Supporting information

Construction of Unimpeded Proton-Conducting Pathways in Solution-Processed Nanoporous Polymer Membranes

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1. Experimental section

Supplementary Materials and Methods

Materials

Phenazine (97%, Bidepharm), 4-bromobenzonitrile (98%, J&K), bromobenzene (99%, J&K), palladium(II) acetate (98%, J&K), sodium tert-butoxide (98%, J&K), triflic acid (99%+, J&K), tri-tert-butylphosphine (10% in toluene, Energy Chemical), 2,4,6-triphenyl-1,3,5-triazine (99%, Shanghai Bidepharm), anhydrous potassium carbonate (99%, Energy Chemical), sodium dithionite (85%, Energy Chemical), anhydrous toluene (99.5%, Aldrich), anhydrous *N*,*N*-dimethylformamide (99.8%, J&K), *N*,*N*-diethylformamide (99.8%, J&K), anhydrous *N*-methyl pyrrolidone (99.8%, J&K), anhydrous *N*,*N*-dimethylacetamide (99.8%, J&K), anhydrous dimethyl sulfoxide (99.8%, J&K), anhydrous 3-dimethyl-2-imidazolidinone (99.8%, J&K), anhydrous methanol (99.5%, Wako), 18.4 M H₂SO₄ (Aldrich) and deuterated solvents (Energy Chemical) for NMR were purchased and used without further purification.

N₂ (99.9999%) and CO₂ (99.9999%) were purchased form TAIYO NIPPON SANSO Company (Japan).

General instrumental analysis

¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE HD III 500M NMR spectrometer. FTIR spectra were recorded on an IFS 66V/S Fourier transform infrared spectrophotometer. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Elemental analysis was performed on an Elementar Vario EL elemental analyzer. TG measurements were performed on a Rigaku Thermo plus EVO2 under N₂, by heating to 500 °C at a rate of 5 °C min⁻¹. Field-emission scanning electron microscopy (FE-SEM) was performed on a Hitachi Regulus 8100 operating at an accelerating voltage of 5.0 kV. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a TEM JEOL 2100F with an acceleration voltage of 300 kV. EPR spectra were measured on a Bruker E500 electron paramagnetic resonance spectrometer. Membrane thicknesses were recorded on a Veeco Dektak 150 atomic profiler. XPS measurements were performed with a Kratos Axis Ulra DLD. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku SmartLab X-ray diffractometer using Cu–K α radiation (λ = 1.54178 Å) in the 20 range of 1.5–30° with a scanning rate of 5° min⁻¹. ¹³C CP-MAS solid-state NMR spectra of GT-POP-1 and protonated state were recorded in JEOL JNM-ECA600 MHz, 3.2-mm rotor, MAS of 20 kHz, recycle delay of 1 sec.

Synthesis

Synthesis of 5,10-dihydrophenazine

Phenazine (3 g, 16.6 mmol) was added into 40 mL of boiling ethanol in a 500 mL two-neck flask with a stirring bar. A suspension of sodium dithionite (26 g) in deionized water (200 mL) was added dropwise into the phenazine solution. Afterwards, the mixture was vigorously stirred for 3 h. The resulting gray-white precipitate was filtered and washed several times with deionized water and ethanol. The collected solid was dried under reduced pressure to afford 5,10-dihydrophenazine (2.91 g, yield = 96%). This material was directly used in the next step without further purification.

Synthesis of 4,4'-(phenazine-5,10-diyl) dibenzonitrile (1)

A mixture of 5,10-dihydrophenazine (1092 mg, 6 mmol), 4-bromobenzonitrile (2730 mg, 15 mmol), potassium carbonate (4968 mg, 36 mmol), tri-tert-butylphosphine (244.8 mg, 1.21 mmol), palladium(II) acetate (100 mg) and toluene (30 mL) was refluxed at 110 °C for 24 h under nitrogen. After the system was cooled, 30 mL of dichloromethane and 20 mL of deionized water were added to the resulting mixture. The organic phase was extracted with dichloromethane for three times. The combined organic layers were dried with MgSO₄ and concentrated under reduced pressure. The obtained solid was purified by chromatography with a mixture of dichloromethane/petroleum ether (v/v = 1/1) as the eluent to afford monomer **1** as an orange solid (1.5 g, yield = 67%). The product was further purified by sublimation under reduced pressure. ¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) = 5.91 (dd, *J* = 5.9, 3.4 Hz, 4H), 6.54 (dd, *J* = 5.9, 3.4 Hz, 4H), 7.62 (d, *J* = 8.5 Hz, 4H), 8.10 (d, *J* = 8.5 Hz, 4H). ¹³C NMR (126 MHz, DMSO-*d*₆): δ (ppm) = 144.29, 134.89, 129.62, 121.65, 117.87, 114.10, 109.65; APCI MS: calcd. for [M]⁺, m/z = 384.14; found m/z = 384.

Synthesis of 5,10-diphenyl-5,10-dihydrophenazine (2)

A mixture of 5,10-dihydrophenazine (1400 mg, 7.7 mmol), bromobenzene (3626.7 mg, 23.1 mmol), sodium tert-butoxide (3326 mg, 34.6 mmol), tri-tert-butylphosphine (46.6 mg, 0.23 mmol), palladium(II) acetate (86 mg) and toluene (40 mL) was refluxed at 110 °C for 24 h under nitrogen. After the system was cooled, 40 mL dichloromethane and 20 mL deionized water were added to the resulting mixture. The organic phase was extracted with dichloromethane for three times. The combined organic layers were dried with MgSO₄ and concentrated under reduced pressure. The obtained solid was purified by chromatography with the mixture of dichloromethane/petroleum ether (v/v = 1/3) as the eluent to afford **2** as a light-green solid (1.3 g, yield = 51%). The product was further purified by sublimation under reduced pressure. ¹H NMR (500 MHz, benzene-*d*₆): δ (ppm) = 5.81 (dd, *J* = 5.9, 3.4 Hz, 4H), 6.27 (dd, *J* = 5.9, 3.4 Hz, 4H), 7.04 (ddd, *J* = 8.7, 4.9, 3.7 Hz, 2H), 7.14 – 7.16 (m, 8H). ¹³C NMR (126 MHz, benzene-*d*₆): δ (ppm) = 113.32, 121.65, 128.55, 131.64, 131.84, 137.38, 141.04. APCI MS: calcd. for [M]⁺, *m*/z = 334.15; found *m*/z = 335.

Synthesis of GT-POP-1

TfOH (2 mL) was added dropwise to a 10 mL Schlenk tube containing 100 mg of monomer **1** at -10 $^{\circ}$ C under N₂ in 15 min and stirred for another 1.5 h. Then, the solution was further stirred for 12 h at 60 $^{\circ}$ C. After cooling to room temperature, the reaction was quenched by 2 M NaOH aqueous solution. The precipitates were filtered and washed with 2 M NaOH and deionized water. The collected solid was Soxhlet extracted with dichloromethane (48

h), acetonitrile (24 h) and methanol (24 h). The powder was dried under vacuum at 80 °C to afford GT-POP-1 as a brownish-red powder (54 mg, yield = 54%).

Preparation of GT-POP-1 solutions and membranes

The GT-POP-1 solutions were prepared by adding GT-POP-1 powders and a certain amount of sulfuric acid to various organic solvents, such as DMF, NMP, DEF, DMAc, DMI and DMSO, followed by simple manual shaking. More concentrated solutions could be obtained by heating the GT-POP-1 solutions for 1 to 5 min. The GT-POP-1 membranes were prepared by drop casting the above solutions onto desired substrates followed by thermal evaporation of the solvents. The membrane thickness in this case was 20 µm.

Gas sorption measurements

 N_2 and CO_2 sorption measurements were performed on BELSORP-mini (Bel Japan, Inc.) automated volumetric sorption analysers. The desired temperatures (77 K for N_2 sorption and 195 K for CO_2 sorption) were controlled by liquid N_2 and a mixture of isopropanol and dry ice, respectively.

The calculation of protonation degree

The protonation degree was calculated by the N1s of XPS data. Theoretically, the protonation degree is the molar ratio of protonated dihydrophenazines to that of total dihydrophenazines. The molar of protonated dihydrophenazines was determined by the area of N in protonated dihydrophenazines (termed N₃). The molar of N in total dihydrophenazines was half of total N in molecule whether in monomer 1 or GT-POP-1. Thus, the protonation degree was calculated by equation S1:

protonation degree =
$$\frac{A_{N_3}}{0.5 A_{N_{total}}}$$
 S1

where A_{N_3} is the area of N in protonated dihydrophenazine, and $A_{N_{total}}$ is the total area of N in GT-POP-1.

Indentation test

The elastic modulus was determined by an indentation test on a tensile-compressive test machine (Instron 6022, Instron Corporation, USA) equipped with a hemisphere steel indenter. The testing velocity was performed at 1 mm min⁻¹, and the force-displacement curve was recorded during the measurement. According to the Hertz's contact theory, the elastic modulus can be described by equation S2:

$$E = \frac{3}{4} I^{\frac{3}{2}} f R^{\frac{1}{2}} (1 - v_p^2)$$

where E, I, f, R, v_p are elastic modulus, displacement of indenter, force and radius of the indenter (= 1mm), and poison's ratio of GT-POP-1 (v_p = 0.5), respectively.

The force and displacement curve of the indentation test was shown in Figure S24. By fitting the data of forcedisplacement curve at the small displacement region, the estimated elastic modulus is 204.8 Mpa.

Fabrication of proton-conducting devices

DMF (1 mL) containing 5, 10, 12, 16 and 20 μ L of 2 M H₂SO₄ was added to sample vials containing 5 mg of GT-POP-1 to form clear solutions. The protonated membranes were prepared by drop casting 400 μ L of the above solutions onto nonconductive glass substrates (1 × 1 cm²) and then drying them at 120 °C under nitrogen for 48 h. Silver electrodes were prepared on the surface of membranes by vacuum deposition through contact shadow masks. The width, length and thickness of the silver electrodes were 1 mm, 1 cm and 500 nm, respectively. The electrode distance was 2 or 6 mm.

Electric conductivity measurements

The electric conductivity was measured by constructing horizontal devices. The distance and length of two electrodes were 50 μ m and 1 mm, respectively. The current density–voltage (*J–V*) profiles were recorded with a Keithley 2400 source meter.

Impedance measurements

The proton conductivities were investigated by AC impedance measurements at frequencies from 1 MHz to 1 Hz with an amplitude of 50 mV at controlled temperatures and RHs. The AC impedance measurements of these membranes were performed by using a Solartron 1255B frequency response analyzer. The RHs and temperatures were controlled in an Espec SH-221 bench-top temperature and humidity chamber. The membranes were stabilized under the test conditions for 10 h before data were recorded.

The proton conductivity of GT-POP-1 membranes were calculated by equation S3:

$$\sigma = rac{\mathrm{d}}{\mathrm{Rlt}}$$
 s3

where σ is the proton conductivity (S cm⁻¹), d is the distance of the two silver electrodes (cm), I is the length of the electrodes, and t and R are the thickness and resistance (Ω) of the membranes, respectively. The resistance value was obtained by taking the higher frequency minimum/intercept along the x axis of the impedance plots. In this study, d was 2 or 6 mm, I was 1 cm and t was 20 μ m.

The activation energy (E_a) for the proton-conduction process was obtained by fitting the proton conductivity at different temperatures to the Arrhenius equation (equation S5, which is derived from equation S4):

$$\sigma = \frac{n \left(Z e \right)^2 D}{KT} \ e^{\frac{-E_a}{KT}}$$

$$\ln (\sigma T) = \ln (A) - \frac{-E_a}{K} \frac{1}{T}$$

where σ is the proton conductivity measured at a certain temperature, A is a constant, and K is the Boltzmann constant.

Broadband dielectrical spectroscopy measurements

The dielectrical properties were conducted on Novocontrol BDS40 at the frequency from 1 to 10^7 Hz. The test temperatures were set from 273 to 333 K. The pristine GT-POP-1 powder was added to a standard 25 mm die and pressed at 30 MPa for 1 min to afford the sample for dielectrical measurements. GT-POP-1 powder (400 mg) was added to H₂SO₄ aqueous solution (0.4 mL, 2 M) and the suspension was stirred for 2 h at room temperature. Then the solid product was filtered off and dried at 120 °C in vacuum for 12 h to afford protonated GT-POP-1. Subsequently, the protonated GT-POP-1 pellet was obtained by the same method.

Electromotive force (EMF) measurements

Proton transport number or transference number (t_{H+}) was measured by the electromotive force measurement technique.^{S1} Protonated GT-POP-1 (f = 78.4) in NMP was coated on a support membrane sheet (OmniporeTM Merck, 10.0 µM), followed by thermal evaporating at 120 °C for 48 h under N₂ atmosphere. The membrane was sandwich between two platinum-coated carbon fiber electrodes (1.5 mg cm⁻², Ø = 7 mm, Chemix Co. Ltd.) and inserted into a single cell with a straight gas flow channel. On one side, H₂/Ar gas (3 vol%) was fed at 100 SCCM. On the other side, variable partial pressure mix gas between H₂/Ar gas (3 vol%) and N₂ (99.99995 vol%) was controlled to maintain the mass flow of 100 SCCM. The precise gas flow was controlled by mass flow controllers (SEC-E40, Horiba, Ltd). The EMF was collected at hydrogen partial pressures ($-ln(P_1/P_2)$) values of 0.23, 0.52, 0.70, 0.92, and 1.62 using BioLogic VSP-300. The (t_{H+}) was calculated via equation S6:

$$E = (t_H +)\frac{RT}{2F}\ln\left(\frac{P_1}{P_2}\right)$$
 S6

where E, T, R, F, P_1 , and P_2 represent EMF, temperature, the gas constant, Faraday constant, partial pressure of H_2 at constant, and variable side, respectively.

DFT simulation

To investigate the H⁺-transport energy barrier for GT-POP-1, we an H⁺-transport model that containing a representative fragment of GT-POP-1 under periodic boundary conditions (PBC), and adopted a "Complete LST/QST" transition state seeking method⁵² to calculate the activation barrier. To investigate the proton conduction process in the aqueous solution, we used the combination of explicit and implicit solvents model to reflect the actual solvation environment. This model includes a solvated proton (in the form of H₃O⁺), a free water that used to accept the passed proton and the GT-POP-1 skeleton; while the effect of the solvent beyond was represented by the COSMO solvation model,^{53–56} implemented using DMol3 module^{57,58} of Materials Studio. Double Numerical basis with Polarization functions (DNP) was selected as the basis set; GGA-PBE⁵⁹ was selected as the exchange-correlation functional. Grimme dispersion correction^{510,511} was employed in all calculations to describe van der Waals (vdW) interactions. All simulation works were performed using the computing resources at National Supercomputing Center in Shenzhen.

2. Characterizations



Figure S1. Synthetic routes of molecules 1 and 2.



Figure S2. ¹H NMR spectra of 1.



Figure S3. ¹³C NMR spectra of 1.



Figure S4. APCI mass spectra of 1.



Figure S5. ¹H NMR spectra of 2.



44 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109 108 107 106 105 f1 (ppm)

Figure S6. ¹³C NMR spectra of 2.



Figure S7. APCI mass spectra of 2.



Figure S8. (a), (b) and (c) SEM images of pristine GT-POP-1 powders with different magnifications. (d), (e) and (f)

SEM images of protonated GT-POP-1 (f = 78.4) powders with different magnifications.



Figure S9. TEM images of (a) pristine GT-POP-1 and (b) protonated GT-POP-1.



Figure S10. TG curve of GT-POP-1.



Figure S11. Solid-state NMR of GT-POP-1 before and after protonation.



Figure S12. PXRD pattern of GT-POP-1.



Figure S13. (a) UV-vis spectra of pristine GT-POP-1 in different solvents. (b) UV-vis spectra of protonated GT-POP-1 in different solvents. The concentrations of GT-POP-1 and TfOH were 0.04 and 2.83 mg mL⁻¹, respectively. The absorption bands from 400 to 900 nm were attributed to the absorption of protonated dihydrophenazine.^{S12-S14}



Figure S14. (a) UV-vis spectra of 2,4,6-triphenyl-1,3,5-triazine containing different concentration of TfOH in NMP. (b) UV-vis spectra of 2 containing different concentration of TfOH in NMP. (c) UV-vis spectra of pristine and protonated GT-POP-1 in NMP. The concentration of 2 was 8×10^{-5} mol L⁻¹. The concentration of GT-POP-1 was 0.04 mg mL⁻¹. The concentration of TfOH were 2.83, 5.66, 8.49 and 11.32 mg mL⁻¹, respectively.

The model compound 2 upon adding TfOH generated two bands at ~460 and 600-800 nm, respectively, while GT-POP-1 upon adding TfOH also exhibited the new peaks at the same position. This consistency revealed that the same dihydrophenazine cationic species formed both in compound 2 and in GT-POP-1, thus the protonation mechanism of the two compounds were the same. On the other hand, the compound 2 was readily protonated because even increasing the TfOH concentration the absorption at 460 nm did not increase at all, which indicated all the compound 2 in the solution were protonated because they can freely diffuse in the solution. In contrast, by adding TfOH to GT-POP-1, the intensity at 460 nm increased with the TfOH concentration, indicating the diffusion of TfOH in the micropores of GT-POP-1 was the rate-determining step of the protonation process.



Figure S15. EPR spectra of 1, 2 and protonated GT-POP-1. Inset shows the magnified spectra of 1 and 2.



Figure S16. Deconvoluted XPS spectra of C1s for (a) pristine GT-POP-1, (b) protonated GT-POP-1 (f = 19.6), (c) protonated GT-POP-1 (f = 39.2), (d) protonated GT-POP-1 (f = 47.6), (e) protonated GT-POP-1 (f = 62.7), (f) protonated GT-POP-1 (f = 78.4).



Figure S17. Deconvoluted XPS spectra of N1s for (a) pristine GT-POP-1, (b) protonated GT-POP-1 (f = 19.6), (c) protonated GT-POP-1 (f = 39.2), (d) protonated GT-POP-1 (f = 47.6), (e) protonated GT-POP-1 (f = 62.7), (f) protonated GT-POP-1 (f = 78.4).



Figure S18. Deconvoluted XPS spectra of F1s for (a) pristine GT-POP-1, (b) protonated GT-POP-1 (f = 19.6), (c) protonated GT-POP-1 (f = 39.2), (d) protonated GT-POP-1 (f = 47.6), (e) protonated GT-POP-1 (f = 62.7), (f) protonated GT-POP-1 (f = 78.4).



Figure S19. (a) N₂ (black curve) and CO₂ (red curve) sorption profiles of GT-POP-1 at 77 and 195 K, respectively. CO₂ (sky-blue curve) sorption profiles of protonated GT-POP-1 at 195 K. The solid and open circles denote the adsorption and desorption, respectively. (b) Pore volume and pore-size distribution of GT-POP-1 before and after protonation.



Figure S20. FTIR spectra of protonated GT-POP-1 with different amount of H₂SO₄.



Figure S21. (a) UV-vis spectra of protonated GT-POP-1 with different amounts of H_2SO_4 . (b) UV spectra of protonated GT-POP-1 by H_2SO_4 and TfOH, respectively.



Figure S22. TG curves of the protonated GT-POP-1 (f = 78.4) membrane (red line) and GT-POP-1 mixed with DMF. To confirm if there was residual solvent (DMF) in the membranes, we mixed GT-POP-1 with several drops of DMF, and measured the TG of the membrane and the mixture. The mixture showed a substantial weight loss in the temperature range of 100 to 250 °C, corresponding to the decomposition of DMF solvent. In contrast, the membrane did not show distinguishable weight loss in this temperature range, demonstrating that there was no residual solvent in the membranes.



Figure S23. ¹H NMR spectra of the protonated GT-POP-1 (f = 78.4) membrane.

We first prepared the membrane by drop casting protonated GT-POP-1 (f = 78.4) DMF solution on the glass substrate, followed by thermal evaporation of DMF. Then the membrane was soaked in D_2O for one day and measure ¹H NMR of the D_2O . If there is any residual DMF, DMF should have desolved in D_2O and the NMR spectra should have displayed peaks at 2.08, 2.90 and 3.06 ppm corresponding to the hydrogens on the CH₃CO-, -NCH₃ and -NCH₃ groups. However, we did not observed these peaks at all. This result demonstrated no solvent (DMF) residual after the forming of the membrane.



Figure S24. SEM image of bent GT-POP-1 (f = 78.4) membrane, showing no crack on the membrane.



Figure S25. The force^{2/3}-displacement curves of the indentation test for protonated GT-POP-1 (f = 78.4) membrane.



Figure S26. The real component of permittivity as a function of frequency. (a) pristine GT-POP-1 and (b) protonated GT-POP-1.



Figure S27. Fitting imaginary component of permittivity of (a) – (c), pristine GT-POP-1 and (d) – (f), protonated GT-POP-1 at 273, 278 and 283 K, respectively.



Figure S28. Fitting imaginary component of permittivity of (a) – (c), pristine GT-POP-1 and (d) – (f), protonated GT-POP-1 at 288, 293 and 298 K, respectively.



Figure S29. Fitting imaginary component of permittivity of (a) – (c), pristine GT-POP-1 and (d) – (f), protonated GT-POP-1 at 303, 308 and 313 K, respectively.



Figure S30. Fitting imaginary component of permittivity of (a) (c) (e) (g), GT-POP-1 and (b) (d) (f) (h), protonated GT-POP-1 at 318, 323, 328 and 333 K, respectively.



Figure S31. The peak maximum frequency of β relaxation as a function of temperature for protonated GT-POP-1. The activation energy (Ea) for β relaxation process was obtained by the peak maximum frequency at different temperatures fitting to Arrhenius equation: $f = f_a e^{\frac{E_a}{KT}}$, where f is the peak maximum frequency measured at certain temperature, f_a is a constant, and K is Boltzmann constant.



Figure S32. Schematic illustration of the H⁺-transport pathway from the starting (a) to the ending (k) of the proton-

exchange process.



Figure S33. (a) CO₂ adsorption isotherms for GT-POP-1 sample in multiple protonation/deprotonation processes. The desorption isotherms were omitted for clarity. (b) Stability of GT-POP-1 sample in multiple protonation/deprotonation processes.

To check the reversibility of the protonation/deprotonation process, we conducted CO₂ adsorption measurements of the samples after multipe treatments of acid and base. (1) Firstly, we measured the CO₂ adsorption isotherms of a neutural GT-POP-1 sample. (2) Secondly, we immersed GT-POP-1 into H₂SO₄ aqurous solution for 1 day, followed by water washing and vacuum evaporation, and measured the CO₂ adsorption isotherms for the protonated GT-POP-1. (3) Thirdly, we immersed the protonated GT-POP-1 into Et₃N MeOH solution for 1 day, followed by MeOH washing and vacuum evaporation, and measured the CO₂ adsorption isotherms for the deprotonated GT-POP-1. The results showed that the protonation/deprotonation process were completely reversible, as showed in the consistance of the adsorption amounts of process (1) and (3). The reversible protonation/deprotonation process was the essence for constructing unimpeded proton-conducting pathways.



Figure S34. (a) ¹H and (b) ¹³C NMR spectra of prestine, protonated and deprotonated GT-POP-1.

We synthesized the neutral polymers and measured the ¹H and ¹³C NMR in the DMSO- d_6 solution. The ¹³C NMR spectrum of the neutral polymer confirmed the presence of the sp² carbons of triazine units by showing a new peak at 178 ppm, whereas the peak of cyano groups in the monomer at 118 ppm was completely vanished, demonstrating the completeness of the reaction. After the NMR measurement, we added one drop of 35% DCl-D₂O solution to the above solutions and measured the ¹H and ¹³C NMR. The addition of acid triggered the protonation process of the dihydrophenazine, which generated radicals and resulted in broad band in the ¹H NMR spectra and very weak ¹³C NMR signals. After the measurement, we neutralized the polymer by base and measured the ¹H and ¹³C NMR. The neutralization completely recovered the NMR spectra, which demonstrated the protonation/deprotonation process was completely reversible.



Figure S35. Configuration and photos of proton-conducting devices.



Figure S36. I–V curves of (a) pristine GT-POP-1 membrane and (b) protonated GT-POP-1 (f = 78.4) membrane.



Figure S37. Nyquist plots of GT-POP-1 membranes with different f at 298 K and 90% RH.



Figure S38. Nyquist plots of protonated GT-POP-1 (f = 78.4) at 298 K and 90% RH measured in different labs. (a) in the labs of S. Horike and S. Kitagawa. (b) in our lab. In both the case (a) and (b), the I and t were 1 cm and 20 μ m, respectively, whereas the d in the case (a) and (b) was 2 and 6 mm, respectively (Figure 4a). The proton conductivity was calculated to be 0.303 and 0.279 S cm⁻¹ in the case (a) and (b), respectively.



Figure S39. Nyquist plots of protonated GT-POP-1 (a) membrane and (b) pressed pellet at 298 K and 90% RH. We immersed GT-POP-1 powder into sulfuric acid for 48 h, followed by vacuum drying to obtain protonated GT-POP-1, and separated the powders into two groups. The powder of Group 1 was directly pressed into pellet, whereas the powder of Group 2 was dispersed in NMP and drop casted into membrane. Thus, the protonated degree of Group 1 and 2 are consistent. We used the two samples to fabricate the proton-conducting devices, which gave the proton conductivity of 0.067 S cm⁻¹ for membrane (horizontal direction) and 0.016 S cm⁻¹ for pellet. The conductivities of the two samples were very similar, and considering the existence of grain boundary resistance and non-preferred orientation of the polymers in the pellet, we could make a conclusion that GT-POP-1 has 3D proton conductivity.



Figure S40. Nyquist plots of protonated GT-POP-1 (f = 78.4) membrane at 298 K and 90% RH under H_2O and D_2O vapor, respectively.



Figure S41. Nyquist plots of GT-POP-1 (f = 78.4) membrane at 298 K and different RHs.



Figure S42. Photo of the GT-POP-1 (f = 78.4) membrane for measuring the H⁺ transport number. The diameter of

the membrane was 15.96 mm.



Figure S43. Cross-section SEM images of (a) GT-POP-1/PMMA, (b) GT-POP-1/PEG and (c) GT-POP-1/PEO hybrid

membranes, showing the defect-free morphology of the membranes.



Figure S44. Nyquist plots of (a) GT-POP-1/PMMA hybrid membrane (50:50 wt%), (b) GT-POP-1/PEG hybrid membrane (50:50 wt%), (c) GT-POP-1/PEO hybrid membrane (50:50 wt%), (d) pure PMMA membrane, (e) pure PEG membrane, and (f) pure PEO membrane at 298 K and 90% RH.

The hybridization of GT-POP-1 with other traditional polymers significantly enhanced the proton conductivity of the polymers, demonstrating that GT-POP-1 could act as a versatile platform for constructing hybrid systems with superior proton conductivity.

	C%	N%	Н%	S%
Calcd.	81.23	14.57	4.20	0
Found	78.34	10.91	4.13	0.02

Table S1. Elemental analysis results of pristine GT-POP-1

molecule	peak (cm ⁻¹)	assignment		
	2231 (s)	C≡N stretching		
	1590 (s)	stretching vibration band of benzene ring		
	1486 (s)	stretching vibration band of benzene ring		
1	1349 (s)	stretching vibration band of benzene ring		
	1283 (s)	C-N stretching band of dihydrophenazine		
	825 (s)	C–H out-of-plane vibration band of benzene		
	742 (s)	C–H out-of-plane vibration band of benzene		
	1671 (s)	stretching vibration band of triazine ring		
	1592 (s)	stretching vibration band of benzene ring		
	1483 (s)	stretching vibration band of benzene ring		
	1321 (s)	stretching vibration band of triazine ring		
GT-POP-1	1283 (s)	C-N stretching band of dihydrophenazine		
	838 (w)	C–H out-of-plane vibration band of benzene		
	787 (w)	C–H out-of-plane vibration band of triazine		
	735 (m)	C-H out-of-plane vibration band of benzene		

Table S2. Peak assignments of FT-IR spectra for 1 and GT-POP-1

chemical structure	chemical shift (ppm)	assignment
	109.65	b
сл Др	114.10	f
	117.87	а
	121.65	e
	129.62	d
	134.89	c and g
	144.29	h
	113.56	f
	121.46	e
	130.21	d
	133.15	С
	136.36	b
	142.83	g
\bigcirc	143.97	h
N ^A N ANA	167.69	g (in protonated state)
	166.26	h (in protonated state)
	178.08	а

Table S3. Peak assignments of liquid-state ¹³C NMR spectra for 1 and GT-POP-1

chemical structure	chemical shift (ppm)	assignment
Ϋ́ΥΥΥ Ϋ́Υ	111.72	d
	121.62	е
Č, D	130.50	b
Ś	142.98	С
N, X, N	170.06	а
`Q _e n, O`		
ŇŢŃ	112 04	h
	130.80	b
CILD	143.25	c
\bigcirc	170.12	а

Table S4. Peak assignments of solid-state ¹³C NMR spectra for GT-POP-1 before and after protonation

	N ₁ (eV)/area	N ₂ (eV)/area	N ₃ (eV)/area	Protonated
	C=N	C-N	C-N ⁺	Degree (%)
f = 0	399.6/4439	400.2/6573	400.8/994	16.5
f = 19.6	399.6/5701	400.2/4563	400.9/2779	42.5
f = 39.2	399.6/6523	400.2/5458	400.9/4634	55.7
f = 47.6	399.6/6972	400.1/6329	400.9/5531	58.7
f = 62.7	399.7/5269	400.5/5756	401.2/4995	62.3
f = 78.4	399.9/1979	400.7/2305	401.5/1898	64.3

Table S5. XPS results and protonated degree of protonated GT-POP-1 membranes

Table S6 Derformar	nco motrics	of roported	nroton	conductivo	matorials
rable 30. Ferrorinar	ice metrics	orreporteu	ριστοπ	conductive	materials

	Proton	Conditions			
Material	conductivities	RH (%)	т (к)	Ref.	
	(S cm ⁻¹)		. ()		
GT-POP-1	0.30	90	298	This work	
HPW@TAPT-DHTA	0.24	100	303	ref. 6	
Co-tri	0.149	98	353	ref. 7	
NP films	0.13	95	298	ref. 35	
BUT-8(Cr)A	0.127	100	353	ref. 8	
PCMOF21/2(Tz)	0.117	90	358	ref. 9	
NKCOFs	0.113	98	353	ref. 10	
UiO-66(SO ₃ H) ₂	0.084	90	353	ref. 11	
TfOH@MIL-101	0.08	15	333	ref. 12	
PTSA@TpAzo	0.078	95	353	ref. 13	
Nafion 117	0.078	100	298	ref. 4	
In-Cr-MOPs	0.058	98	295.5	ref. 14	
TJU-102	0.052	98	363	ref. 15	
Fe-CAT-5	0.05	98	298	ref. 16	
CB[6] 2	0.043	98	293	ref. 17	
3D MOF	0.042	98	298	ref. 18	
NUS-10(R)	0.0396	97	298	ref. 19	
Co(DCDPP)	0.039	97	353	ref. 20	
PCMOF10	0.0355	95	343	ref. 21	
BIP	0.032	95	368	ref. 22	

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