate and water. The crude product was purified by column chromatography (PE/DCM=1/3vol/vol) to obtain light gray solid 2 (160mg, yield:60%). ¹H NMR (400 MHz, DMSO) δ 7.70 (s, 1H), 7.68 (s, 1H), 7.50 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.45 (d, *J* = 1.5 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H), 6.87 (d, *J* = 9.0 Hz, 4H), 6.82 (d, *J* = 8.9 Hz, 4H), 6.77 – 6.72 (m, 2H), 3.73 (s, 6H), 3.70 (s, 6H). ¹³C NMR (101 MHz, DMSO) δ 158.53, 156.23, 153.68, 152.88, 149.14, 140.41, 139.42, 137.24, 130.94, 130.79, 129.12, 128.79, 126.93, 121.74, 119.44, 117.15, 115.35, 114.28, 64.00, 55.69, 55.49. HRMS (*m/z*): found: [M+H]⁺ 683.1666, calculated: C₄₁H₃₄BrNO₄, 683.1666.

9-(7-(bis(4-methoxyphenyl)amino)-9,9-bis(4-methoxyphenyl)-9H-fluoren-2-yl)-*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine (MF-ACD):

Add product 2 (150mg, 0.22mmol), 3 (150mg, 0.24mmol), Pd₂(dba)₃ (9mg, 0.01 mmol), ^tBu₃P•BF₄ (6mg, 0.02 mmol), ^tBuONa (63mg, 0.66mmol) successively to the flask, add 30mL toluene as solvent, run nitrogen into the flask for ten minutes to drain the air, The reaction was stirred at 120°C in nitrogen atmosphere for 12 hours. After the reaction, it was cooled to room temperature, and the crude product was extracted with ethyl acetate and water. The crude product was purified by column chromatography (PE/EA =3/1vol/vol) to obtain dark yellow solid MF-ACD (220mg, yield:82%). ¹H NMR (400 MHz, DMSO) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.45 (d, *J* = 15.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 7.2 Hz,

10H), 6.81 (dd, $J = 22.6, 13.5$ Hz, 26H), 3.70 (s, 6H), 3.63 (d, $J = 6.7$ Hz, 18H). ^{13}C NMR (101 MHz, DMSO) δ 158.48, 156.17, 154.76, 153.22, 148.91, 142.37, 141.69, 140.47, 137.59, 137.49, 131.27, 129.12, 126.90, 124.96, 124.37, 123.81, 117.07, 115.33, 115.11, 114.27, 110.97, 64.00, 60.21, 55.67, 55.60, 55.42. HRMS (m/z): found: $[\text{M}+\text{H}]^+$ 1224.4986, calculated: $\text{C}_{81}\text{H}_{68}\text{N}_4\text{O}_8$, 1224.5032.

9,9'-(9,9-bis(4-methoxyphenyl)-9H-fluorene-2,7-diyl)bis(N^3,N^3,N^6,N^6 -tetrakis(4-methoxyphenyl)-9H-carbazole-3,6-diamine) (MF-CD2): Add product 1 (200mg, 0.37mmol), 3 (466mg, 0.75mmol), $\text{Pd}_2(\text{dba})_3$ (9mg, 0.01 mmol), $^t\text{Bu}_3\text{P}\cdot\text{BF}_4$ (6mg, 0.02 mmol), $^t\text{BuONa}$ (108mg, 1.12mmol) successively to the flask, add 30mL toluene as solvent, run nitrogen into the flask for ten minutes to drain the air, the reaction was stirred at 120°C in nitrogen atmosphere for 12 hours. After the reaction, it was cooled to room temperature, and the crude product was extracted with ethyl acetate and water. The crude product was purified by column chromatography (PE/EA=3/1vol/vol) to obtain light green solid MF-CD2 (500mg, yield: 83%). ^1H NMR (400 MHz, DMSO) δ 8.25 (d, $J = 7.9$ Hz, 2H), 7.67 – 7.56 (m, 6H), 7.15 (d, $J = 8.7$ Hz, 8H), 7.01 (s, 6H), 6.89 – 6.74 (m, 34H), 4.04 (s, 1H), 4.02 (s, 1H), 3.67 (s, 24H), 3.61 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.70, 154.76, 153.96, 142.55, 141.86, 137.83, 137.31, 137.27, 137.20, 129.10, 125.68, 124.46, 121.38, 116.55, 114.60, 113.92, 110.64, 60.39, 55.53, 55.28. HRMS (m/z): found: $[\text{M}+\text{H}]^+$ 1616.6518, calculated: $\text{C}_{107}\text{H}_{88}\text{N}_6\text{O}_{10}$, 1616.6556.

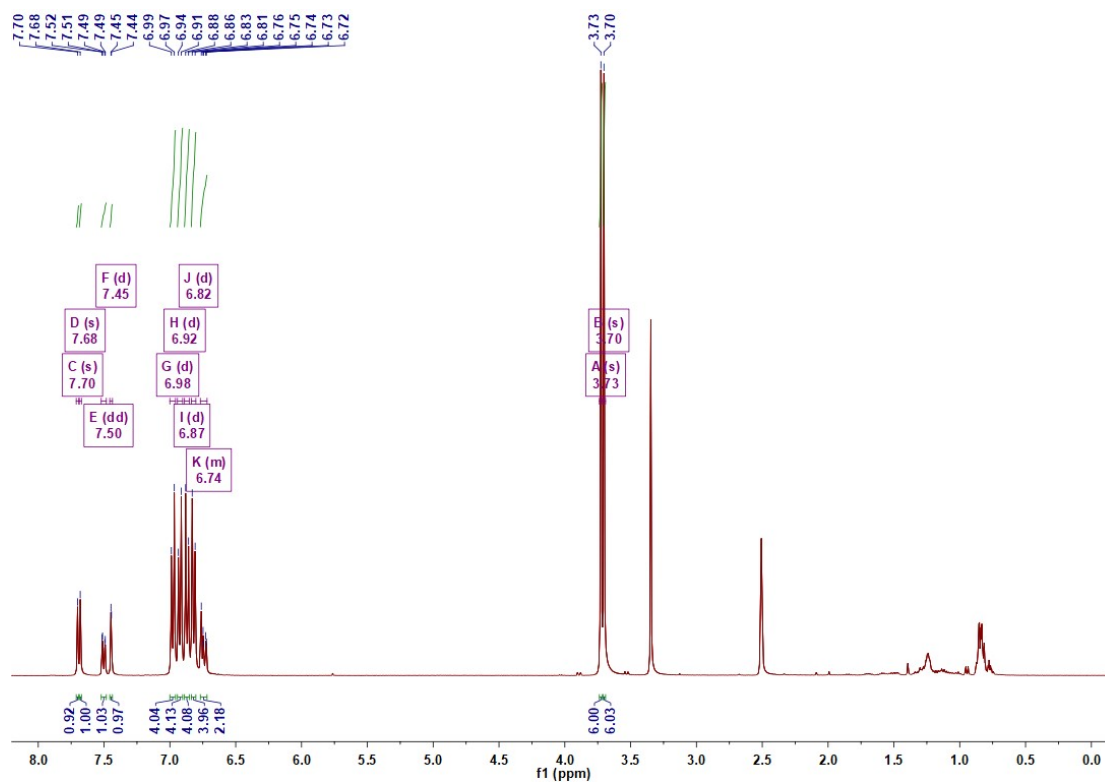


Figure S1. $^1\text{H-NMR}$ spectrum of **2** recorded in $d_6\text{-DMSO}$

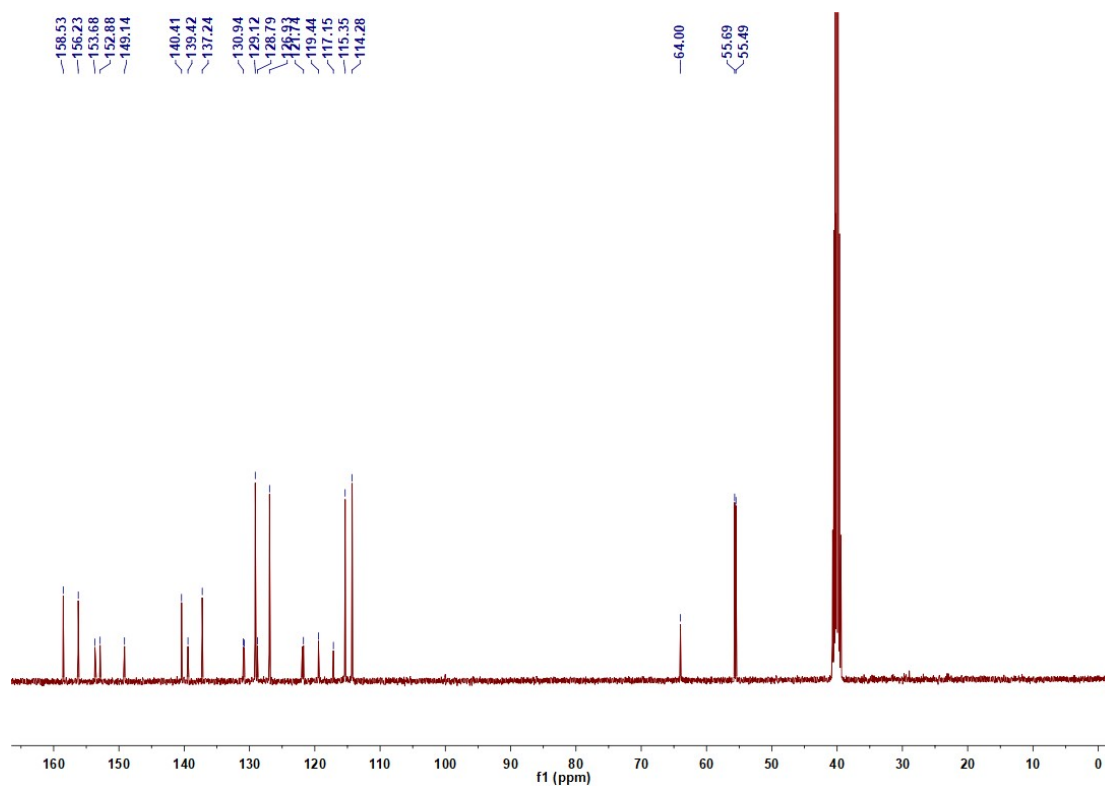


Figure S2. $^{13}\text{C-NMR}$ spectrum of **2** recorded in $d_6\text{-DMSO}$

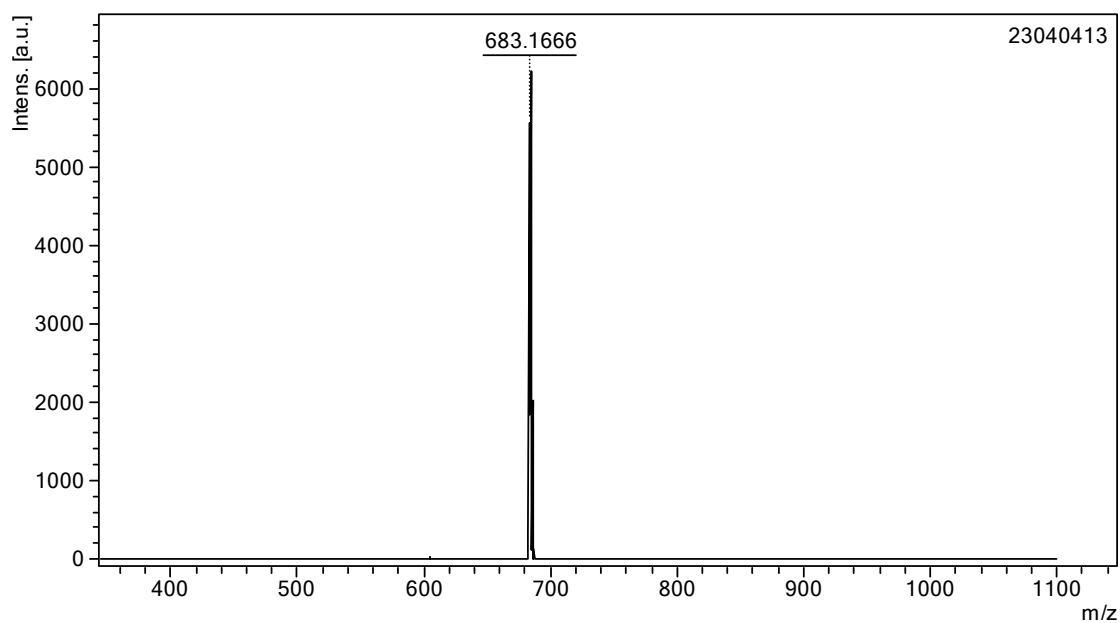


Figure S3. HRMS of 2

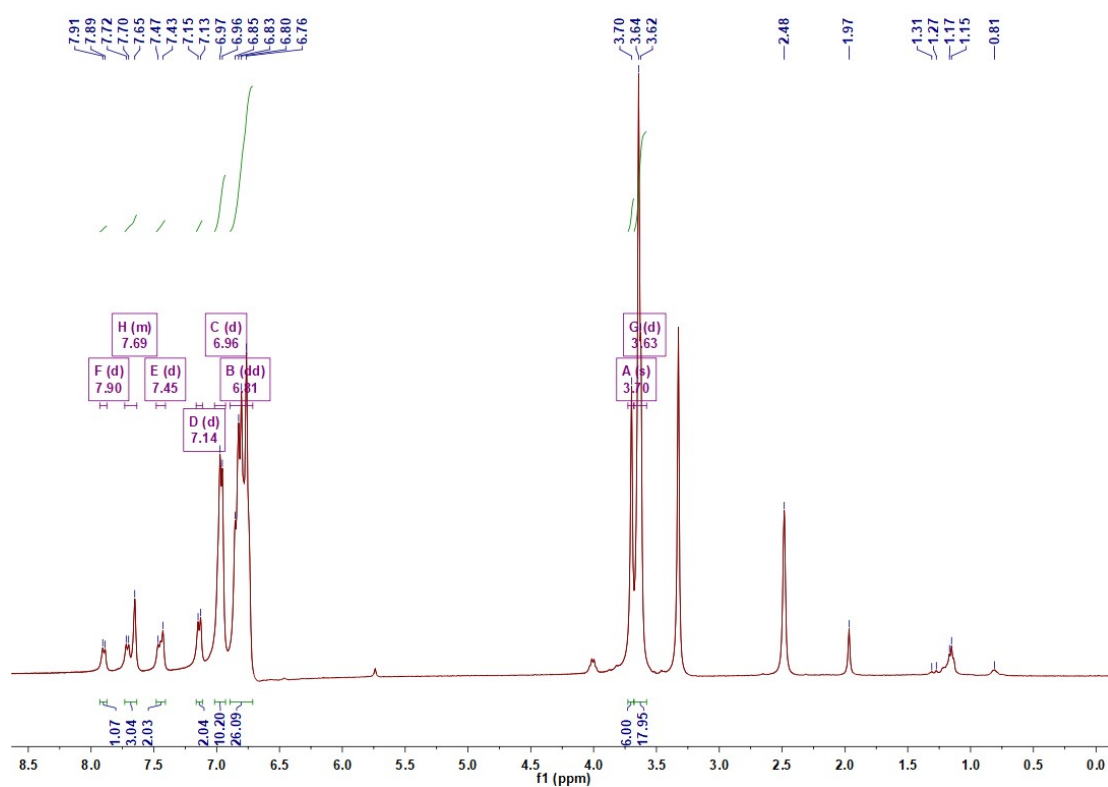


Figure S4. ¹H-NMR spectrum of MF-ACD recorded in *d*₆-DMSO

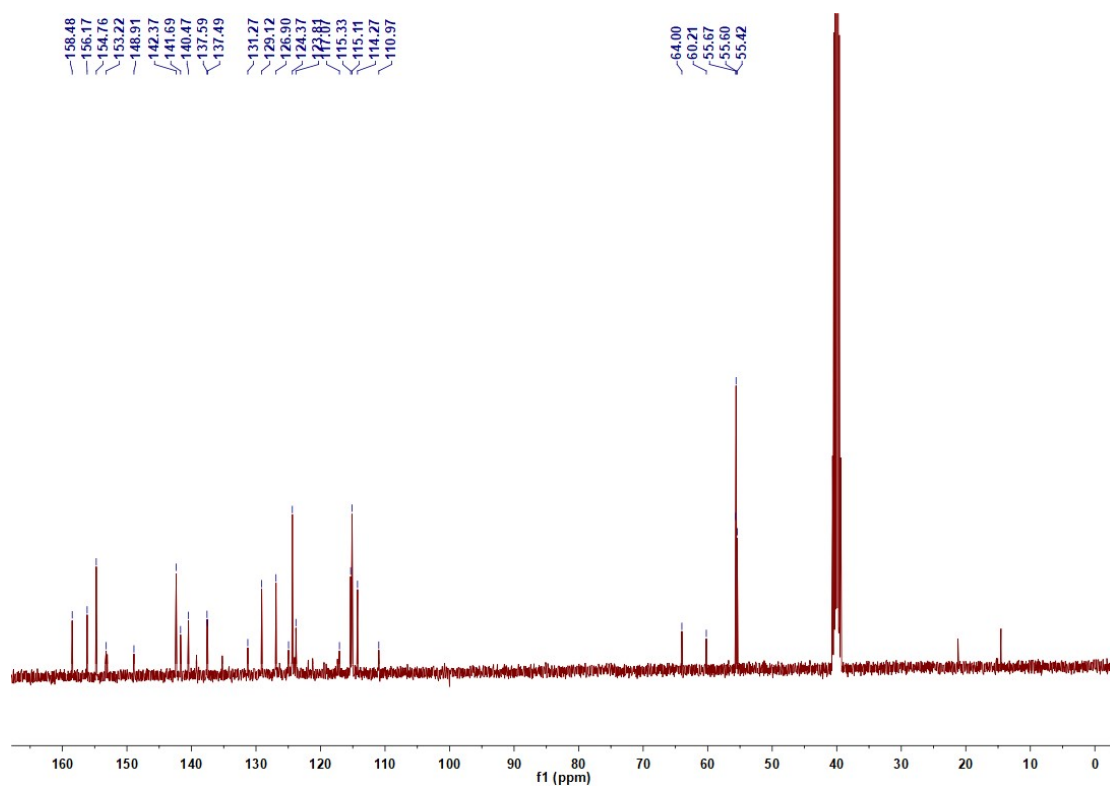


Figure S5. ^{13}C -NMR spectrum of **MF-ACD** recorded in d_6 -DMSO

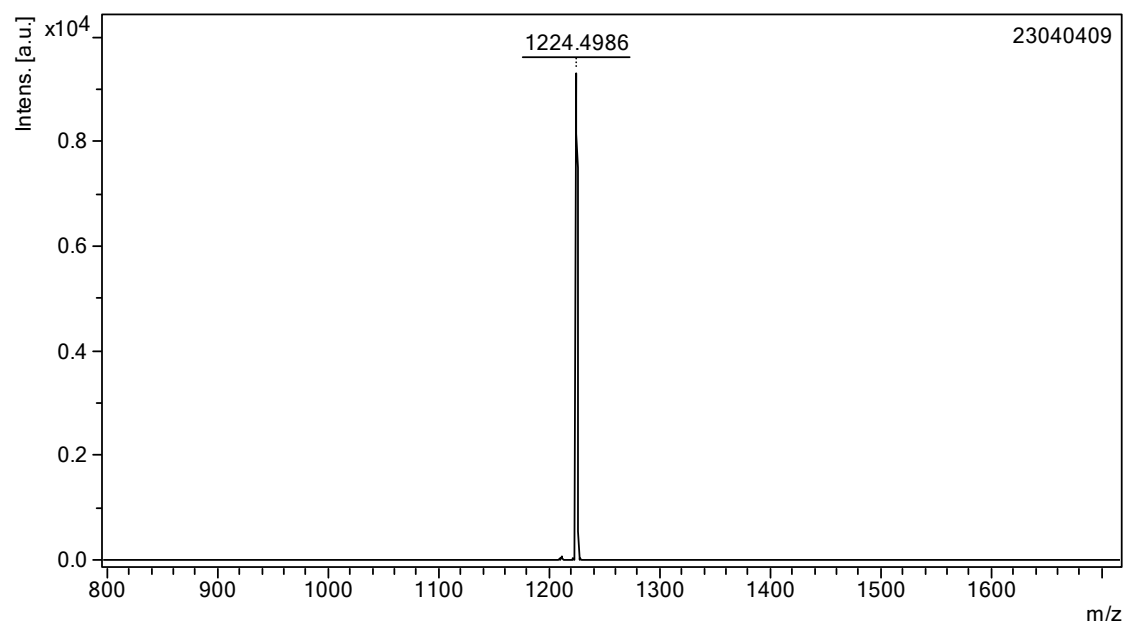


Figure S6. HRMS of **MF-ACD**

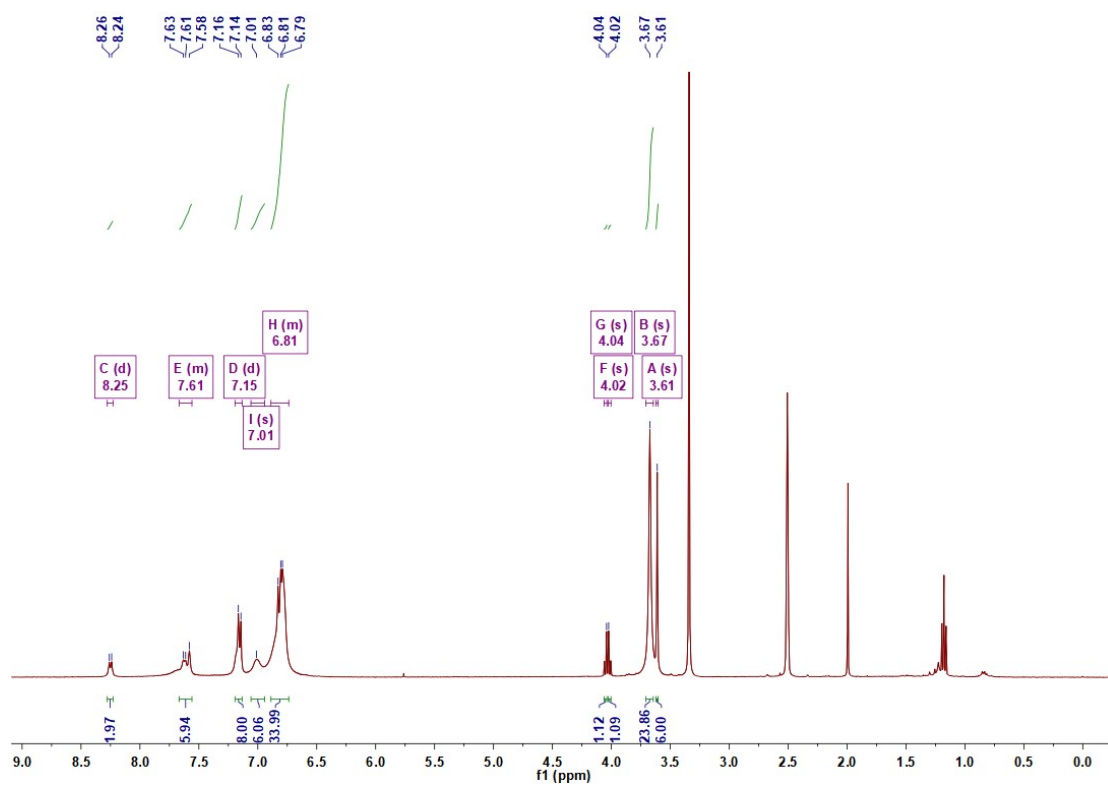


Figure S7. ^1H -NMR spectrum of **MF-CD2** recorded in d_6 -DMSO

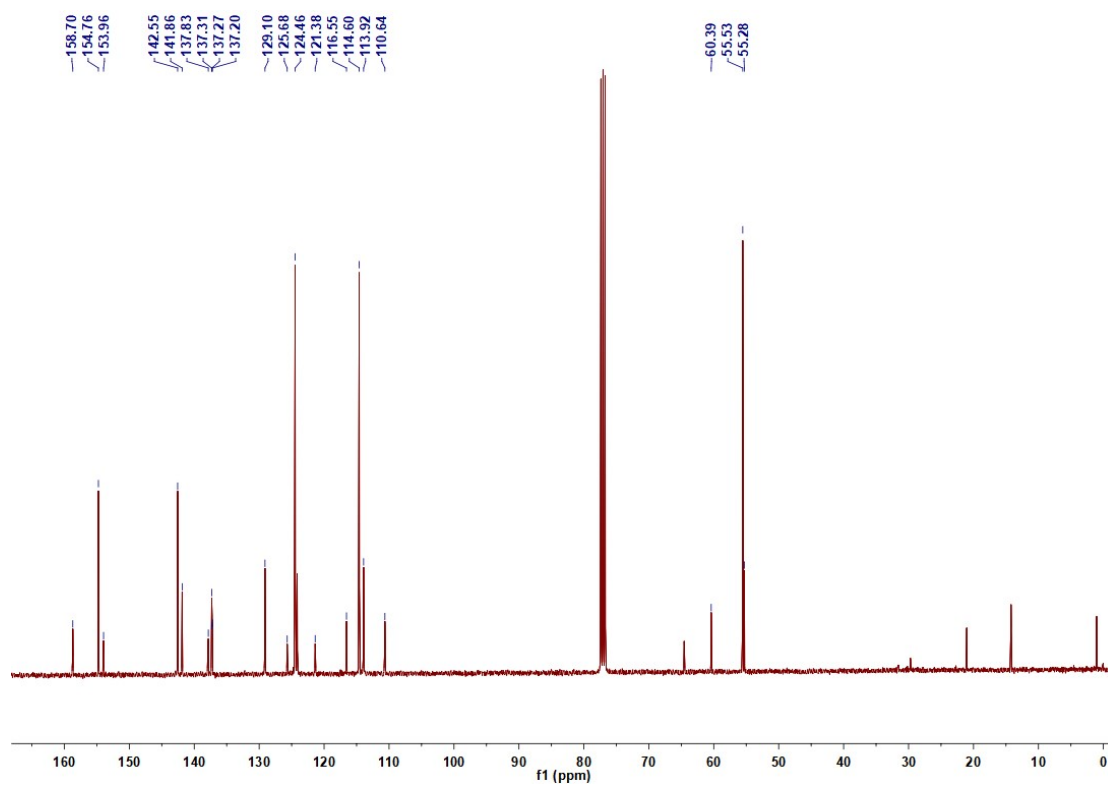


Figure S8. ^{13}C -NMR spectrum of **MF-CD2** recorded in CDCl_3

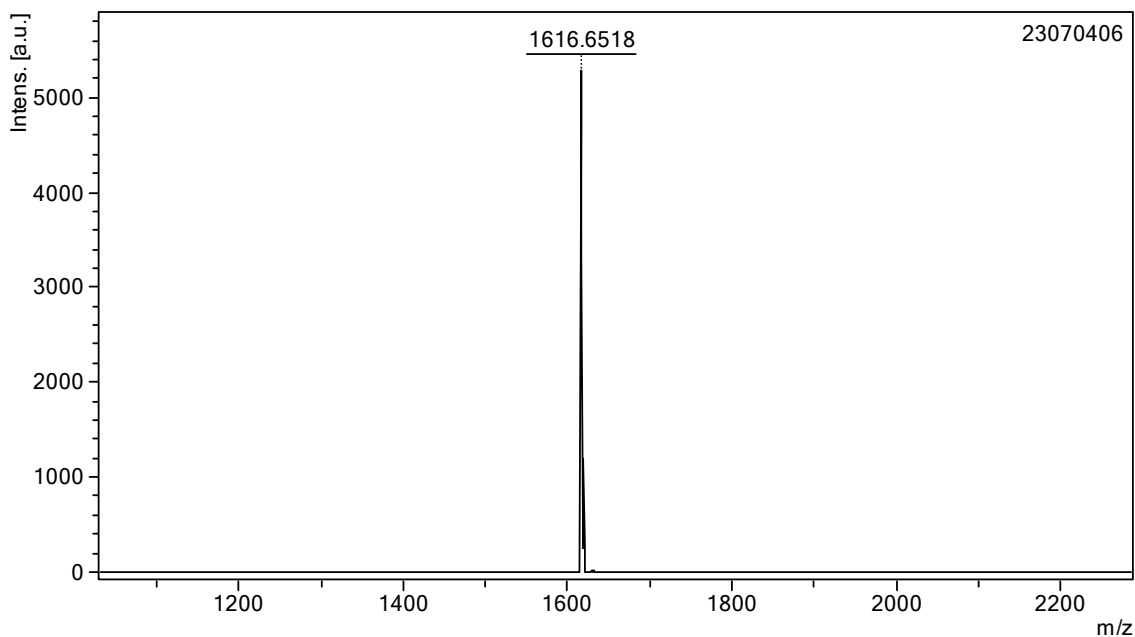


Figure S9. HRMS of **MF-CD2**

2. Preparation of perovskite solar cells

2.1 Etching and cleaning of FTO conductive glass

The FTO conductive glass is cut into 30mm×120mm strips and etched in the middle of the strip, and the etched area is 5.5mm×120mm. The sample was put into a glass cleaning vessel, and ultrasounded for 30min by adding ultra-pure water, acetone and ethanol in turn. Put the cleaned conductive glass in the oven to dry and store it for later use.

2.2 Preparation of electron layer of c-TiO₂

Bis (2, 4-glutaronic acid) bis (2-propanolic acid) titanium (IV) (75% isopropanol solution) and anhydrous ethanol were mixed in a ratio of 1:9 by volume. Then a certain amount of solution was filtered by a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.22μm as the precursor of the dense layer. The

conductive glass after cleaning and drying is placed on a hot table with the conductive side facing upward. When the temperature of the hot table is gradually heated to 500°C, the precursor liquid is evenly sprayed on the FTO conductive glass with a spray gun and held at 500°C for 1h. After cooling to room temperature, each conductive glass was cut into 16 (15mm×15mm) square samples.

2.3 Preparation of SnO₂ electron layer

Weigh 20mg polyacrylic acid (PAA) and add 19mL ultra-pure water at room temperature, stir for 1h, and add 1ml 15% SnO₂ aqueous solution, stirred at 80°C for 3h, after cooling to room temperature, it was filtered by polyether sulfone (PES) membrane with a pore size of 0.22 μm. The sample was cleaned by ultraviolet ozone for 30min, and 30μL solution drops were absorbed by pipette gun and added on TiO₂ dense layer for spin coating. The speed of the homogenizer was set at 4000r/min and rotated for 30s, and then moved to the hot table for heating at 160°C for 30min.

2.4 Preparation of perovskite film

Weigh FAI 240.8mg, PbI₂ 705.2mg, MACl 33.8mg, MAPbBr₃ 5.8mg, add 1mL DMF and DMSO mixed solution, the volume ratio is 8:1, stir for 12h, polyvinylidene fluoride (PVDF) membrane with a pore size of 0.22μm was used for filtration. The samples were cleaned by ultraviolet ozone for 10min and transferred to an air glove box. Use a pipette gun to absorb 30μL precursor droplets and add them to the surface of SnO₂ electronic layer for spin coating, set the speed of the homogenizer to 1000r/min for 10s, 6000r/min for 30s, and then add anti-solvent chlorophenol 100μL when countdown 10s, and then move to the hot table to heat at 120°C for 60min.

2.5 Preparation of hole transport layer

YT-2, MF-ACD and MF-CD2 were each weighed 50mg, and Spiro-OMeTAD 73mg, add 1mL chlorobenzene to dissolve, 17.5μL LiTFSI (520 mg/mL acetonitrile) and

28.8 μLTBP were added to homogenize the mixture. A polyvinylidene fluoride (PVDF) membrane with a pore size of $0.22\mu\text{m}$ was filtered, and then $30\mu\text{L}$ solution drops were absorbed by a pipette gun and added to the surface of perovskite for spin coating. The speed of the homogenizer was set to $3000\text{r}/\text{min}$ and rotated for 30s .

2.6 Preparation of the opposite electrode

Use a high vacuum evaporation coating machine to steam the sample. Before steaming, use a knife to scrape off the top part of the FTO opposite the etched edge of the sample (the scraping area is $3\text{mm}\times 15\text{mm}$). The high purity gold was selected and uniformly steamed to the surface of the prepared hole material at A rate of about $0.5\text{ \AA}/\text{s}$, and the evaporation thickness was 100 nm .

3. Test section of perovskite solar cells

3.1 Hole mobility and hole conductivity measurements

The hole mobility of HTM was measured by space charge limiting current method (SCLC), and the device structure is ITO/PEDOT:PSS/HTM/Au. The device structure of the conductivity is Glass/ TiO_2 /HTM/Au, Figure S10. is the correlation structure diagram.

The formula for calculating the hole mobility is shown below:

$$J = \frac{9}{8} \mu \varepsilon_0 \varepsilon_r \frac{V^2}{D^3}$$

Where J is the current density, μ is the hole mobility, ε_0 and ε_r are the vacuum dielectric constant ($8.85\times 10^{-12}\text{ F}/\text{m}$) and the dielectric constant of HTM (generally 3 for organic semiconductors), V is the applied bias, and D is the HTM thickness.

The formula for calculating the conductivity is below:

$$\sigma = \frac{W}{RLD}$$

Where σ is the conductivity, W is the channel width 2 mm, L is the channel length 10 mm, D is the common thickness of TiO_2 and HTM, and R is the film resistance calculated from the slope of the conductivity curve.

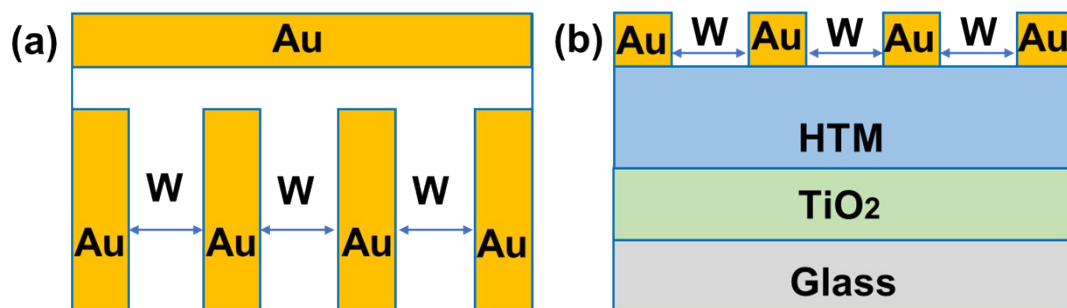


Figure S10. (a) Schematic view of the conductivity device (b) schematic cross-section

3.2 DFT calculation details

The molecular dipole is calculated by DFT calculation and the value is obtained directly after calculation. Geometries optimization and frequency analysis were performed at the level of B3LYP /6-311G(d,p). The molecular orbitals and dipole moments were analyzed, the energy gaps between HOMO and LUMO were obtained. All calculations are based on Density Functional Theory (DFT) with Gaussian09 package.

4. SEM images

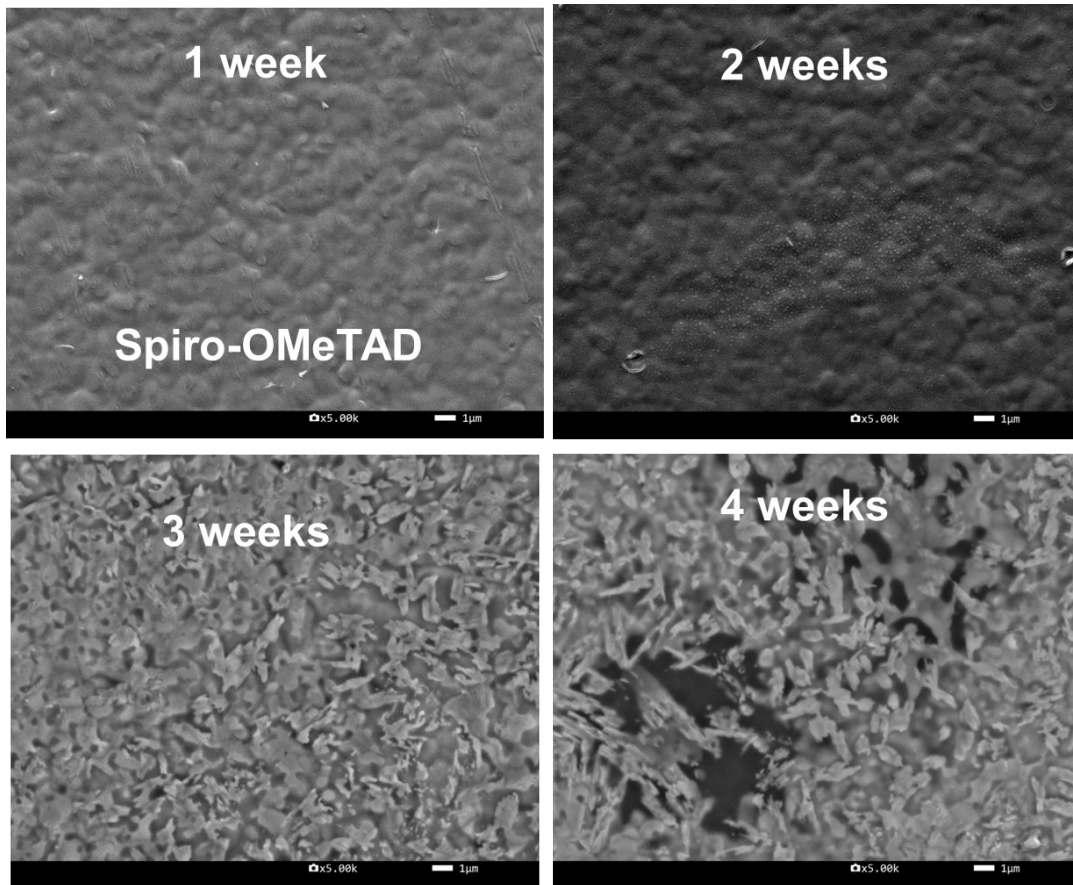


Figure S11. Long-term stability of unencapsulated PSC devices based on Spiro-OMeTAD under the ambient condition of 20-25 °C and 40-60% RH

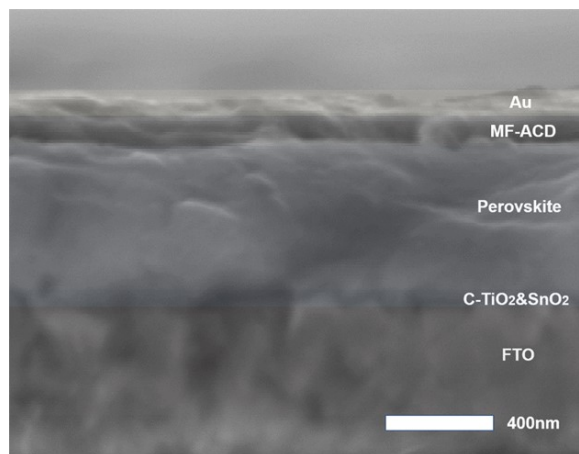


Figure S12. SEM images of the device cross section

5.The rest part

Table S1 TRPL parameters of the different HTMs

Sample	τ_1/ns	Rel.%	τ_2/ns	Rel.%	$\tau_{\text{ave}}/\text{ns}$
With Spiro-OMeTAD	2.11	221.90	84.42	55.94	77.01
With YT-2	2.08	183.39	145.09	88.99	145.53
With MF-CD2	1.95	224.88	99.16	55.69	92.01
With MF-ACD	1.34	232.22	73.27	48.46	67.72

$$\text{Note: } \tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

1. M. Zhai, A. Wang, C. Chen, F. Hao, H. Wang, L. Ding, X. Yang and M. Cheng, *Chemical Engineering Journal*, 2021, **425**, 131675.
2. Y. Shi, K. Hou, Y. Wang, K. Wang, H. Ren, M. Pang, F. Chen and F. Zhang, *J. Mater. Chem. A*, 2016, **4**, 5415-5422.
3. F. Liu, Z. Tu, Y. Fan, Q. Li and Z. Li, *ACS Omega*, 2019, **4**, 18609-18615.