

Electronic Supplementary Information (ESI)

Selective CO₂ adsorption and proton conductivity in the two-dimensional Zn(II) framework with protruded water molecules and flexible ether linkers

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Experimental Details

Preparation.

1,3,5-Tri(4-carboxyphenoxy)benzene (**H₃TCPB**) was synthesized using the reported method.^{s1}

[Zn₃(TCPB)₂(H₂O)₂]·4DMF·3H₂O (1·4DMF·3H₂O): A solution of Zn(NO₃)₂·6H₂O (0.20 g, 0.68 mmol) in DMF/EtOH/H₂O (7/7/5, v/v, 5 mL) mixed solvent and a solution of H₃TCPB (0.15 g, 0.31 mmol) in DMF/EtOH/H₂O (7/7/5, v/v, 5 mL) mixed solvent were combined and sealed in a 25 mL vial. The resulting solution was heated in an oven at 70 °C, and allowed to react solvothermally for 2 d. The mother liquor was decanted and the colorless rod crystals were washed with EtOH. The product was dried in air. Yield: 63%. Elemental analysis (%) calcd for C₆₆H₆₈N₄O₂₇Zn₃: C 51.29, H 4.44, N 3.63; found: C 51.45, H 4.03, N 3.45.

[Zn₃(TCPB)₂(H₂O)₂] (1'): The activated sample was prepared by heating under vacuum at 50 °C for 4 hours. Elemental analysis (%) calcd for C₅₄H₃₄O₂₀Zn₃: C 54.09, H 2.86; found: C 54.07, H 2.71.

Crystallographic structure determination.

X-ray data for **1** were collected on a Bruker SMART APEXII diffractometer equipped with CCD area detector and operated at 1.5 kW (50 kV, 30 mA) to generate Mo K α radiation ($\lambda = 0.71073$ Å). Preliminary orientation matrix and cell parameters were determined from three sets of ω scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structure of **1** was solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL-97 program. Lattice water and DMF molecules in **1** are significantly disordered and could not be modeled properly, thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. All hydrogen atoms except for those of coordinated water molecules were calculated at idealized positions and refined with the riding models. Crystal data of **1** (squeezed): empirical formula = C₅₄H₃₀O₂₀Zn₃, Mr = 1194.95, $T = 100$ K, trigonal, space group $P-31c$, $a = 16.7421(2)$ Å, $b = 16.7421(2)$ Å, $c = 14.3737(3)$ Å, $V =$

3489.15(13) Å³, $Z = 2$, $D_{\text{calc}} = 1.137 \text{ g cm}^{-3}$, $\mu = 1.082 \text{ mm}^{-1}$, 45022 reflections collected, 2889 unique ($R_{\text{int}} = 0.1016$), $R1 = 0.0638$, $wR2 = 0.1722$ [$I > 2\sigma(I)$].

Physical measurements.

Elemental analysis for C, H, and N was performed at the Elemental Analysis Service Center of Sogang University. Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min in a N₂ flow using a Scinco TGA N-1000 instrument. PXRD data were recorded using Cu K α ($\lambda = 1.5406 \text{ \AA}$) on a Rigaku Ultima III diffractometer with a scan speed of 2 °/min and a step size of 0.02°.

Gas adsorption measurements.

Gas sorption isotherms were measured using a BEL Belsorp mini II gas adsorption instrument up to 1 atm of gas pressure. The highly pure N₂ (99.999 %), H₂ (99.999 %), CO₂ (99.999 %), CH₄ (99.999 %), CO (99.999 %) were used in the sorption experiments. The gases isotherms were measured at 77 K (N₂ and H₂), 195 K (CO₂), 273 K (CO₂, N₂, CH₄, CO, and H₂), 298 K (CO₂, N₂, CH₄, CO, and H₂).

Impedance analyses.

AC impedance data were obtained using a pellet (0.6 cm in diameter) pressed at 5,000 kg for a couple of minutes. The thickness of the pellet was ranging from 0.10 to 0.14 cm. Measurements were carried out using a Solartron SI 1260 Impedance/Gain-Phase Analyzer and 1287 Dielectric Interface with Pt-pressed electrodes and applied AC voltage amplitude of 100 mV and frequency range of 10⁶–0.1 Hz.

Water adsorption measurement.

Water adsorption experiment was performed by volumetric method using a Micrometrics ASAP2020 instrument at 298 K.

(s1) K. Matsumoto, T. Higashihara, M. Ueda, *Macromolecules* 2008, **41**, 7560-7565.

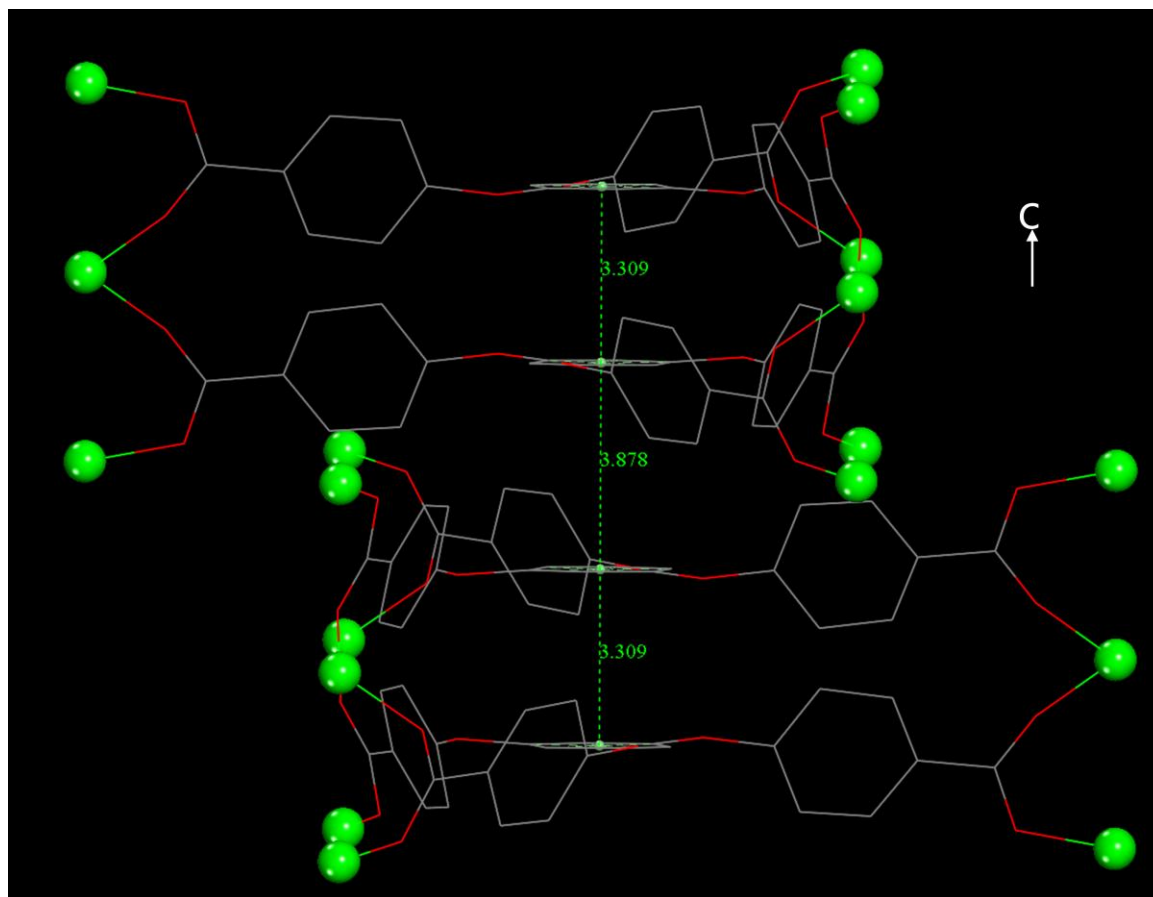


Fig. S1. Side view of **1** showing π - π contacts between benzene rings. The intralayer centroid distance is 3.309 Å, while the interlayer centroid distance is 3.878 Å.

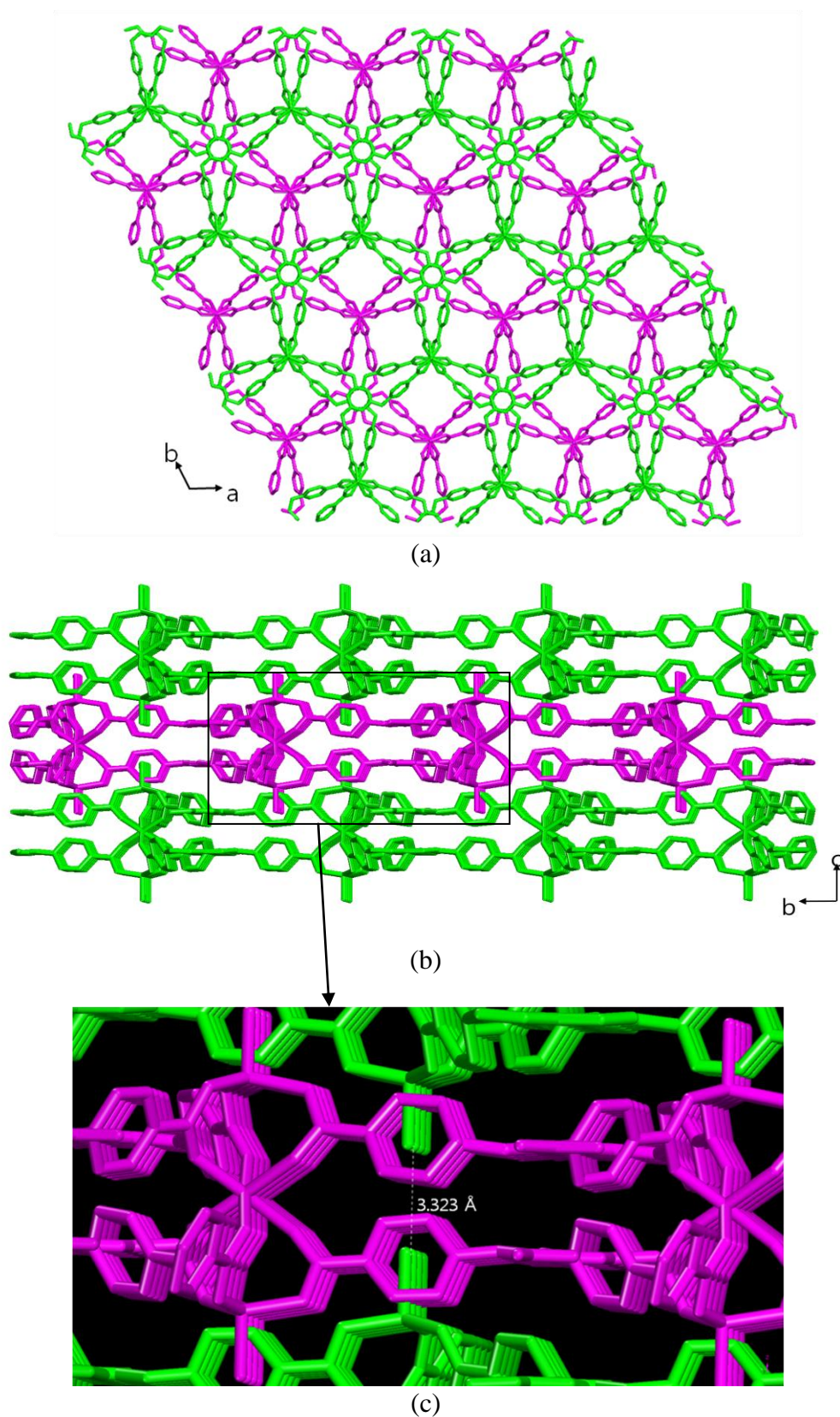


Fig. S2. View of the layered structure (a) in the *ab* plane and (b) in the *bc* plane. Colors represent different sheets. (c) Enlargement of the indicated area in (b) showing the contacts between water oxygens in the green layers.

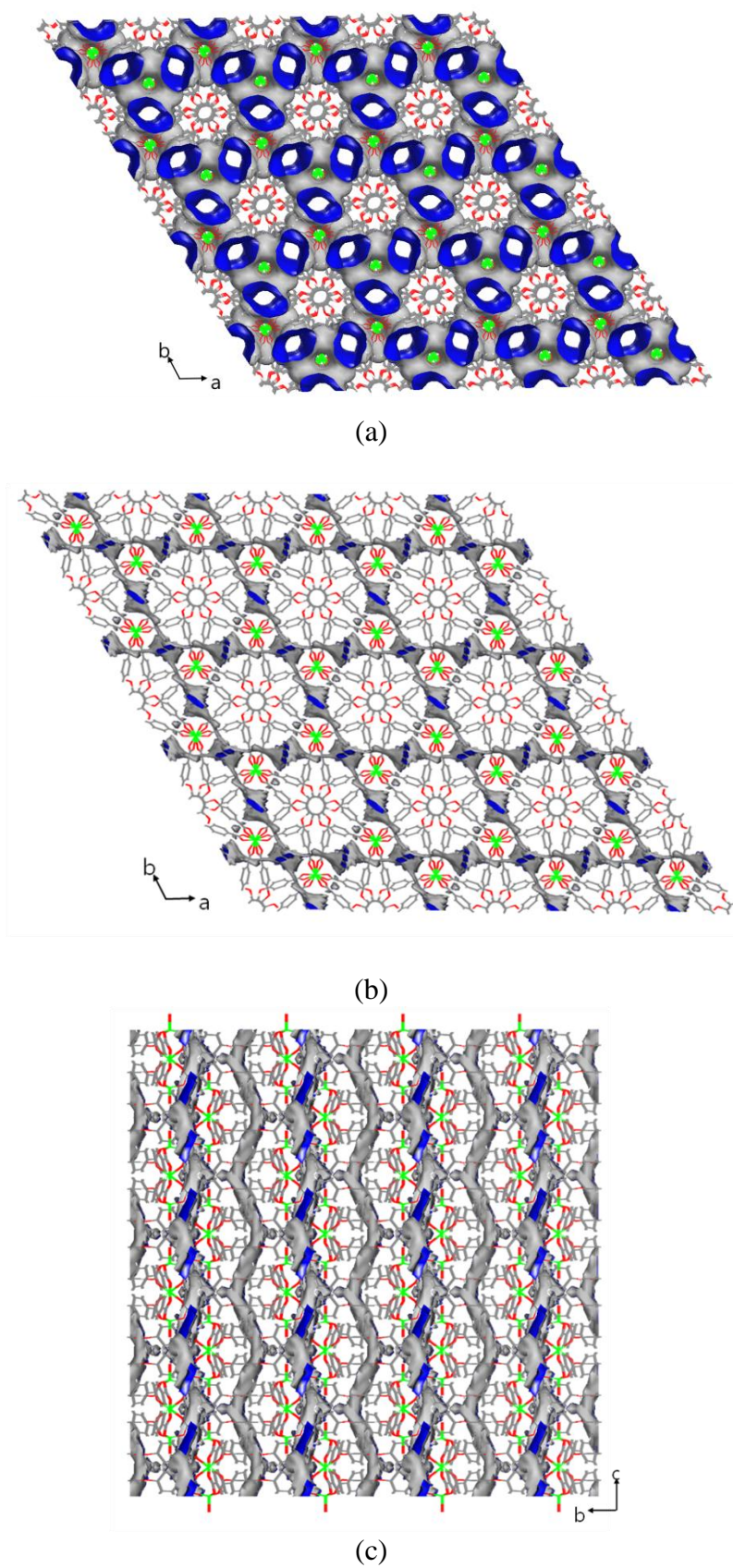
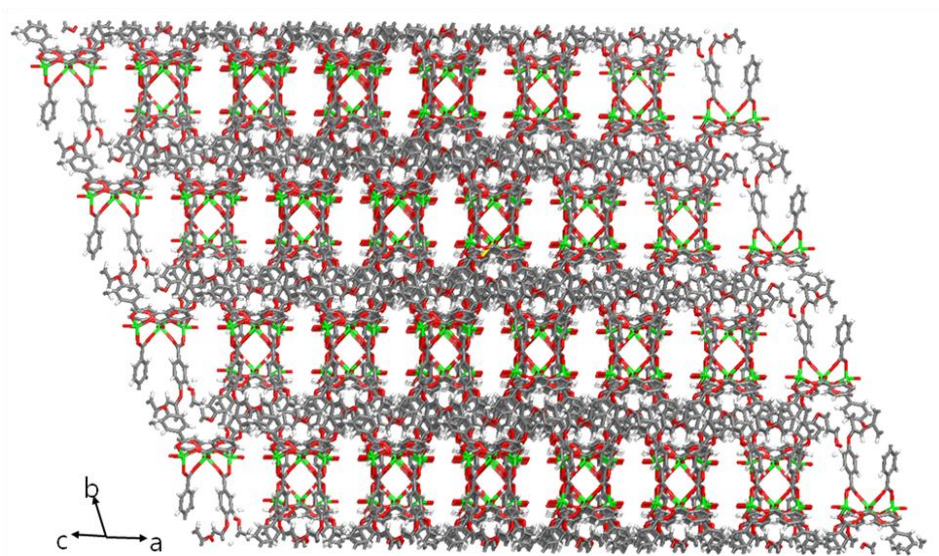
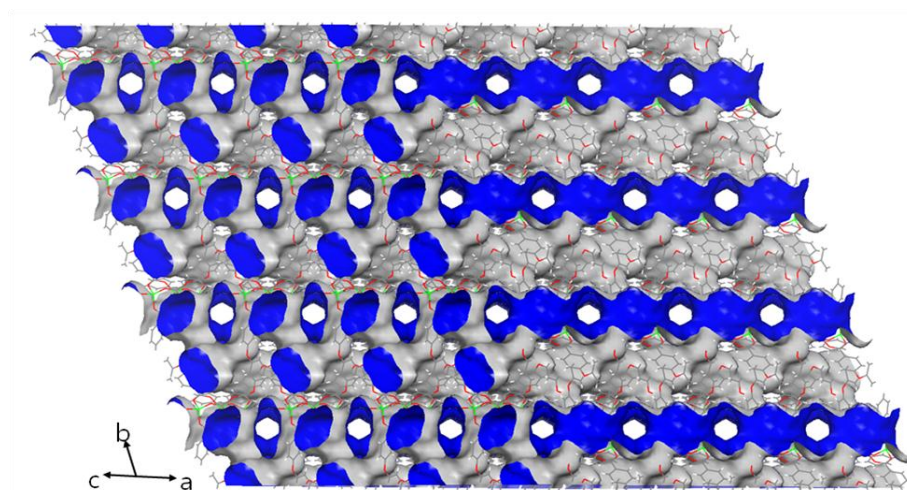


Fig. S3. (a) Connolly surface of **1**. Solvent surfaces of **1** with a probe radius of 1.65 Å (b) in the *ab* plane and (c) in the *bc* plane.



(a)



(b)

Fig. S4. (a) Extended structural view exhibiting 1D channels with water molecules exposed toward the channels. (b) Connolly surface of the corresponding structure.

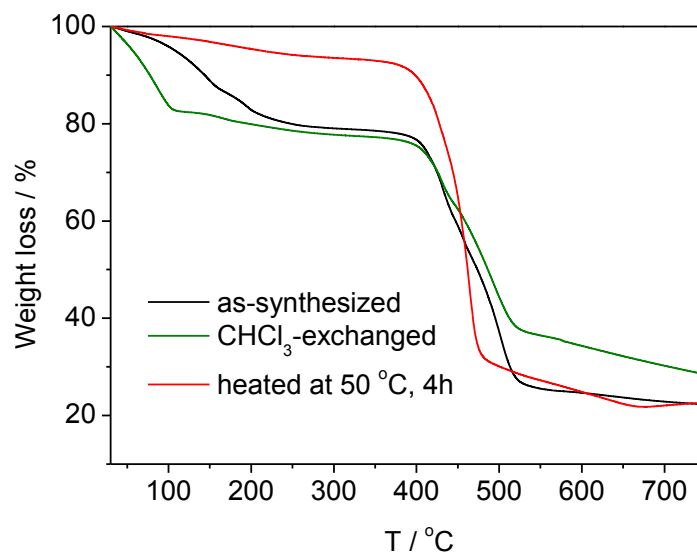


Fig. S5. TG curves of the as-prepared, CHCl₃-exchanged, and activated-1.

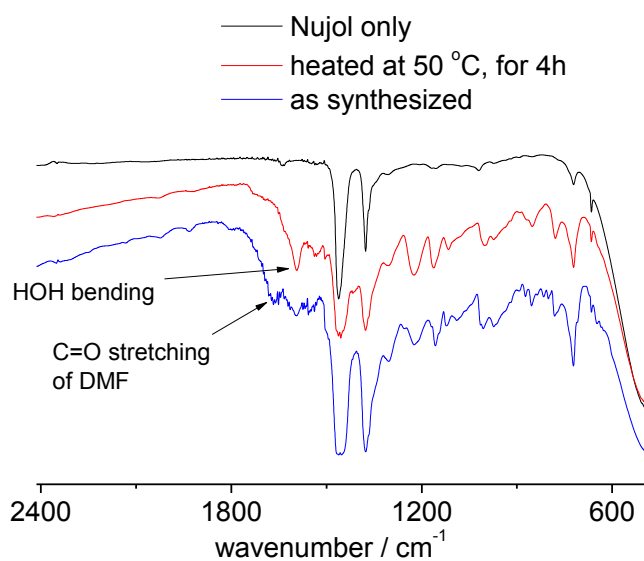


Fig. S6. Nujol IR spectra of the as-prepared and activated-1 showing H₂O bending and CO stretching modes.

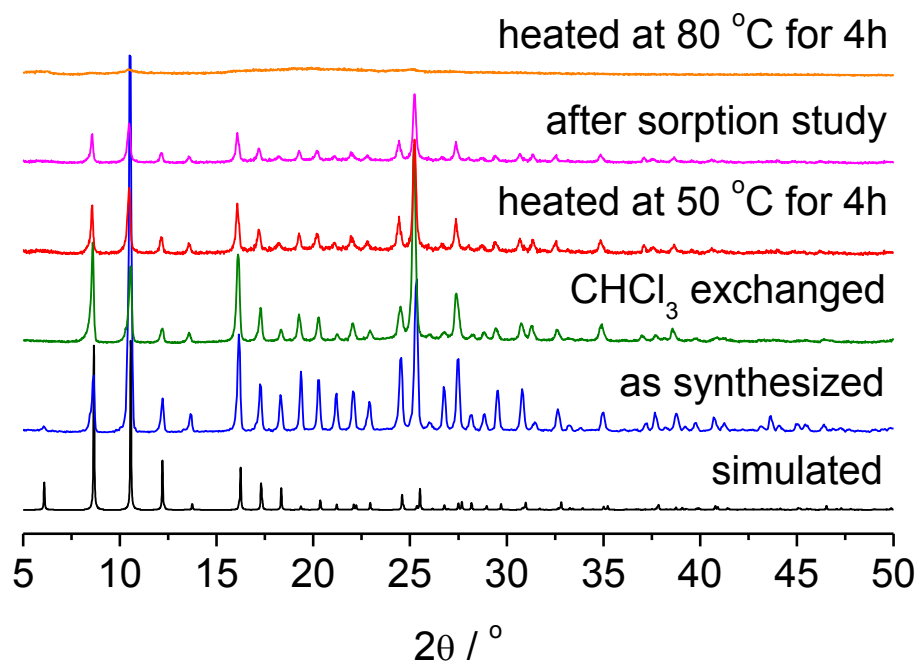


Fig. S7. PXRD data of the as-prepared (**1**), CHCl₃-exchanged, activated solids (**1'**), and samples after sorption and heated at 80 °C.

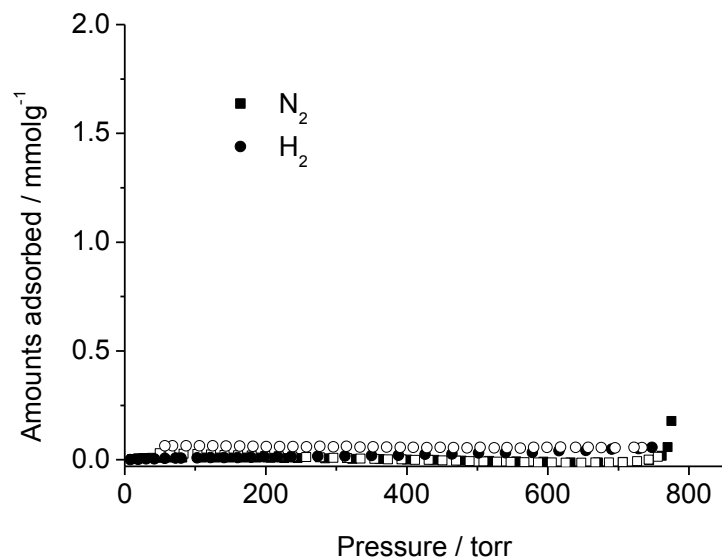


Fig. S8. N₂ and H₂ sorption isotherms of **1'** at 77 K.

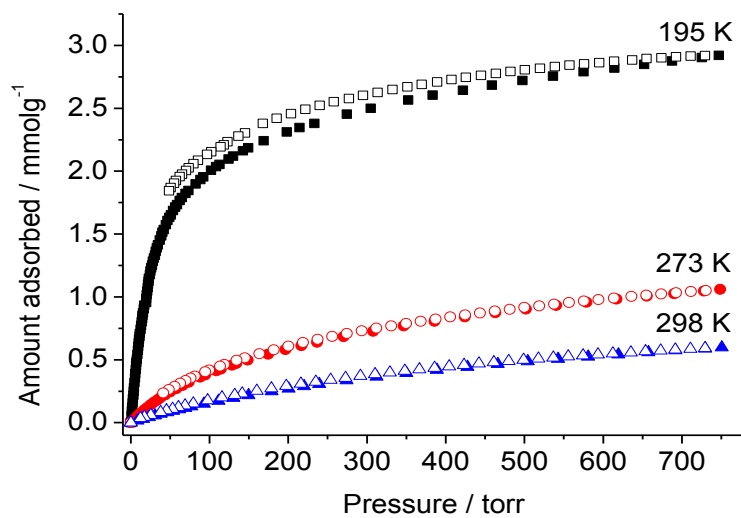


Fig. S9. CO₂ adsorption isotherms of **1'** at three temperatures.

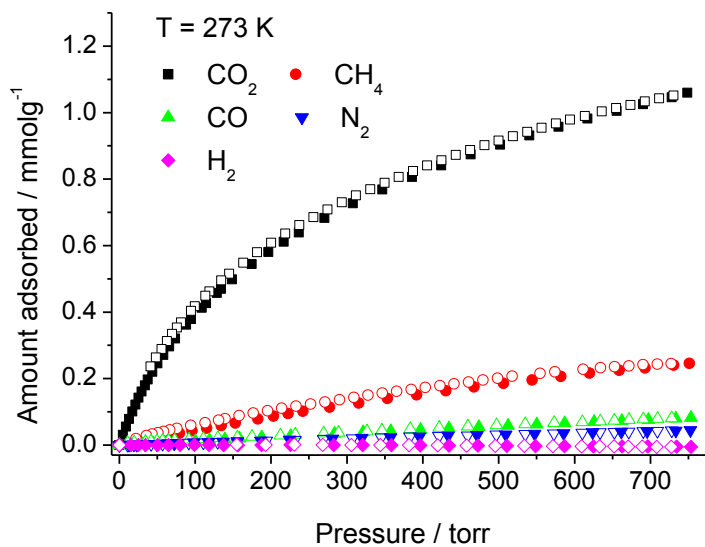


Fig. S10. CO₂ sorption isotherms of **1'** at 273 K.

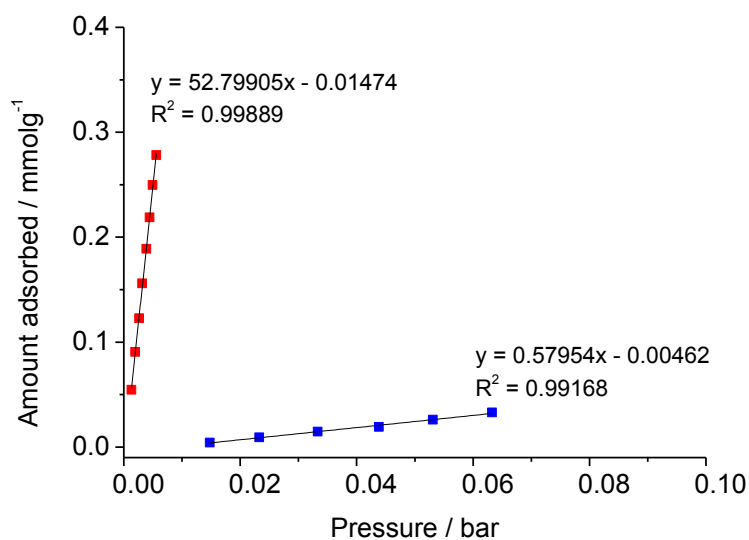


Fig. S11. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and N₂ (blue) at 195 K.

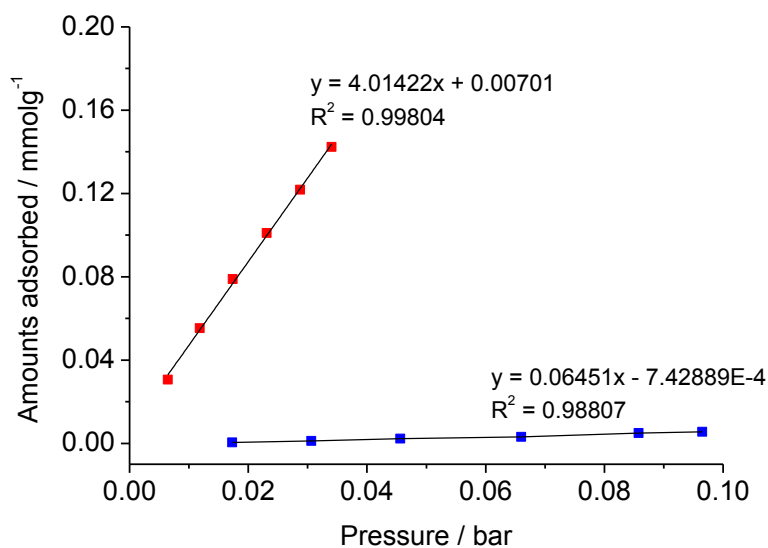


Fig. S12. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and N₂ (blue) at 273 K.

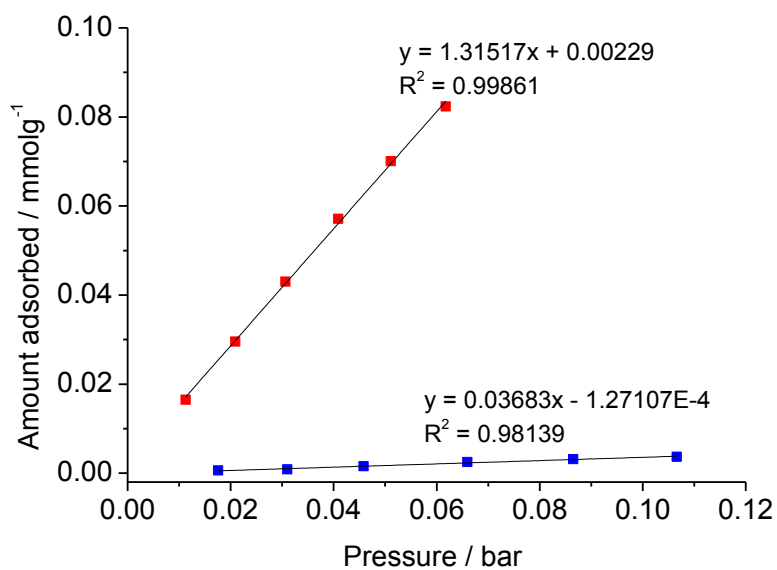


Fig. S13. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and N₂ (blue) at 298 K.

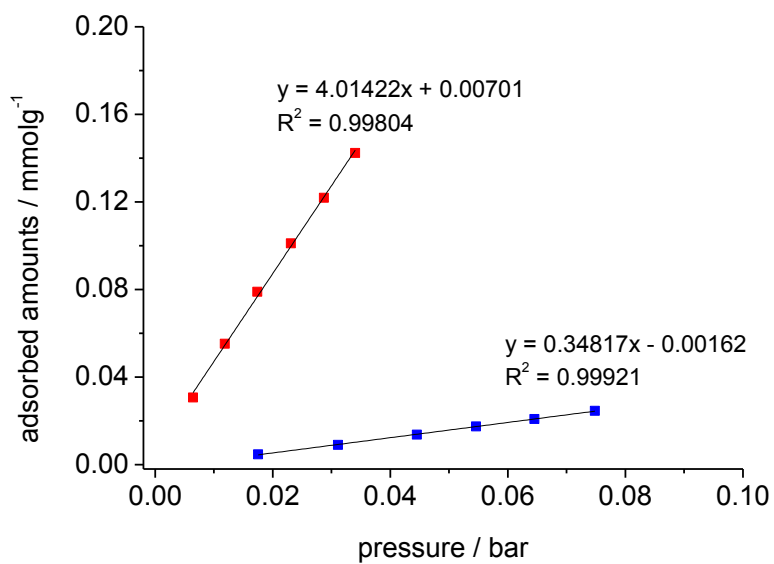


Fig. S14. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and CH₄ (blue) at 273 K.

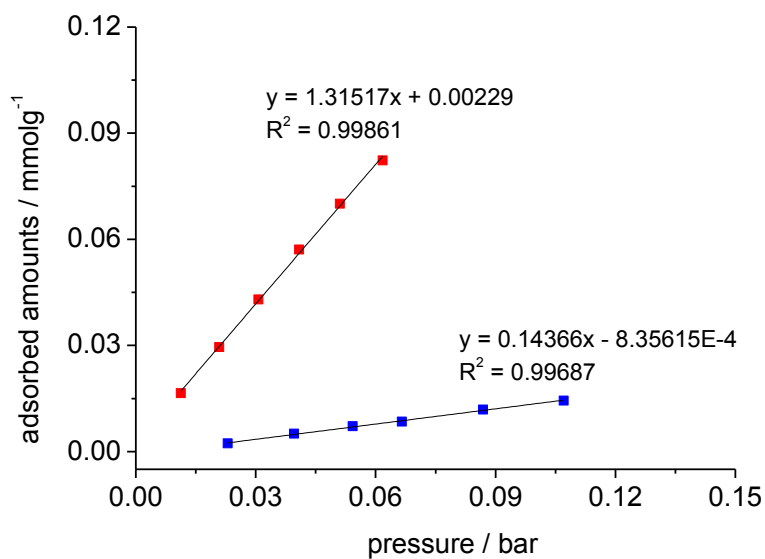


Fig. S15. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and CH₄ (blue) at 298 K.

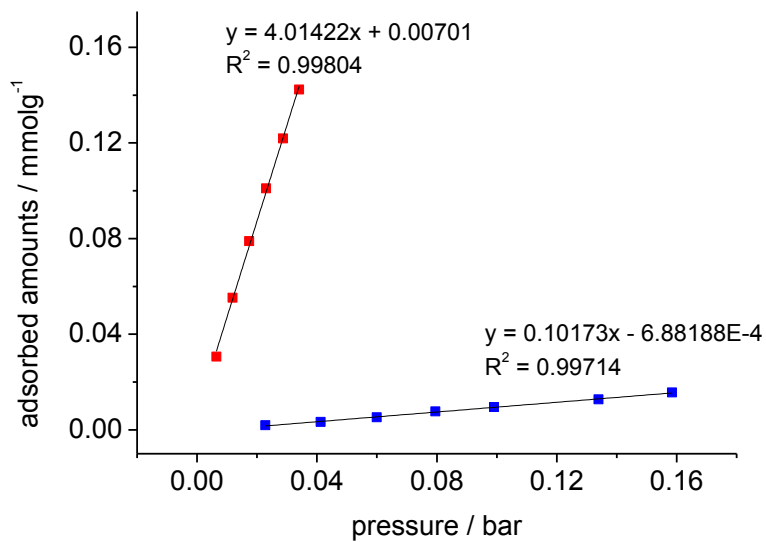


Fig. S16. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and CO (blue) at 273 K.

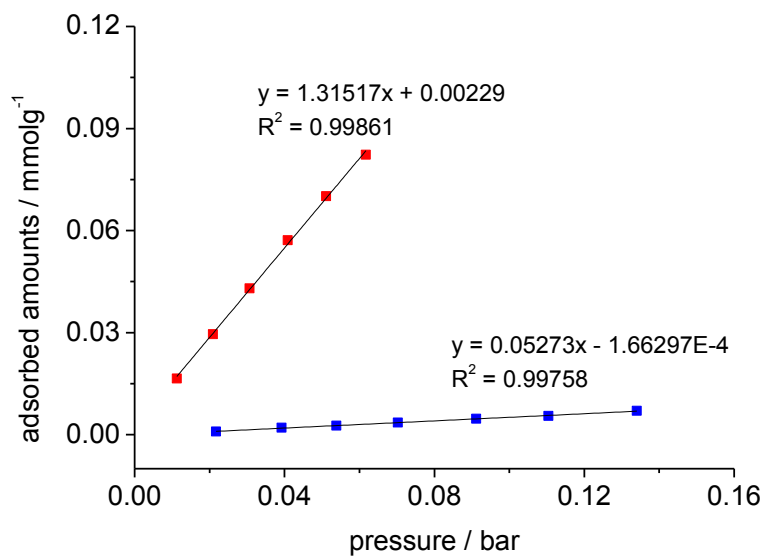


Fig. S17. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and CO (blue) at 298 K.

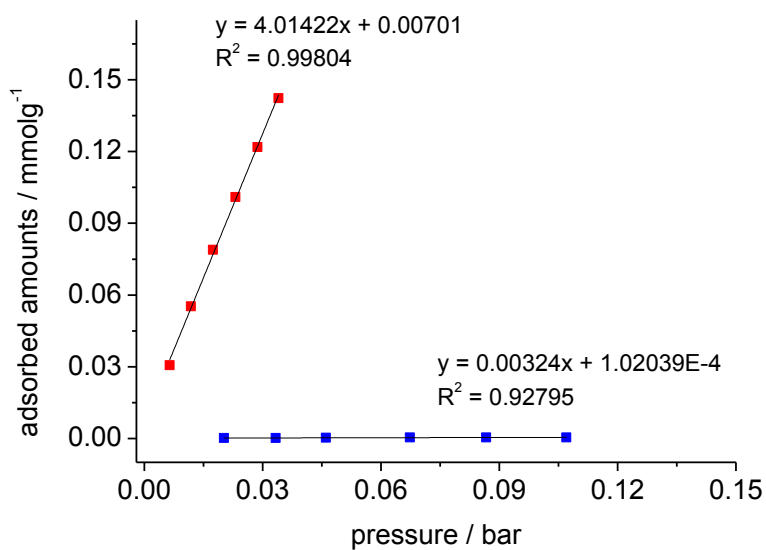


Fig. S18. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and H₂ (blue) at 273 K.

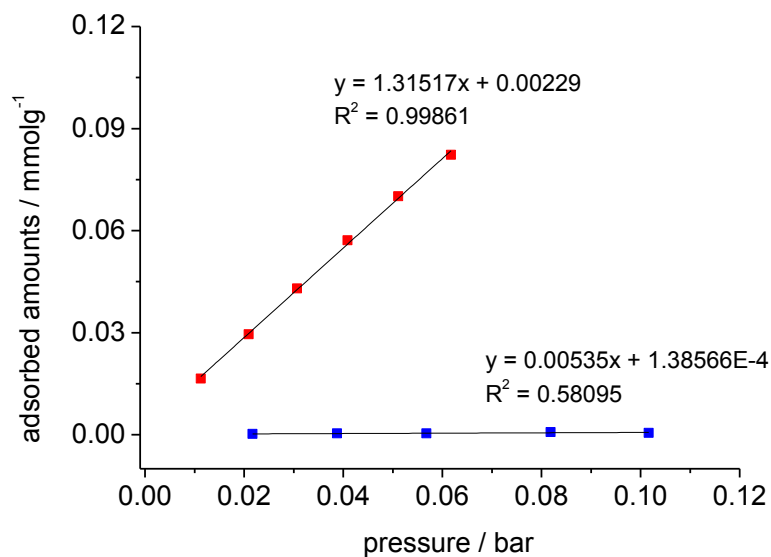


Fig. S19. Linear fit of the low-pressure adsorption data in the Henry region for CO₂ (red) and H₂ (blue) at 298 K.

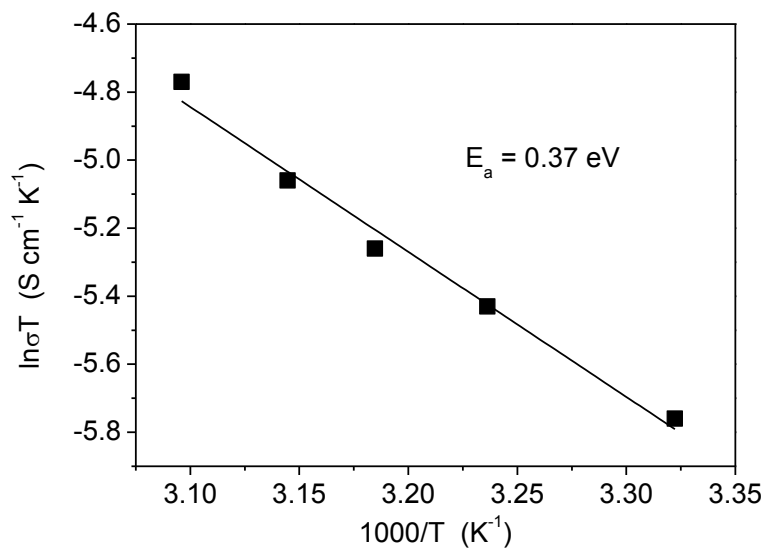


Fig. S20. Arrhenius plot of proton conductivity of **1'** at 98% RH.

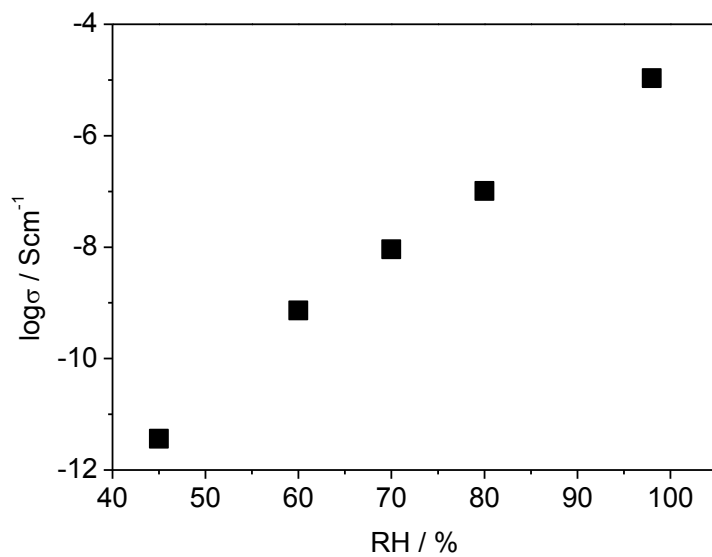


Fig. S21. Relative humidity dependence of the proton conductivity for **1'** at 28 °C

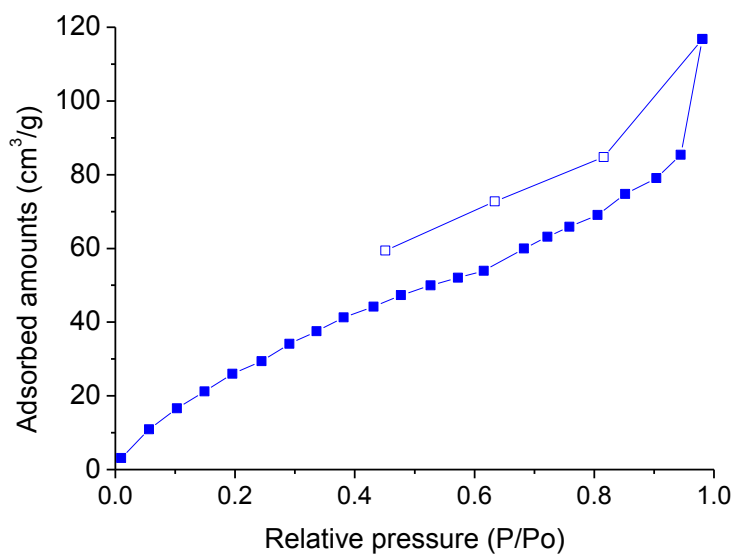


Fig. S22. Water vapor sorption isotherm of **1'** at 25 °C.