

Supporting Information

Chemicals

Phloroglucinol, hexamethylenetetramine, Trifluoroacetic acid, Pd/C, 5,6-Dimethylbenzimidazole, and Imidazole were purchased from Aladdin Chemical Reagent Co. All other chemicals were of analytical grade and were used without any further purification.

Measurements

The Powder X-ray diffraction measurements were carried out on a Bruker D2 Phaser with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), and the scan speed was $10^\circ/\text{min}$ over the 2θ range of $2\text{-}30^\circ$ at room temperature. The morphology of the sample was observed by scanning electron microscopy (SEM) with a JEOL JSM-6400F field emission microscope operated at 15 kV acceleration voltages directly on samples. Transmission electron microscopy (TEM) characterization was performed using a FEI tecnai G2 F20S-Twin with an acceleration voltage of 200 kV. Nitrogen sorption isotherms of samples were measured by a Quantachrome Instruments Quadrasorb SII at 77 K, and samples were degassed at 80°C for 5h in a vacuum before measurements. Solid-state C-NMR spectra were recorded using a Bruker Avance III spectrometer at 14KHz and 4 mm MAS probe, ZrO₂ rotor with MAS spin rate at 13k Hz was used to acquire all spectra. Fourier transform infrared (FTIR) spectra were recorded at room temperature in a KBr matrix on a Nicolet IS 5. Thermogravimetric investigations were carried out with a SETARAM LabsysEvo TG-DTA instrument at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere. Proton Conductivity measurements were performed on sample pellets using Solartron 1260 frequency response analyzer over a frequency range from 1 Hz to 1 MHz and with an input voltage amplitude of 100 mV. The sample pellets were tightly connected between two gold electrodes, by means of spring, to ensure good contact between sample and each electrode. The sample pellets for conductivity measurements with a diameter of 6mm and a thickness of $\sim 1\text{mm}$ were prepared under a pressure of $\sim 1.2 \text{ GPa}$. The thickness of sample pellets was measured using a vernier caliper under absolutely anhydrous containers for testing.

Measurements were taken under anhydrous conditions and done at thermal equilibrium by holding for 10 min in the temperature range from 30°C to 130 °C.

Synthesis of Tp-DADMB

Monomer DADMB and Tp were synthesized according to the previously reported method [1,2]. 4,7-Diamino-5,6-dimethylbenzimidazoles (61.1 mg, 0.35 mmol) and Triformylphloroglucinol (48.3 mg, 0.23 mmol) followed by 8 mL of dry anisole and 2 mL of 12 M acetic acid were placed in a 30 mL Schott Duran glass bottle with a Teflon sealed PBT cap. The reaction mixture was heated for 96 h at 120 °C. A reddish brown precipitate was filtered off with a Frit funnel and washed with 100 mL of acetone. The obtained CMP powder was immersed in 5 mL of anisole in a 30 mL schott duran glass bottle and heated at 120 °C for another 24 h. Afterward the powder was filtered and washed with 100 mL of acetone to afford the Tp-DADMB.

Preparation of Imidazole-loaded Tp-DADMB

After syntheses Tp-DADMB was degassed by heating to 120°C under reduced pressure for 5 h to remove residual solvent molecules. The thermal sublime diffusion method was employed for loading imidazole into the pores of Tp-DADMB. A mixture of Tp-DADMB and imidazole was placed in a Pyrex tube and sealed under pressure. The tube was heated at 120°C for 48 h to yield the composites.

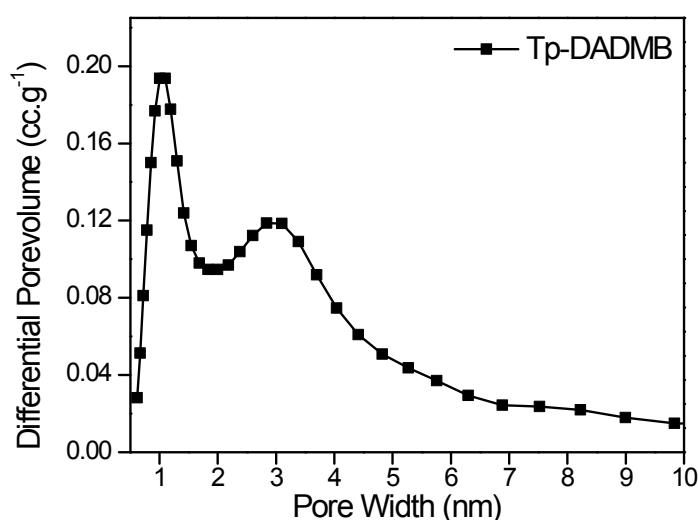


Figure S1. Pore size distribution of Tp-DADMB

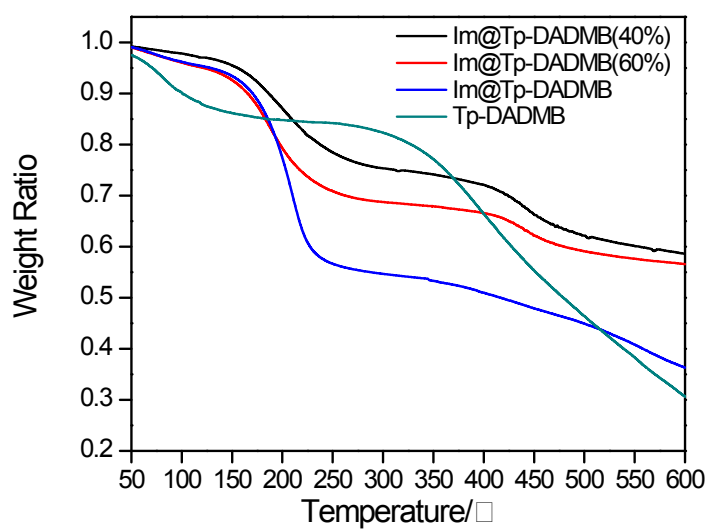


Figure S2. TGA curves of Tp-DADMB and the composites

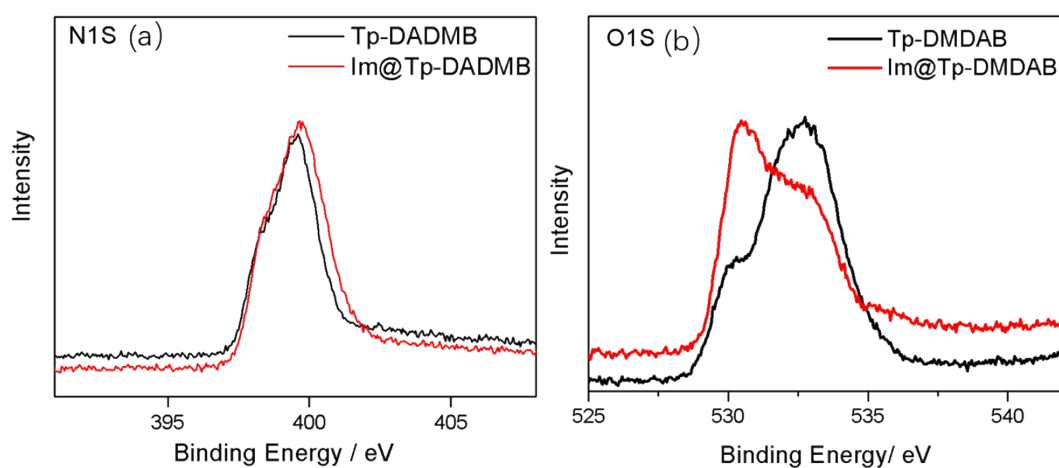


Figure S3. XPS spectrum of Tp-DADMB and Im@Tp-DADMB for N1S (a) and O1S (b).

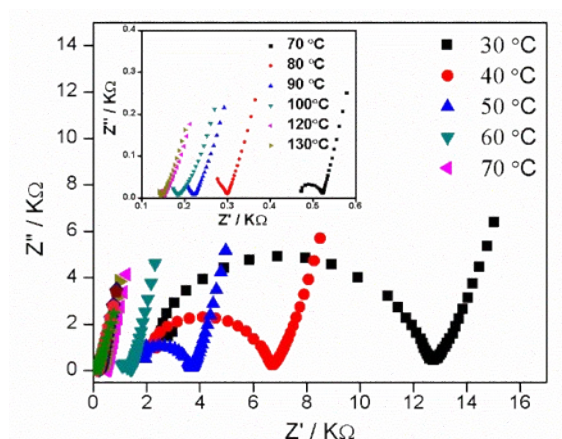


Figure S4. Nyquist plots of Im@Tp-DADMB at different temperatures

Table S1. Comparison of proton conductivity of Tri@MS-PrNH₂-1 with the reported porous materials.

Materials	Conductivity (S/cm)	Ea (eV)	Measurement Conditions	Ref
His@[Al(OH)(ndc)] _n	1.7×10 ⁻³	0.25	Anhydrous, 150°C	<i>Angew. Chem. Int. Ed.</i> 2011, 50, 11706
β-PCMOF-2(Tz) _{0.45}	5.0×10 ⁻⁴	0.34	Anhydrous, 150°C	<i>Nat. Chem.</i> 2009,1,75
In-IA-2D-2	1.2×10 ⁻⁵	0.48	Anhydrous, 90°C	<i>Chem. Commun.</i> 2013,49,6197
Im@{Al(μ ₂ -OH)(1,4-bdc)} _n	2.2×10 ⁻⁵	0.90	Anhydrous, 120°C	<i>Nat. Mater.</i> 2009,8,831
[ImH ₂][Cu(H ₂ PO ₄) _{1.5} (HPO ₄) _{0.5} •Cl _{0.5}]	2.0×10 ⁻²	1.10	Anhydrous, 130°C	<i>Chem. Commun.</i> 2014,50,10241
PA@Tp-Azo	6.7×10 ⁻⁵	0.11	Anhydrous, 67°C	<i>J. Am. Chem. Soc.</i> 2014,136,6570
[Zn ₃ (H ₂ PO ₄) ₆](Hbim)	1.3×10 ⁻³	0.50	Anhydrous, 120°C	<i>J. Am. Chem. Soc.</i> 2013,135,11345
Im@Td-PPI 2	3.49×10 ⁻⁴	0.30	Anhydrous, 90°C	<i>J. Am. Chem. Soc.</i> 2015,137,913
[Zn(HPO ₄)(H ₂ PO ₄) ₂](ImH ₂) ₂	2.5×10 ⁻⁴	0.47	Anhydrous, 130°C	<i>J. Am. Chem. Soc.</i> 2012,134,7612
Im@Tp-DADMB	2.4×10⁻³	0.16	Anhydrous 130°C	This work

Reference:

- [1] Chong, J. H., Sauer, M., Patrick, B. O., and MacLachlan, M. J., *Organic Letter*, **2003**, 5, 3823-3826.
- [2] Edelman, M. J., Raimundo J.-M., Utesch, N. F., and Diederich F., *Helvetica Chimica Acta*, **2002**, 85, 2195-2213.