

Electronic Supplementary Information

Synthesis and Fine-Tuning the Pore Properties of a Thiophene Based Porous Organic Framework by the Post-Oxidation

Yanze Liu,^{#a} Yiming Zuo,^{#a} Shuai Li,^a Jiani Li,^a Li Li,^a Caixia Liu,^a Shumalia Ashraf,^a
Pengfei Li,^{*ab} and Bo Wang^{*bc}

- Advanced Research Institute of Multidisciplinary Science, Beijing Institute of Technology, Beijing, 100081, China.
- Key Laboratory of Cluster Science Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China.
- Department of Chemistry, Tsinghua University, Beijing, 100084, China.

E-mail: lipengfei@bit.edu.cn and bowang@bit.edu.cn

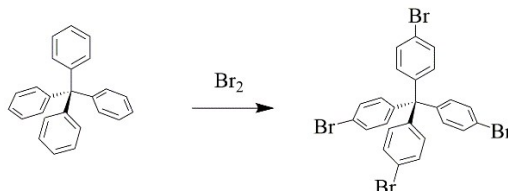
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1. Synthetic Procedures

All chemicals and solvents were purchased from J&K Scientific Co. Ltd., Innochem Co. Ltd. and Aladdin Reagent Co., Ltd. They were directly used without further purification unless otherwise noted.

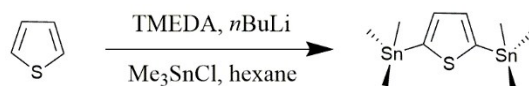
1.1 Synthesis of tetrakis(4-bromophenyl)methane (Br₄TPM)



Scheme S1. Synthesis of tetrakis(4-bromophenyl)methane (Br₄TPM)

Br₄TPM was prepared according to the literature.^[1] At 0 °C, the liquid bromine (3.2 mL, 63.0 mmol) was added carefully to a 100 mL 2-neck round-bottom flask containing tetraphenylmethane (1.0 g, 3.1 mmol). The reaction mixture was stirred for 3 h at room temperature. When finished, it was cooled to -78 °C by an ice/acetone bath. Ethanol (40 mL) was added slowly, and the resulting mixture was allowed to warm to room temperature overnight. Then aqueous solution of saturated Na₂S₂O₃ was added cautiously to remove the excess bromine until the orange color disappeared. The precipitate was collected, washed with plenty of water and ethanol. Further purification by recrystallization from chloroform/ethanol (V:V = 2:1) afforded a white solid. Then dried by vacuum at 100 °C for 12 h. Yield: 1.68 g (2.64 mmol, 85%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.39 (d, *J* = 8.0 Hz, 8H); 7.01 (d, *J* = 8.0 Hz, 8H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 144.42, 132.35, 131.08, 120.80, 63.63.

1.2 Synthesis of 2,5-Bis(trimethylstannyl) thiophene (BTSTP).



Scheme S2. Synthesis of 2,5-Bis(trimethylstannyl) thiophene (BTSTP)

2,5-Bis(trimethylstannyl)thiophene was prepared according to the literature.^[2] *n*-butyl lithium (8.0 mL, 20.0 mmol, 2.5 M in *n*-hexane) was added dropwise carefully to the solution of 3.0 mL (20.0 mmol) of TMEDA (Tetramethylethylenediamine), 2.3 mL (10 mmol) of thiophene, and 30 mL of hexane at 0 °C under N₂. Then the mixture was

heated at reflux for 1h, and slowly cooled to 0 °C, followed by the addition of 4 g (20.0 mmol) trimethyltin chloride in 20 mL of anhydrous hexane. The reaction mixture was warmed to room temperature and stirred for 24 h. The reaction mixture was quenched with water, extracted with hexane and washed with distilled water for several times. The organic phase was collected and dried over anhydrous Na₂SO₄, and the solvents were removed under reduced pressure to obtain a white solid. Recrystallization from ethanol afforded the target compound. Yield: 3.42 g (8.35 mmol, 83%). ¹H NMR (400 MHz, *d*₆-DMSO) δ (ppm): 7.34 (s, 2H), 0.32 (s, 18H). ¹³C NMR (100 MHz, *d*₆-DMSO) δ (ppm): 143.25, 136.39, -7.34.

2. ^1H NMR and ^{13}C NMR Spectra

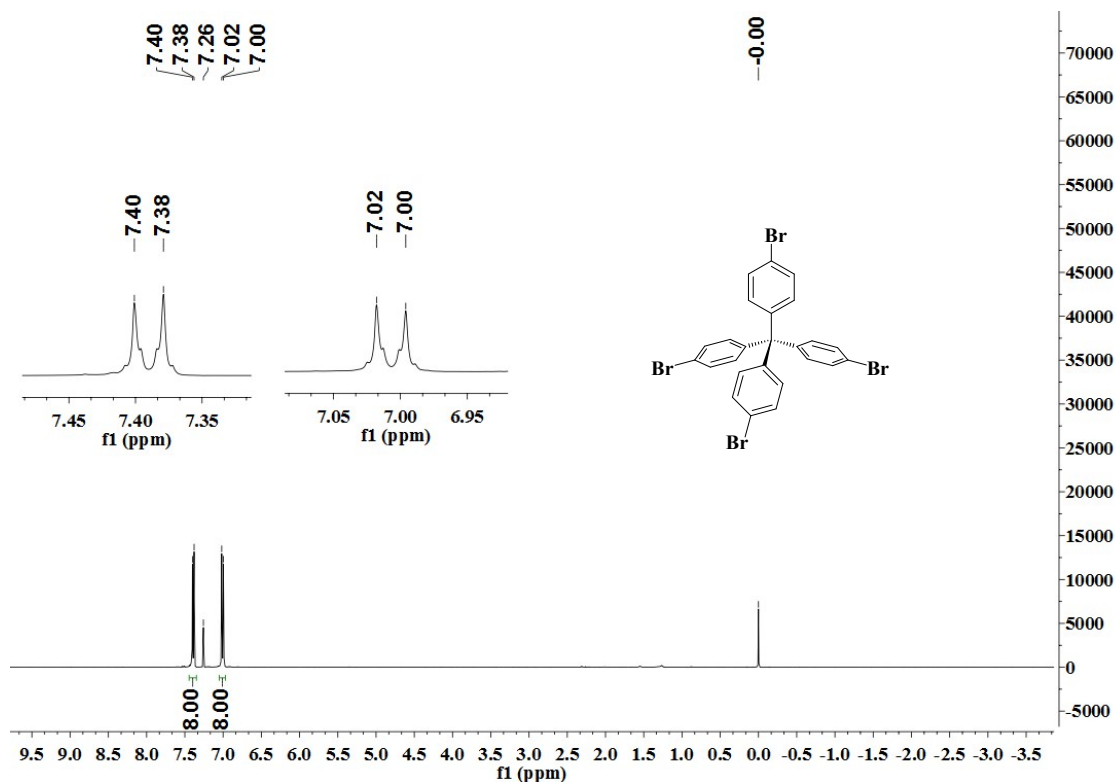


Fig. S1. ^1H NMR of Br_4TPM (CDCl_3 , 400 MHz).

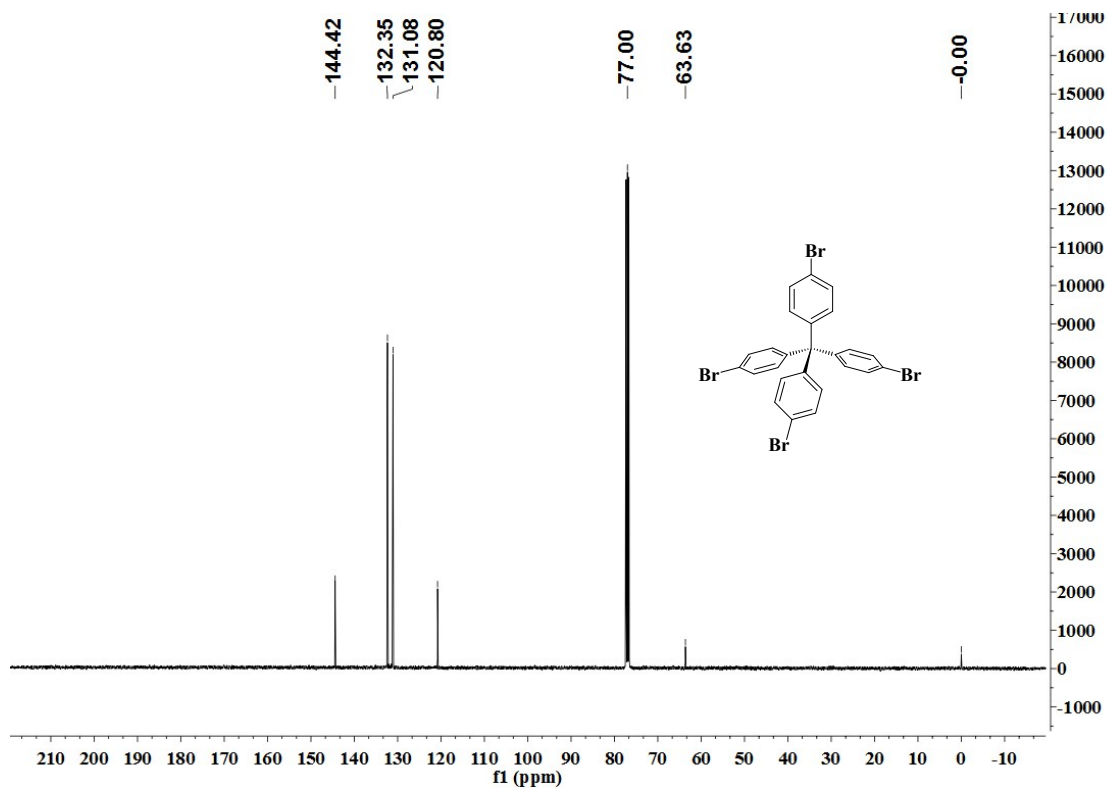


Fig. S2. ^{13}C NMR of Br_4TPM (CDCl_3 , 100 MHz).

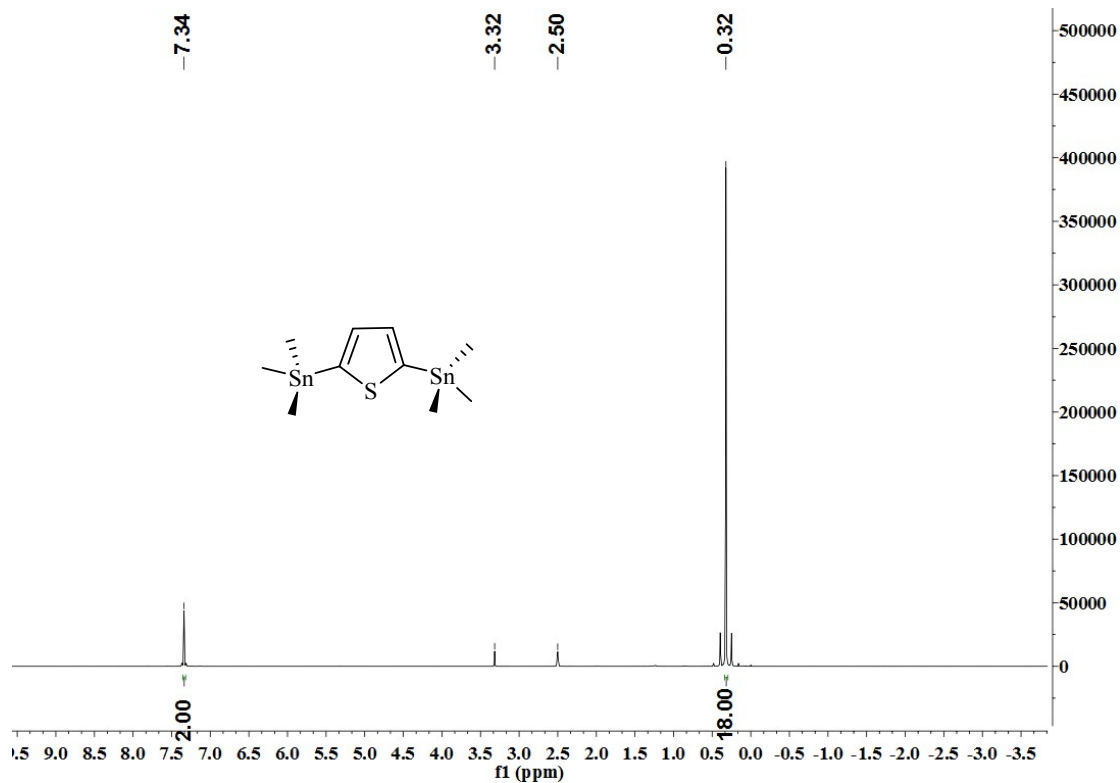


Fig. S3. ^1H NMR of BTSTP (d_6 -DMSO, 400 MHz).

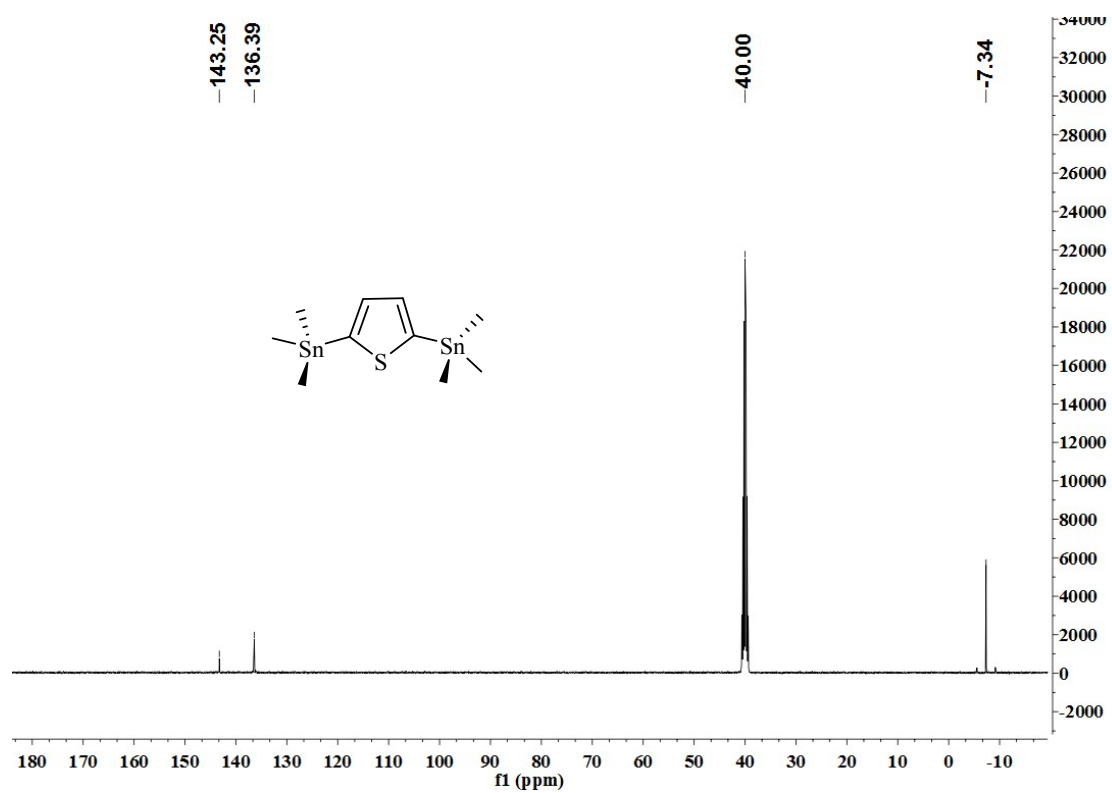


Fig. S4. ^{13}C NMR of BTSTP (d_6 -DMSO, 100 MHz).

3. FT-IR Spectra

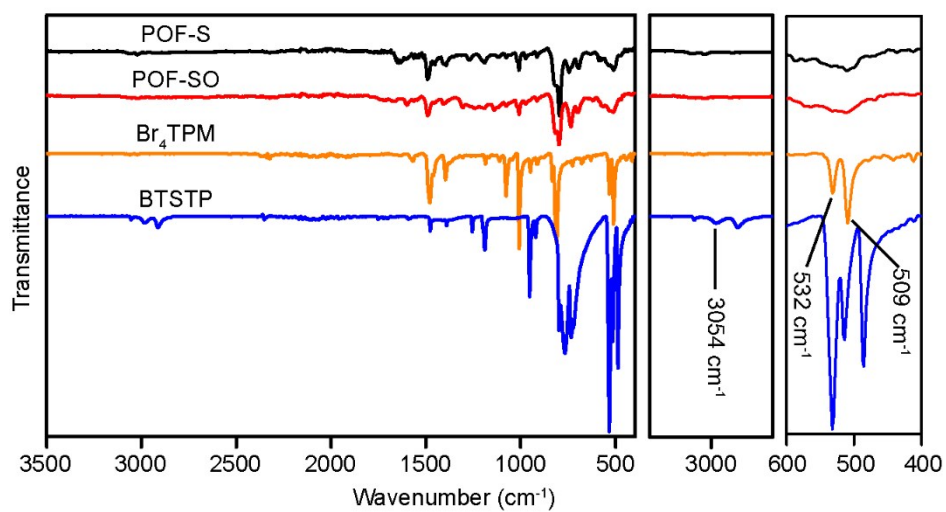


Fig. S5. FT-IR spectra comparison of Br₄TPM, BTSTP, POF-S and POF-SO(1.0).

4. Powder X-Ray Diffraction (PXRD)

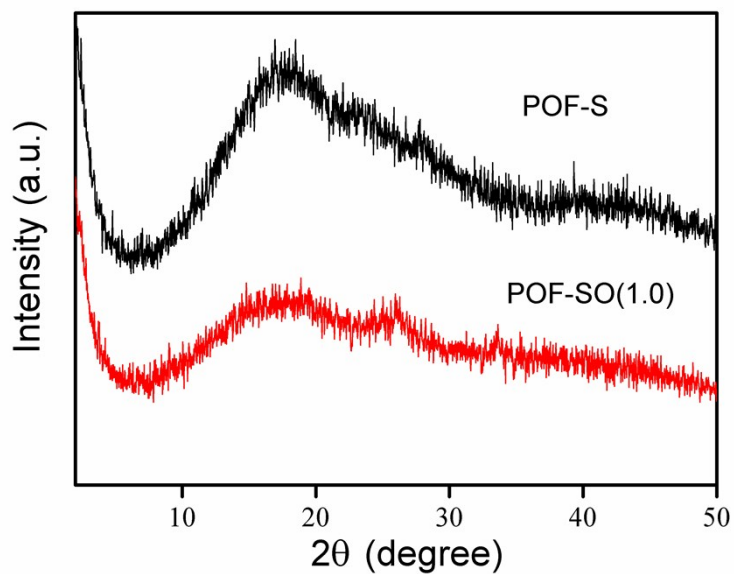


Fig. S6. PXRD pattern of POF-S and POF-SO(1.0).

5. Scanning Electron Micrographs (SEM)

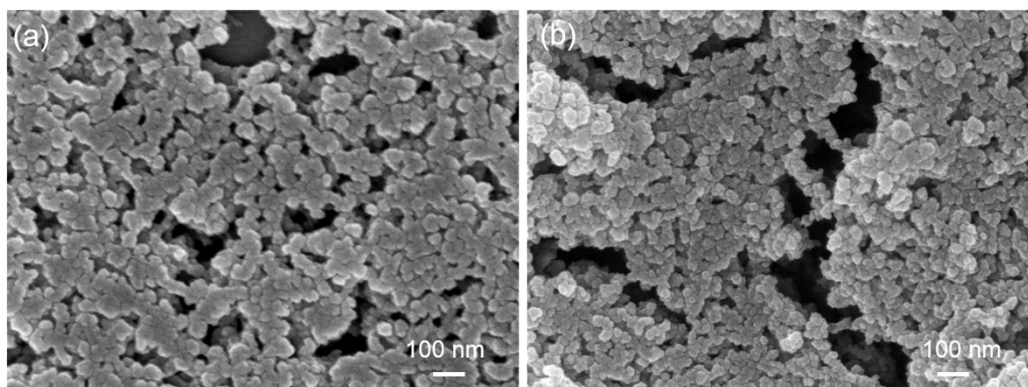


Fig. S7. SEM images of POF-S (a) and POF-SO(1.0) (b).

6. Thermogravimetric Analysis (TGA)

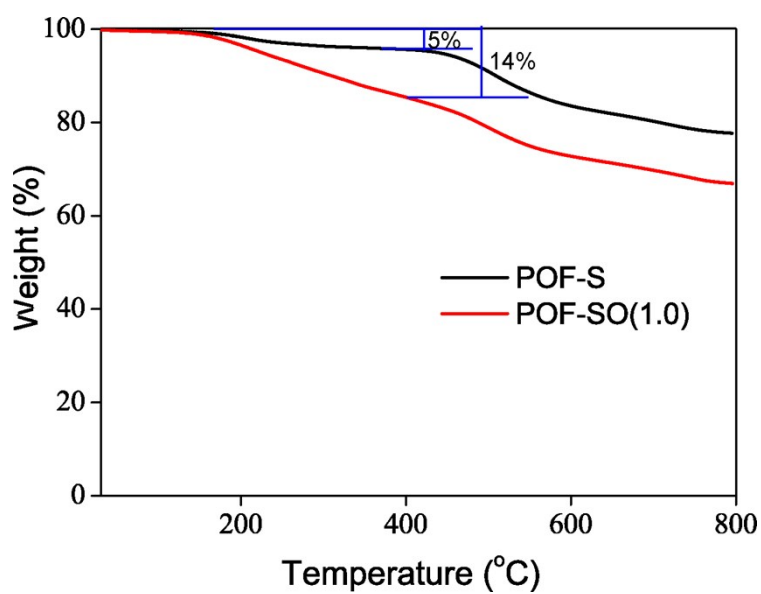


Fig. S8. TGA of POF-S and POF-SO (1.0) under N₂ atmosphere.

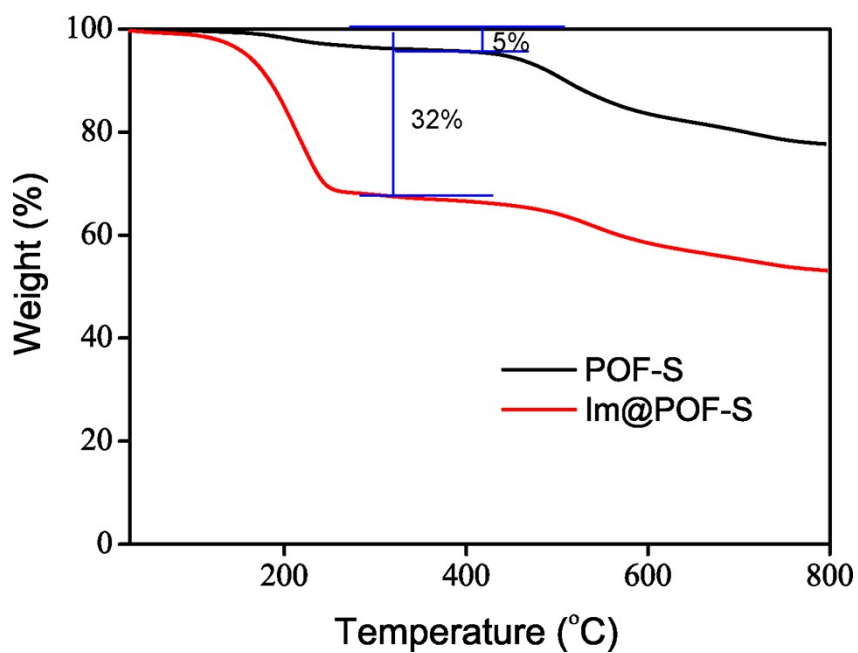


Fig. S9. TGA data of Im@POF-S under N₂ atmosphere.

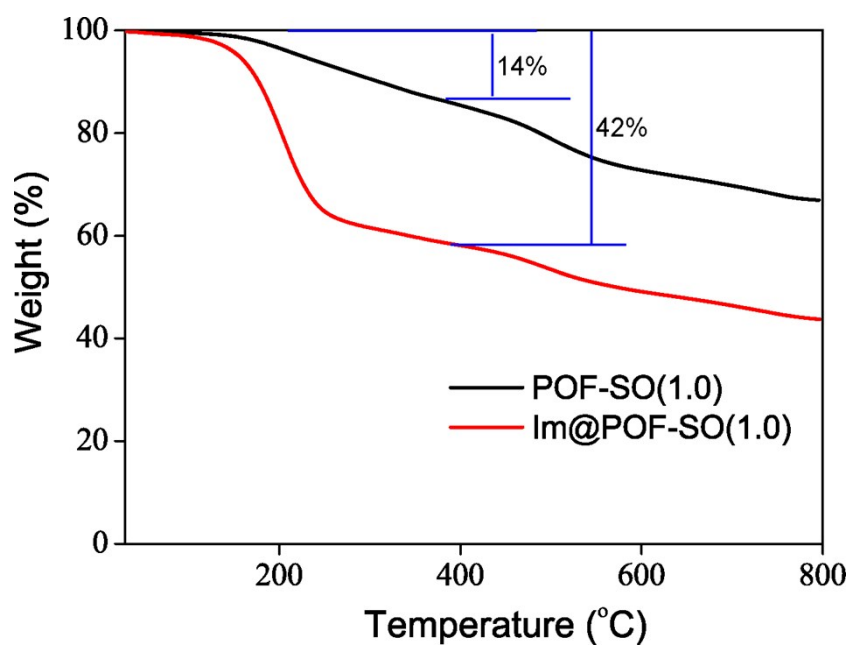


Fig. S10. TGA data of Im@POF-SO (1.0) under N₂ atmosphere.

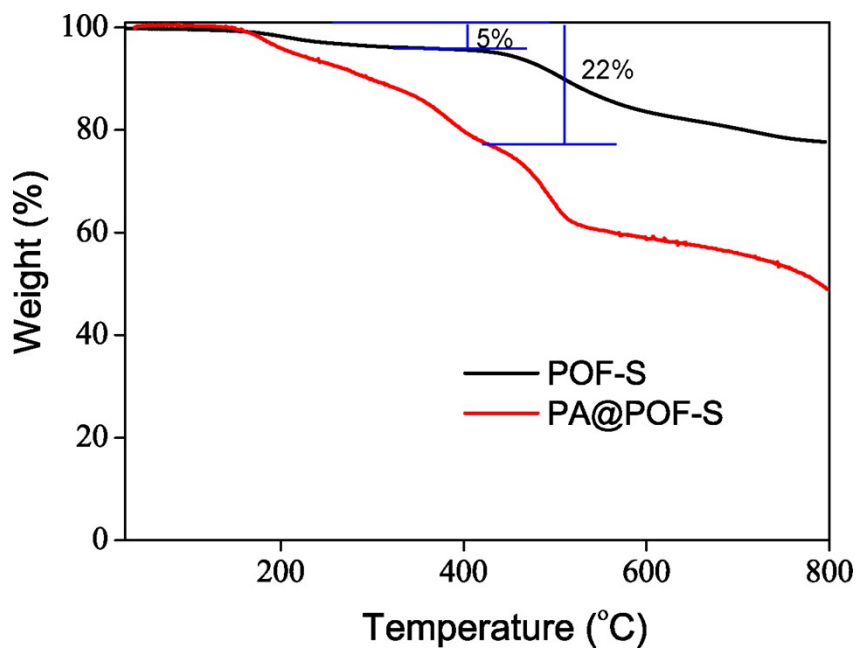


Fig. S11. TGA data of PA@POF-S under N₂ atmosphere.

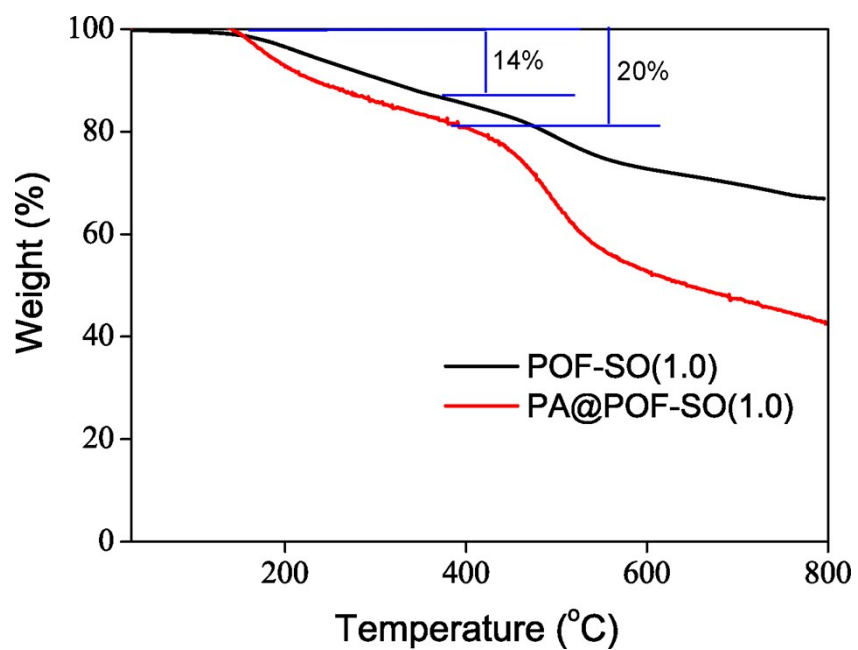


Fig. S12. TGA data of PA@POF-SO (1.0) under N₂ atmosphere.

7. Gas Adsorption Studies

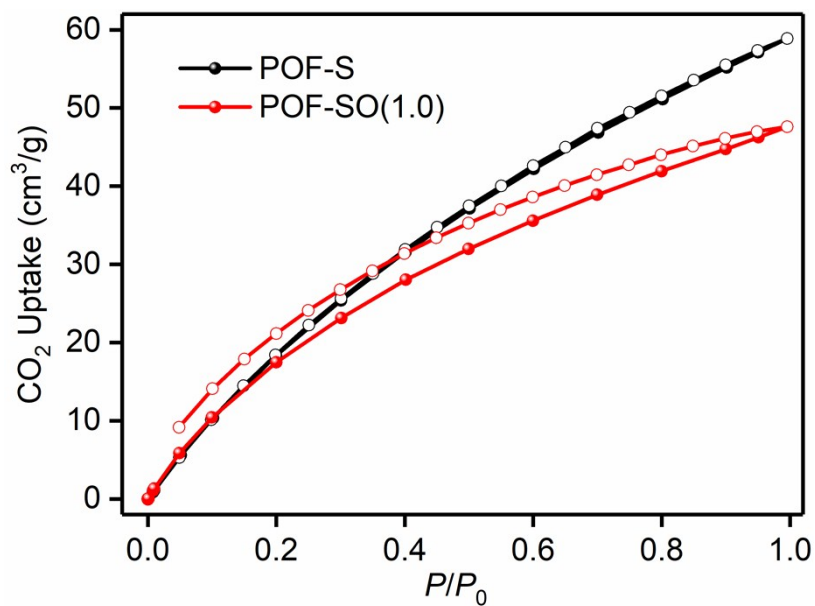


Fig. S13. CO₂ adsorption isotherms of POF-S and POF-SO(1.0) at 273K.

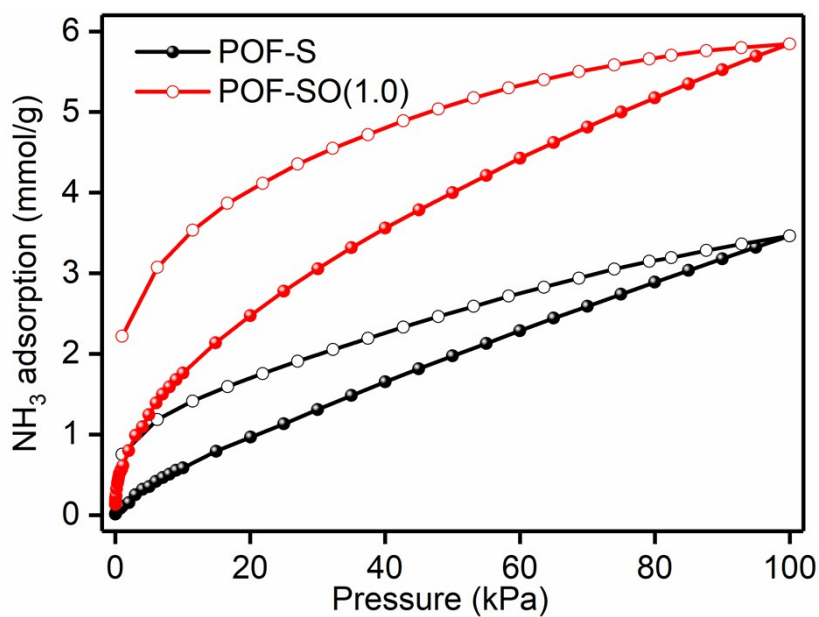


Fig. S14. NH₃ adsorption isotherms of POF-S and POF-SO (1.0) at 298K.

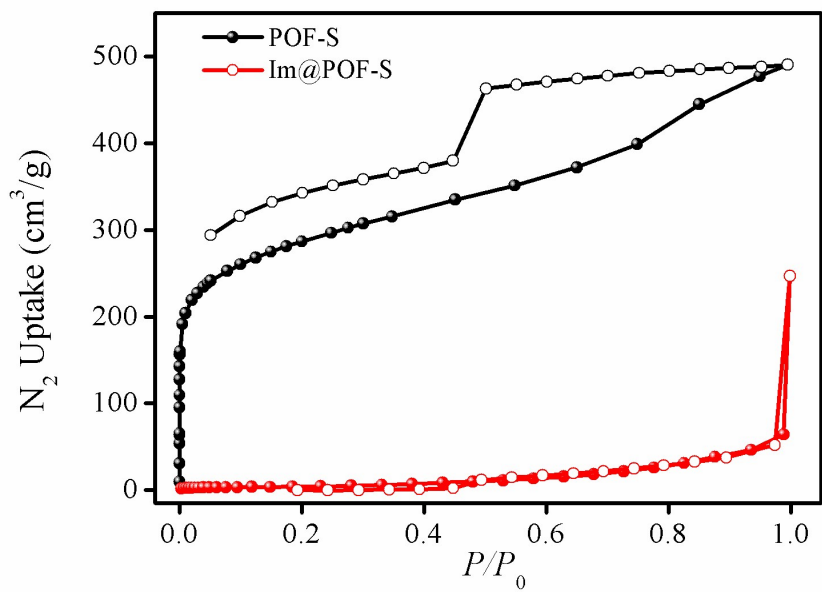


Fig. S15. N₂ adsorption isotherms of POF-S and Im@POF-S at 77K.

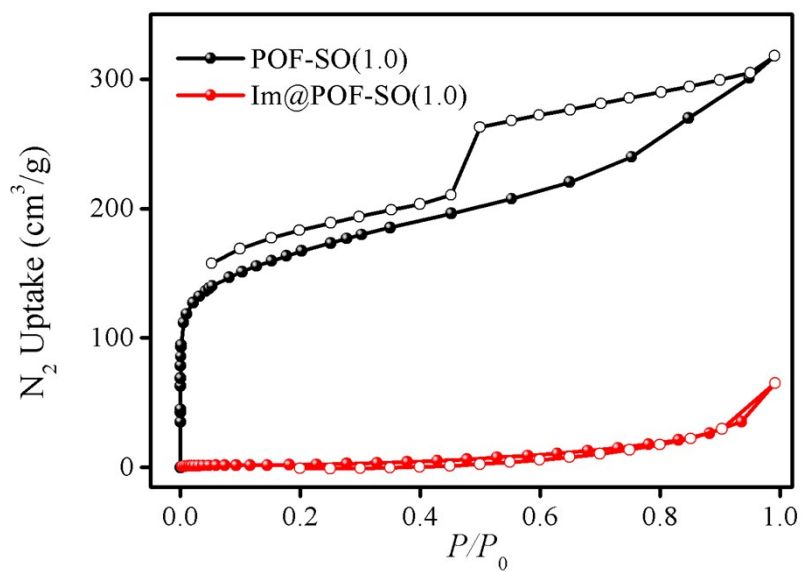


Fig. S16. N₂ adsorption isotherms of POF-SO(1.0) and Im@POF-SO(1.0) at 77K.

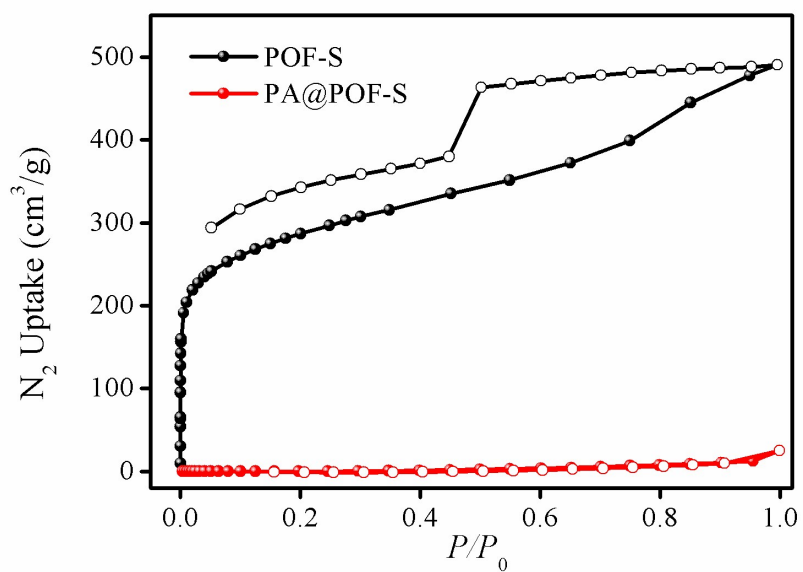


Fig. S17. N₂ adsorption isotherms of POF-S and PA@POF-S at 77K.

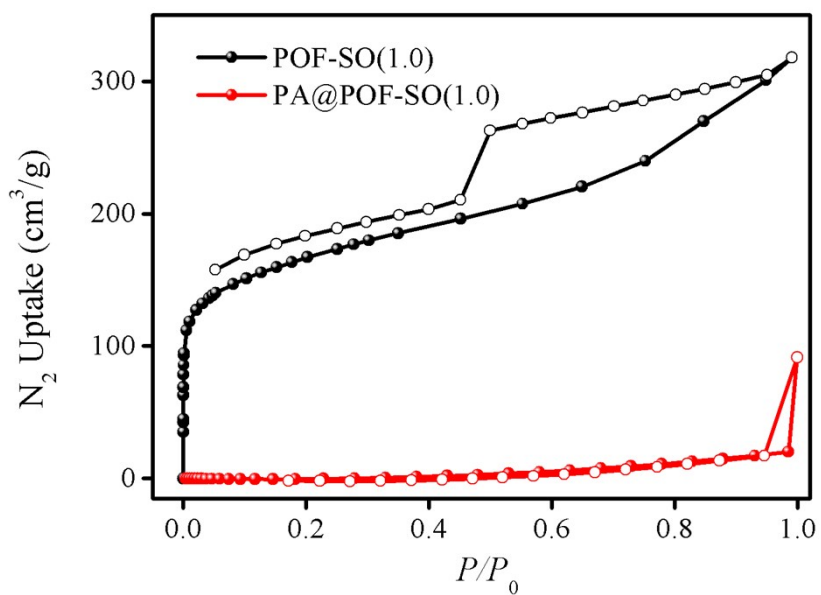


Fig. S18. N₂ adsorption isotherms of POF-SO(1.0) and PA@POF-SO(1.0) at 77K.

8. Proton conductivity comparison

Table S1: Comparison of the anhydrous proton conductivity of porous materials

	Compound Name	Conductivity (S cm ⁻¹)	Ea(eV)	Temperature	References
1	β -PCMOF2(Tz) _{0.3}	2×10^{-4}	0.51	150 °C	Nat. Chem., 2009 , 1, 705–710
2	[Al(μ_2 -OH)(1,4-ndc)] _n ⊃Im	2.2×10^{-5}	0.6	120 °C	Nat. Mater., 2009 , 8, 831–836
	[Al(μ_2 -OH)(1,4-bdc)] _n ⊃Im	1.0×10^{-7}	0.9		
3	PA@MIL-101	3×10^{-3}	0.42	150 °C	J. Am. Chem. Soc., 2012 , 134, 15640–15643
4	[Zn(H ₂ PO ₄) ₂ (Tz) ₂] _n	1.1×10^{-4}	0.6	130 °C	J. Am. Chem. Soc., 2012 , 134, 12780–12785
5	PA@Tp-Azo	6.7×10^{-5}	0.11	67 °C	J. Am. Chem. Soc., 2014 , 136, 6570–6573
6	Im@Td-PNDI	9.04×10^{-5}	0.33	120 °C	J. Am. Chem. Soc., 2015 , 137, 913–918
	Im@Td-PPI	3.49×10^{-4}	0.30		
7	Im@TPB-DMTP-COF	3.78×10^{-3}	0.21	120 °C	Nat. Mater., 2016 , 15, 722–726
	Tz@TPB-DMTPCOF	9.60×10^{-4}	0.25		
8	PON-1	5.2×10^{-4}	0.39	130 °C	J. Mater. Chem. A, 2018 , 6, 21542–21549
	PON-2	7.3×10^{-5}	0.39		
	PON-3	2.1×10^{-7}	0.53		
	PON-4	9.7×10^{-6}	0.58		
	PON-5	2.0×10^{-5}	0.35		
	PON-6	4.9×10^{-6}	0.44		
9	Im@POF-SO(1.0)	1.3×10^{-3}	0.37	120 °C	This work
	PA@POF-SO(1.0)	2.6×10^{-3}	0.20		

Note: PA = H₃PO₄, Im = Imidazole, Tz = *IH*-1,2,4-triazole

9. References:

1. R. Rathore, C. L. Burns, M. I. Deselnicu, *Org. Lett.*, 2001, **3**, 2887–2890.
2. J. Liu, E. N. Kadnikova, Y. Liu, M. D. McGehee, J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2004, **126**, 9486–9487.