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Intrinsic proton conduction in 2D sulfonated covalent organic framework through the post-synthetic strategy

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Materials

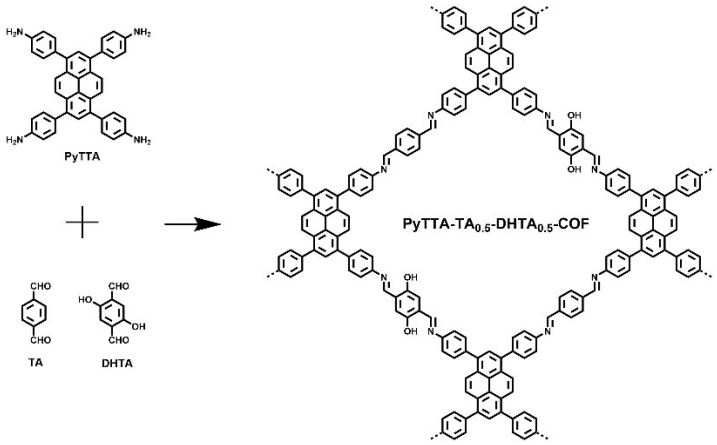
1,3,6,8-tetrabromopyrene, 4-aminophenylboronic acid pinacol ester, 1,3-propane sultone, sodium hydroxide and other chemicals were obtained from TCI, Wako, and Sigma-Aldrich. 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline and 2,5-dihydroxyterephthalaldehyde were synthesized according to reported methods.[S1-S3]

Methods

Field emission scanning electron microscope was performed on HITACHI Miniscope TM3030. Energy-dispersive X-ray spectroscopy (EDS) mapping was measured by TM3030Plus miniscope. The X-ray photoelectron spectroscopy (XPS) measurement was implemented on a DLD spectrometer (Kratos Axis-Ultra; Kratos Analytical Ltd). Nitrogen sorption isotherms were measured at 77 K by BELSORP-max. Water uptake were measured by performed by using a Micrometrics ASAP2050 analyzer. Fourier transforms Infrared spectra (FT-IR) were measured from 650 to 4000 cm^{-1} on a FT-IR spectrometer (Nicolet 6700; Thermo Fisher Scientific Inc.). Powder X-ray diffraction (PXRD) data were recorded on fully automatic horizontal multipurpose X-ray diffractometer (Rigaku Smartlab) from 2θ = 1.5° up to 30° with 0.02° increment. Thermogravimetric analysis (TGA) was implemented on TG-DTA 2010 SA (NETZSCH) Japan under nitrogen flow at 10°C min^{-1}. Proton conductivity measurement of COF samples was examined through impedance spectroscopy measurements using a frequency response analyzer (SI1260; Solartron Analytical) equipped with a high-frequency dielectric interface (SI1260; Solartron Analytical). Proton conductivity (σ) was calculated as, $\sigma = L / (R \times S)$, where R denotes the resistance value obtained from the impedance, S and L respectively stand for the contact electrode area and the thickness of the membrane. The activation energy (E_A) of S-POPs was calculated as, $\sigma T = \sigma_0 \times \exp(-E_A / (k_B \times T))$, where σ is the proton conductivity, σ_0 is the pre-exponential factor, k_B is the Boltzmann constant, and T is the temperature.

Synthetic procedures

Synthesis of PyTTA-DHTA-COF: The PyTTA-DHTA-COF was synthesized using a reported methods.[S3] 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetraaniline (PyTTA) (60 mg, 0.11 mmol), 2,5-dihydroxyterephthalaldehyde (36 mg, 0.22 mmol), 2 mL of o-DCB, 2 mL of n-BuOH, and 0.2 mL of 6 M HAc were added the flask and degassed through three freeze-pump-thaw cycles. The mixture was heated at 120 ºC for 72 h under Argon atmosphere. The formed precipitate was collected and washed with water and acetone, then extracted by THF overnight, and dried under vacuum at room temperature for 24 h to afford a red powder in 89% isolated yield.



Scheme S1. Synthesis of PyTTA-$TA_{0.5}$-$DHTA_{0.5}$-COF.

Synthesis of PyTTA-$TA_{0.5}$-$DHTA_{0.5}$-COF: T 4,4',4",4'"-(pyrene-1,3,6,8-tetrayl)tetraaniline (PyTTA) (60 mg, 0.11 mmol), 1,4-phthalaldehyde (18 mg, 0.11 mmol), 2,5-dihydroxyterephthalaldehyde (14.5 mg, 0.11 mmol), 2 mL of o-DCB, 2 mL of n-BuOH, and 0.2 mL of 6 M HAc were added the flask and degassed through three freeze-pump-thaw cycles. The mixture was heated at 120 ºC for 72 h under Argon atmosphere. The formed precipitate was collected and washed with water and acetone, then soxhleted by THF overnight, and dried under vacuum at room temperature for 24 h to afford a red powder in 86% isolated yield.

Synthesis of PyTTA-DHTA-COF-SO_3H: The PyTTA-DHTA-COF-SO_3H was synthesized using reported methods.[S4] Under Argon atmosphere, PyTTA-DHTA-COF (180 mg) and NaOH (52 mg, 1.30 mmol) was added in DMF 15 mL. The mixture was stirred at 60 ºC for three hours, and cooled down to room temperature. The 1,3-propane sultone (200 μL, 1.7 mmmol) was added into system. The mixture was stirred overnight under Argon atmosphere. The powder was collected and washed by water and acetone, and dried under vacuum for 2 h. The powder was added into 50 ml of 1 M HCl for 2 h, collected and washed by water and acetone, and dried under vacuum. The process was repeated for ten times. Finally, a black powder was collected (225 mg). PyTTA-$TA_{0.5}$-$DHTA_{0.5}$-COF-$SO_3H_{0.5}$ was synthesized by the same route.

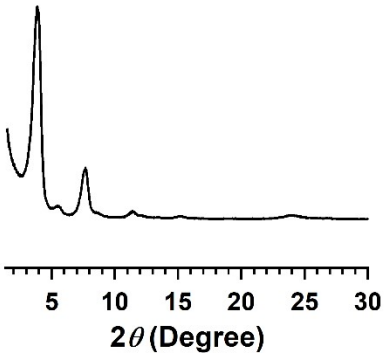


Fig. S1. PXRD pattern of PyTTA-DHTA-COF in 1 M NaOH at room temperature for 12 h.

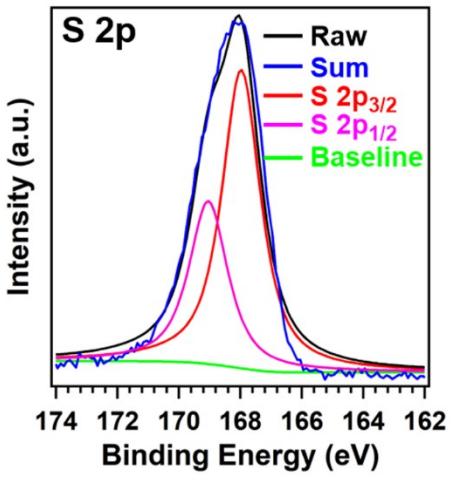


Fig. S2. XPS spectra of S 2p for PyTTA-DHTA-COF-SO_3H.

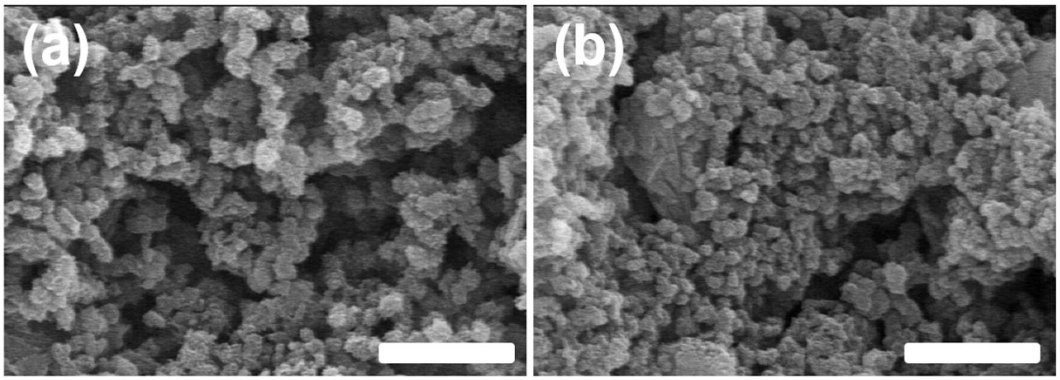


Fig. S3. FE SEM images of (a) PyTTA-DHTA-COF and (b) PyTTA-DHTA-COF-SO_3H. (Scale bar: 5 μm).

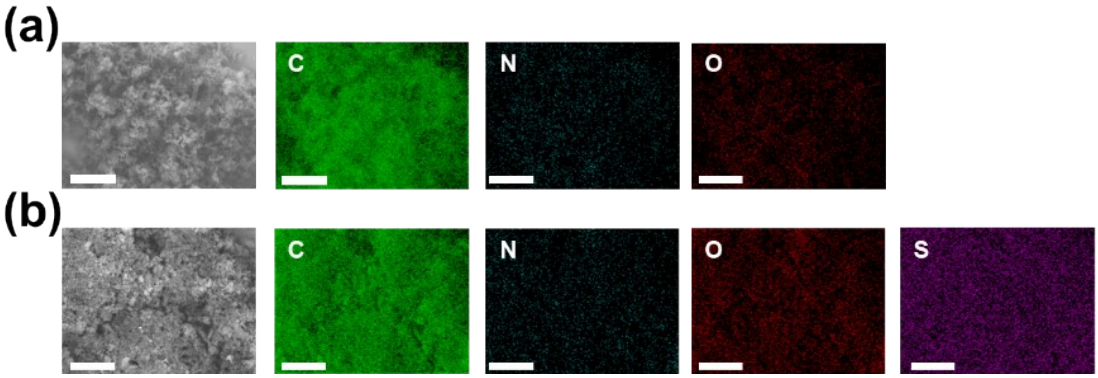


Fig. S4. EDS mapping images of (a) PyTTA-DHTA-COF and (b) PyTTA-DHTA-COF-SO_3H. (Scale bar: 25 μm).

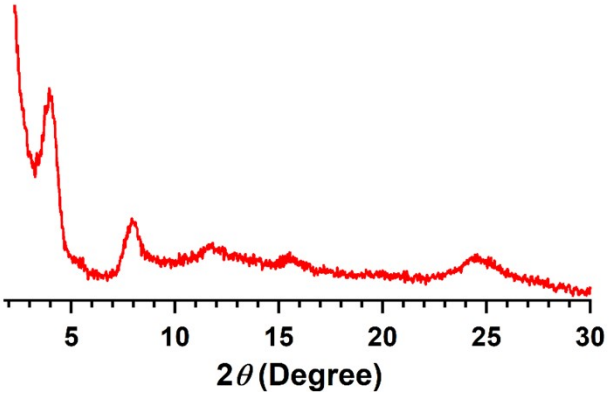


Fig. S5. PXRD pattern of PyTTA-DHTA-COF-SO_3H.

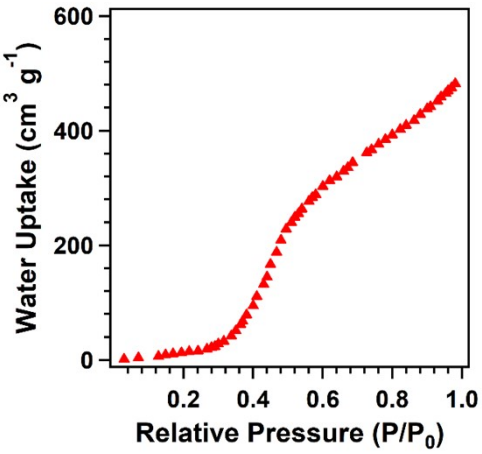


Fig. S6. Water vapor adsorption curve of PyTTA-DHTA-COF-SO_3H.

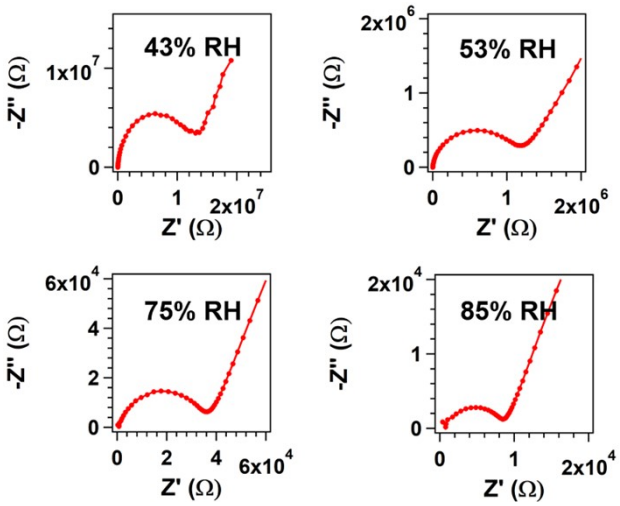


Fig. S7. Nyquist plots of PyTTA-DHTA-COF-SO_3H recorded under different humidity.

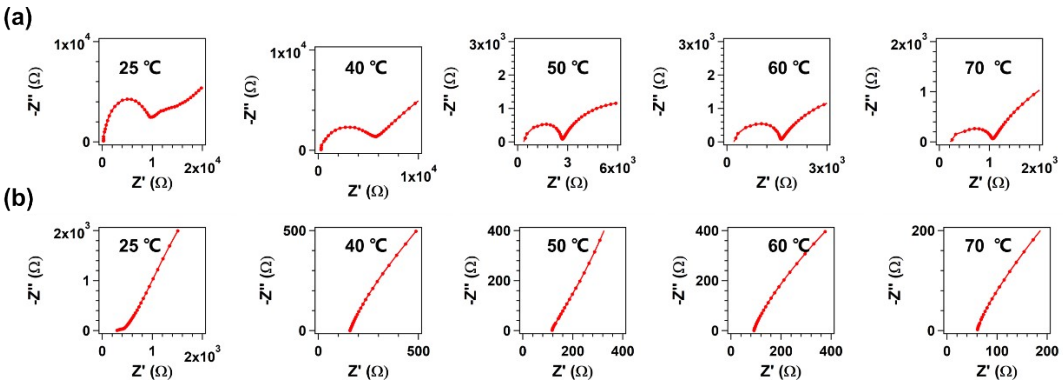


Fig. S8. Nyquist plots of (a) PyTTA-DHTA-COF and (b) PyTTA-DHTA-COF-SO_3H recorded at the different temperature and 100% relative humidity.

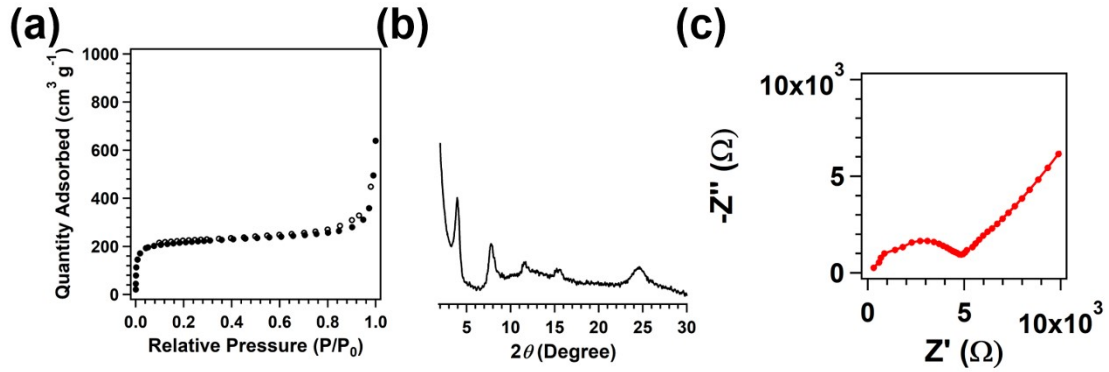


Fig. S9. (a) Nitrogen sorption isotherms measured at 77 K, (b) PXRD pattern and (c) Nyquist plots of PyTTA-$TA_{0.5}DHTA_{0.5}$-COF-$SO_3H_{0.5}$ recorded at room temperature and 100% relative humidity.

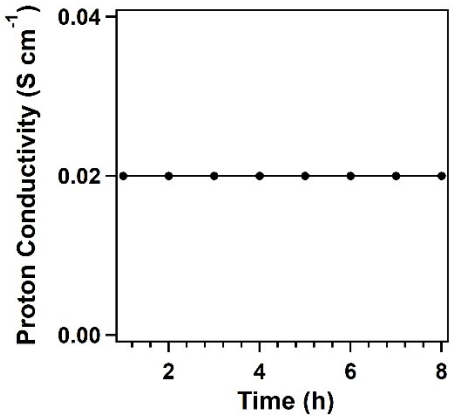


Fig. S10. Time dependent proton conduction in PyTTA-DHTA-COF-SO_3H at 70 ºC and 100% relative humidity.

Tab.S1. Elemental analysis of PyTTA-DHTA-COF and PyTTA-DHTA-COF-SO_3H.

Sample		C (%)	N (%)	H (%)	S (%)
PyTTA-DHTA-COF	theoretical	81.34	6.78	4.14	-
	observed	82.67	7.30	5.36	-
PyTTA-DHTA-COF-SO_3H	theoretical	62.09	9.87	2.66	9.75
	observed	60.40	10.01	3.33	7.82

References

S1. D. Bessinger, L. Ascherl, F. Auras, T. Bein, *J. Am. Chem. Soc*., 2017, 139, 12035.

S2. Y. Zhi, P. Shao, X. Feng, H. Xia, Y. Zhang, Z. Shi, Y. Mu and X. Liu, *J. Mater. Chem. A*, 2018, 6, 374.

S3. X. Chen, N. Huang, J. Gao, H. Xu, F. Xu and D. Jiang, *Chem. Commun*., 2014, 50, 6161.

S4. K. Krishnan, H. Iwatsuki, M. Hara, S. Nagano and Y. Nagao, *J. Mater. Chem. A*, 2014, 2, 6895.