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Supporting information for:

Introducing fluorene into organic hole transport materials to improve mobility and photovoltage for perovskite solar cells

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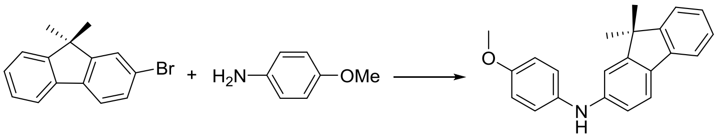
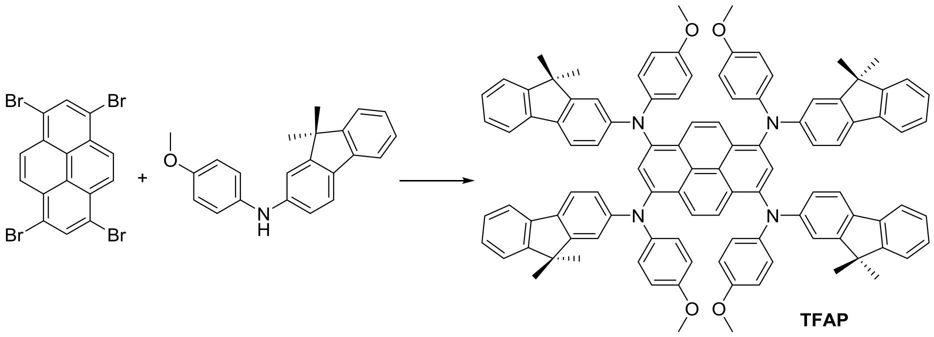
Experimental section

Synthesis of TFAP

Commercially available starting materials were purchased and used without any further purification. Solvents were purified by standard methods and dried if necessary. NMR spectra were recorded in the designated solvent on Bruker Avance 300 MHz or 400 MHz spectrometer. Spectra are reported in ppm values from residual protons of deuterated solvent. Mass data were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is α-cyano-4-hydroxycinnamic acid.



Synthesis of *N*-(*p*-methoxyphenyl)-*N*'-(9,9-dimethylfluoren-2-yl)amine: A suspension of 2-bromo-9,9-dimethyl-9H-fluorene (1.1 g, 4.0 mmol), *p*-anisidine (0.52 g, 4.2 mmol), $Pd_2(dba)_3$ (0.18 g, 0.2 mmol), dppf (0.11 g, 0.2 mmol) and NaO^tBu (0.38 g, 4.0 mmol) in 40 mL of dry toluene was stirred under nitrogen atmosphere for 24 h at 80 ^{o}C. After cooling to room temperature, the reaction mixture was concentrated. The residue was purified by chromatography on silica gel (eluting with petroleum ether/CH_2Cl_2, 5/1 v/v) to give 1.0 g of *N*-(*p*-methoxyphenyl)-*N*'-(9,9-dimethylfluoren-2-yl)amine in 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.38 (s, 6H), 3.73 (s, 3H), 6.89 (d, J = 8.0 Hz, 3H), 7.05 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.17 (t, J = 8.0 Hz, 1H), 7.26 (t, J = 6.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.58-7.62 (m, 2H), 8.00 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.63, 46.64, 55.69, 109.7, 114.3, 115.1, 119.0, 120.9, 121.2, 122.9, 125.9, 127.3, 129.9, 136.7, 139.7, 145.7, 152.9, 154.4, 155.3. EI-MS (m/z): 315 for $[M]^+$. HRMS-EI calcd for $C_{22}H_{21}NO$: 315.1623. Found: 315.1618.



Synthesis of **TFAP**: A suspension of 1,3,6,8-tetrabromopyrene (310 mg, 0.60 mmol), *N*-(*p*-methoxyphenyl)-*N*'-(9,9-dimethylfluoren-2-yl)amine (787 mg, 2.5 mmol), $Pd_2(dba)_3$ (110 mg, 0.12 mmol), dppf (67 mg, 0.12 mmol), and NaO^tBu (240 mg, 2.5 mmol) in 30 mL of toluene was heated at 120 ^oC for 96 h under N_2 atmosphere. The system was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by chromatography on silica gel (eluting with petroleum ether/CH_2Cl_2, 1/1 v/v) to yield 347 mg of **TFAP** as a yellow solid in 39.7% yield. m.p.: 365 ^oC. ^1H NMR (400 MHz, DMSO-d_6): δ 1.20 (s, 24H), 3.65 (s, 12H), 6.75 (d, J = 8.4 Hz, 4H), 6.82 (d, J = 8.4 Hz, 8H), 6.98 (s, 4H), 7.06 (d, J = 8.0 Hz, 8H), 7.15-7.24 (m, 8H), 7.39 (d, J = 6.8 Hz, 4H), 7.53 (d, J = 8.0 Hz, 4H), 7.58 (d, J = 7.2 Hz, 4H), 7.66 (s, 2H), 8.00 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.44, 22.53, 27.26, 31.43, 46.71, 55.57, 114.4, 115.3, 118.8, 119.6, 121.3, 122.9, 123.1, 125.8, 126.5, 126.6, 127.4, 128.5, 129.4, 132.0, 138.9, 140.9, 142.6, 149.1, 153.3, 155.1, 155.7. MALDI-TOF-MS (m/z): 1454.5 for $[M]^+$. HRMS-MALDI-TOF calcd for $C_{104}H_{86}N_4O_4$: 1454.6643. Found: 1454.6638.

Fabrication of solar cell devices

The conductive glass substrates (ITO-coated glass, < 10 Ω/square) were cleaned by ultrasonication in isopropanol (1 h), suds (1 h), deionized water (30 min), acetone (15 min) and isopropanol (30 min), respectively. The cleaned ITO were dried under a flux of nitrogen and further cleaned in the UV-O_3 cleaner for 30 min. The precursor solution of the electron transport layer (ETL, SnO_2) was spin-coated onto ITO at 3000 rpm for 30 s, then annealed at 150 ^oC for 30 min. The perovskite precursor solution was prepared according to the reported method.[1] To fabricate the perovskite films, the precursor solution was spin-coated onto the SnO_2-coated ITO at 4000 rpm for 25 s in air atmosphere and 2 mL of diethyl ether was dripped on rotating substrate in 2 s before the surface changed to be turbid. The prepared perovskite film was annealed at 65 ^oC for 1 min and 100 ^oC for 2 min. The optimized concentration in 1 mL of chlorobenzene were found to be 65 mM for spiro-OMeTAD and 20 mM for TFPA and Py-C respectively. In addition, 30 μL of 4-tert-butylpyridine (> 96.0%, TCI), and 35 μL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) (99.95%, Sigma-Aldrich) solution (260 mg Li-TFSI in 1 mL acetonitrile, 99.8%, Sigma-Aldrich) were added as additives. Then the HTM solution was spin-coated onto the perovskite layer at 3000 rpm for 30 s. Due to the relatively low solubility of TFPA and Py-C, the HTM solution as well as the substrate were heated to 100 ℃ for spin coating. Finally, 100 nm of gold was deposited on the HTM-coated films at a metallization chamber.

The hole-only devices were fabricated by spin-coating PEDOT:PSS (1-3% in water) onto pre-cleaned, patterned ITO substrates. A film of the HTM was spin-coated on top of the PEDOT:PSS layer from its chlorobenzene solution with a concentration as the same as that for perovskite devices fabrication. As a counter electrode, a Au layer of 100 nm thick was deposited on the top by vacuum evaporation. The current density-voltage curves of the devices were recorded with a Keithley 2400 source. The hole mobility is estimated by using Mott-Gurney's equation, $J = 9\varepsilon_r\varepsilon_0\mu_h V^2/8L^3$, where ε_r is the relative dielectric constant of the transport medium (ε_r is 3 for organic materials), ε_0 is the permittivity of free space (8.85×10^{-12} C V^{-1} m^{-1}), L is the thickness of the HTM layer, μ_h is the hole mobility and V is the voltage drop through the device.[2]

Characterization

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGAQ600 with a ramp of 10 ℃ min^{-1} under N_2 from 40 to 800 ℃. Morphology and microstructure characterization of different layers were investigated using an S-4800 high resolution field emission scanning electron microscope (FESEM) (Hitachi, Japan). The current density-voltage (*J*-*V*) curves were measured using a solar simulator manufactured by Enli Technology Co., Ltd with a source meter (keitheley 2400) at 100 mA/cm^2 illumination (AM 1.5G). The light intensity was adjusted with an NREL calibrated silicon solar cell. The active area (0.012 cm^2) was defined with a mask with aperture. Transient-state photoluminescence was measured by FLS980 (Edinburgh Instruments Ltd) with an excitation wavelength of 600 nm. The conditions of all measurement of solar cells were conducted at room temperature under ambient atmosphere without encapsulation.

Computational Methods

DFT calculations are carried out using the exchange correlation functional B3LYP and 6-31G* basis set implemented in the Gaussian 09 package. No symmetry constraints were used in the optimization (nosymm keyword). Solvation effects in CH_2Cl_2 were included for all calculations using the conductor-like polarizable continuum model (CPCM). All orbitals have been computed at an isovalue of 0.02 e/bohr^3. TDDFT calculations were performed at the same level of theory.

Table S1. Calculation of the synthetic cost of **TFAP**.

Chemical	**Weight reagent or solvent (g/g)**	**Weight workup (g/g)**	**Price of Chemical (US$ /kg)**	**Chemical cost (US$ /g product)**	**Cost per step (US$/g)**
p-anisidine	0.52		58	0.03	
2-bromo-9,9-dimethyl-9H-fluorene	1.10		436	0.48	
$Pd_2(dba)_3$	0.18		12790	2.30	
dppf	0.11		523	0.05	
NaO^tBu	0.38		43	0.01	
Toluene	35		3.7	0.13	
Petroleum ether		1280	3.7	4.73	
CH_2Cl_2		331	2.6	0.86	
Silica gel		100	5.4	0.54	
***N*-(*p*-methoxyphenyl)-*N*'-(9,9-dimethylfluoren-2-yl)amine**					9.13
***N*-(*p*-methoxyphenyl)-*N*'-(9,9-dimethylfluoren-2-yl)amine**	0.787			7.1	
1,3,6,8-tetrabromopyrene	0.31		1162	0.36	
$Pd_2(dba)_3$	0.11		12790	1.41	
dppf	0.067		523	0.03	
NaO^tBu	0.24		43	0.01	
Toluene	26		3.7	0.09	
Petroleum ether		1280	3.7	4.73	
CH_2Cl_2		662	2.6	1.72	
Silica gel		100	5.4	0.54	
TFAP					46.08

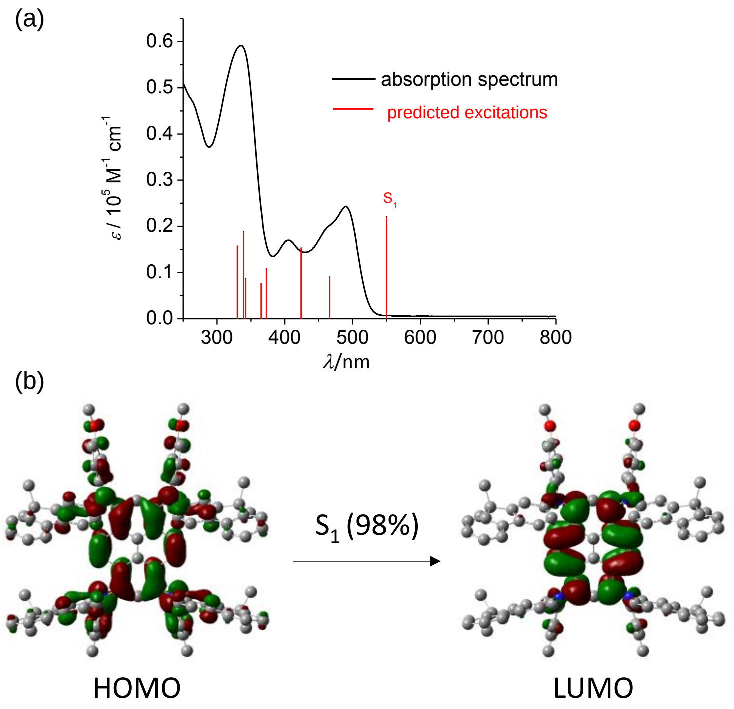


Fig. S1 TDDFT results of TFAP. (a) Predicted excitations together with the experimental absorption spectrum. (b) HOMO and LUMO orbitals responsible for the first singlet (S_1) excitation.

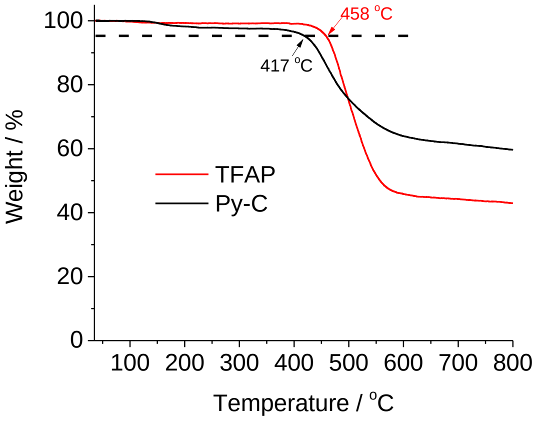


Fig. S2 Thermogravimetric analysis of TFAP and Py-C (scan rate: 10 ℃ min^{-1}). The decomposition temperature was determined at the point with 5% weight loss.

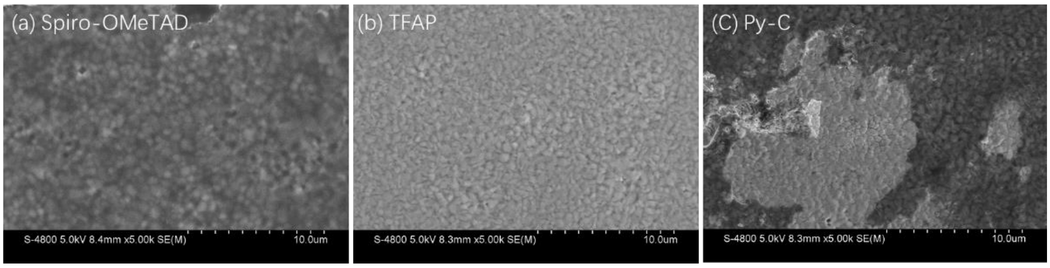


Fig. S3 SEM images of the perovskite film coated with different HTM.

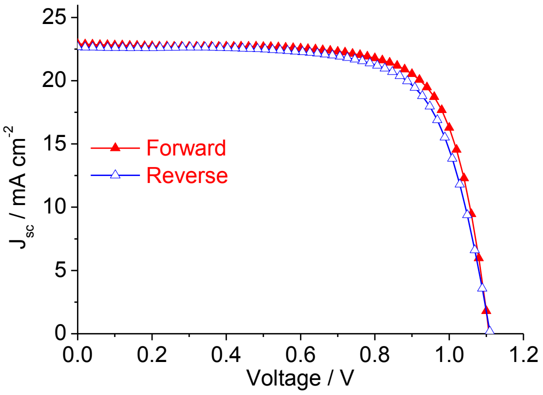


Fig. S4 Forward and reverse scanning *J*-V curves and photovoltaic parameters of a device with TFAP.

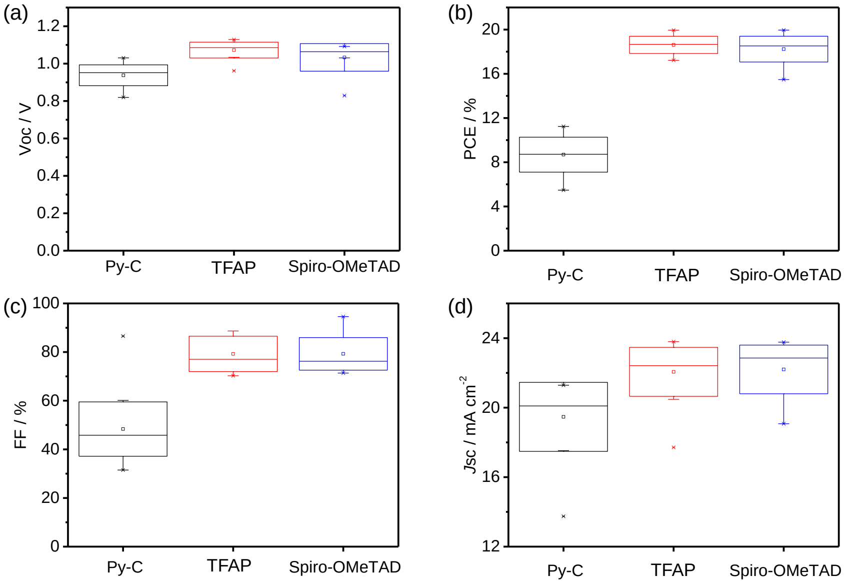


Fig. S5 Box plots of the photovoltaic parameters (V_{oc}, PCE, *FF*, and J_{sc} respectively) of PSCs with different HTMs.

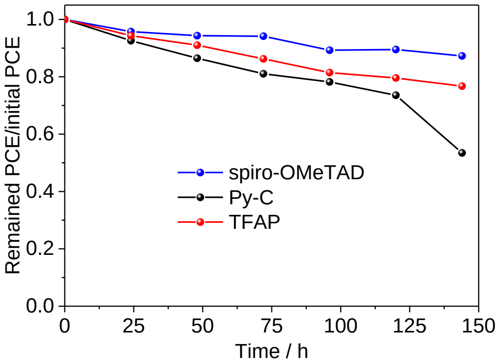


Fig. S6 Performance stability test under ambient conditions of the device with different HTM without encapsulation.

Table S2. Time-resolved PL decay fitting parameters.

film	τ_1 (ns)	τ_2 (ns)
perovskite/Py-C	11.5	147.0
perovskite/spiro-OMeTAD	9.8	74.7
perovskite/TFAP	8.4	139.8
perovskite	13.0	230.5

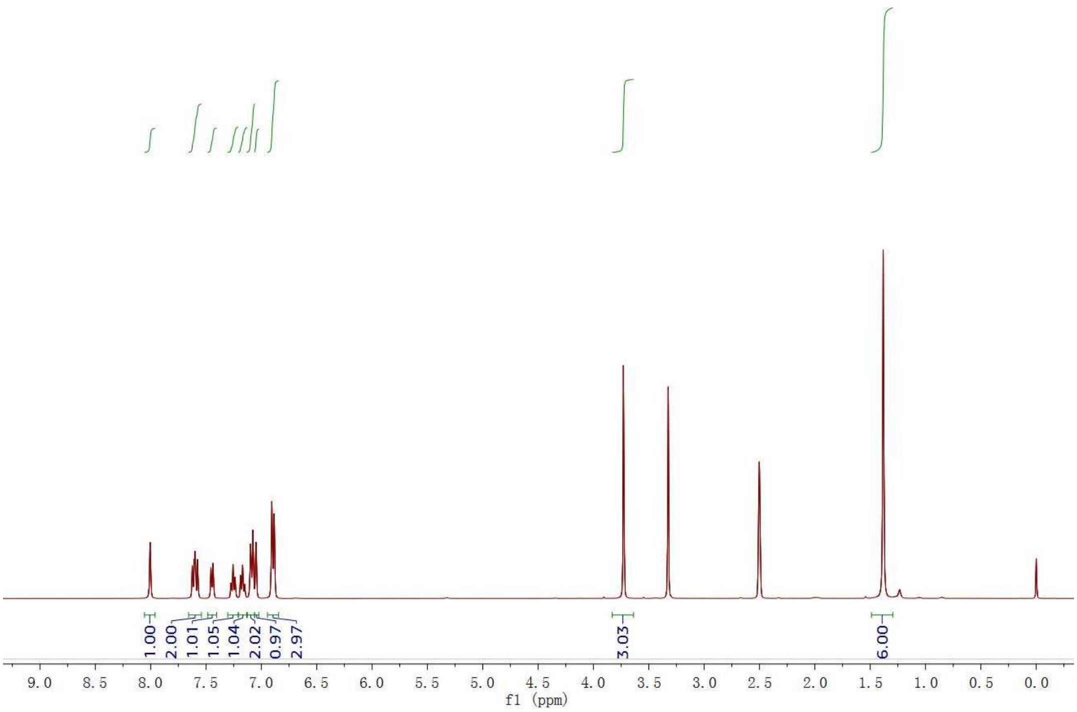


Fig. S7 ^{1}H NMR spectrum of N-(*p*-methoxyphenyl)-N’-(9,9-dimethylfluoren-2-yl)amine (400 MHz, DMSO-d_6, 298 K).

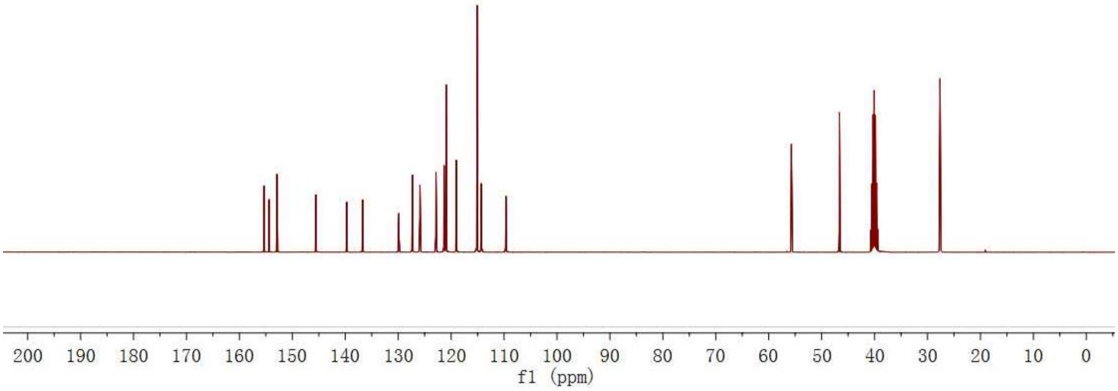


Fig. S8 ^{13}C NMR spectrum of *N*-(*p*-methoxyphenyl)-*N*’-(9,9-dimethylfluoren-2-yl)amine (75 MHz, DMSO-d_6, 298 K).

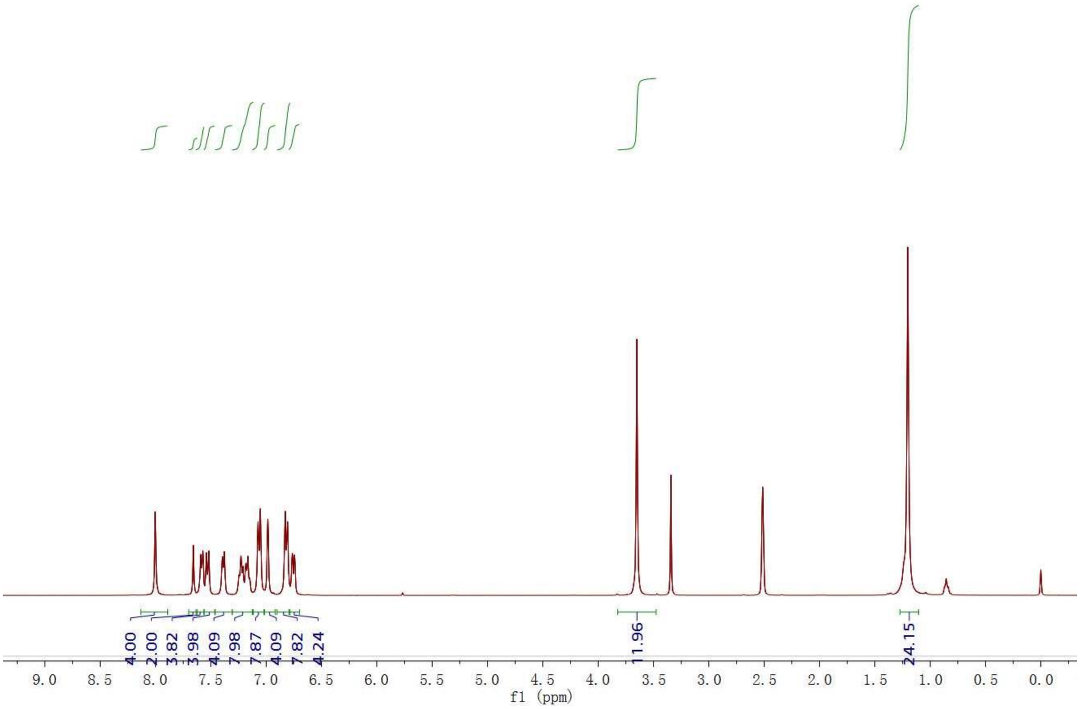


Fig. S9 ^{1}H NMR spectrum of **TFAP** (400 MHz, DMSO-d_6, 298 K).

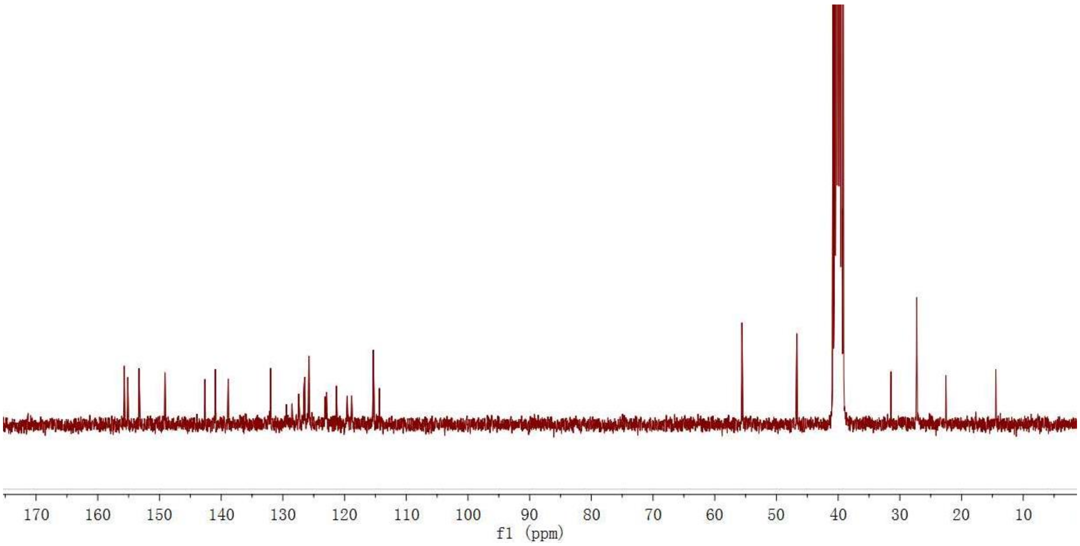


Fig. S10 ^{13}C NMR spectrum of **TFAP** (75 MHz, DMSO-d_6, 298 K).

References

S1. N. Ahn, D. Y. Son, I. H. Jang, S. M. Kang, M. Choi and N. G. Park, *J. Am. Chem. Soc*., **2015**, *137*, 8696.

S2. (a) F. Tang, K. Wu, Z. Zhou, G. Wang, B. Zhao and S. Tan, *ACS Appl. Energy Mater*., 2019, **5**, 3918; (b) X. Yin, J. Zhou, Z. Song, Z. Dong, Q. Bao, N. Shrestha, S. S. Bista, R. J. Ellingson, Y. Yan and W. Tang, *Adv. Funct. Mater*., 2019, 1904300.