Electronic Supplementary Information (ESI)

Reversible structural transformation and selective gas adsorption in an aqua-bridged Mn(II) metal-organic framework

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Experimental Details

Preparations: All chemicals and solvents in the synthesis were reagent grade and used as received. The source and purity of the reagents are as follows: Tri-*m*-tolylphosphine (TCI, >98.0%), Pyridine (DAE JUNG, >99.5%), $KMnO_4$ (Aldrich, ≥99.0%), HCl (DAE JUNG, >99.5%), $MgBr_2 \cdot 6H_2O$ (Aldrich, 99%), DEF (TCI, >99.0%), MeOH (DAE JUNG, >99.5%), $MnCl_2 \cdot 4H_2O$ (Aldrich, 99%), and DMF (DAE JUNG, >99.5%).

Tris-(3-carboxylphenyl)phosphine oxide (= H_3mTPO): Tri-*m*-tolylphosphine (3 g, 9.86 mmol) in 80 mL pyridine was heated to 70 °C. Warm water (40 mL, 70 °C) was slowly added to the solution and refluxed for 24 h with air flowing, and the color of the mixture turned violet. $KMnO_4$ (20 g, 43.25 mmol) was poured to the mixture and reacted at 70 °C for 48 h. The filtered solution was heated to dryness under reduced pressure. The white solid was dissolved in water and the resulting solution was acidified with neat HCl until no precipitates formed. The solid was collected by filtration and washed with water several times to produce a pure product. Yield: 90%. ^1H NMR (DMSO, 300 MHz): 7.68-7.74 (m, 3H), 7.82-7.89 (m, 3H), 8.14-8.19 (m, 6H). Elemental analysis (%) calcd for $C_{21}H_{16.8}O_{7.9}P$ (**H_3mTPO**•0.9H_2O): C 59.13, H 3.97; found: C 59.54, H 4.40.

[Mg_2(HmTPO)$_2$(μ-H_2O)(H_2O)$_2$]•2DEF (1): $MgBr_2 \cdot 6H_2O$ (44 mg, 0.15 mmol) and H_3mTPO (41 mg, 0.10 mmol) were put in a 5 mL vial and dissolved in DEF/MeOH/H_2O (3:3:1 v/v, 1 mL). The vial was placed in a preheated oven (100 °C) and reacted for 48 h. Colorless crystals were formed, which were washed with DEF/MeOH/H_2O and dried in air. Yield: 30%. Elemental analysis (%) calcd for $C_{52}H_{56}Mg_2N_2O_{20}P_2$ (**1**•H_2O): C 54.81, H 4.95, N 2.46; found: C 54.61, H 4.56, N 2.18.

[Mn_3(mTPO)$_2$(μ-H_2O)(H_2O)$_4$]•2DMF•H_2O (2): $MnCl_2 \cdot 4H_2O$ (30 mg, 0.15 mmol) and H_3mTPO (41 mg, 0.10 mmol) in a 5 mL vial were dissolved in DMF/H_2O (2:1 v/v, 1 mL). The vial was placed in an oven (100 °C) and retained for 48 h. Colorless crystals were precipitated, washed with DMF, and dried in air. Yield: 30%. Elemental analysis (%) calcd for $C_{48}H_{50}Mn_3N_2O_{22}P_2$: C 46.73, H 4.09, N 2.27; found: C 46.37, H 4.26, N 2.47.

Desolvated sample (**2b**): Compound **2** was soaked in MeOH at 40 °C for 24 h. The MeOH exchanged sample (**2a**) was dried in air. The desolvated sample of **2b** was obtained by heating the MeOH-exchange sample at 50 °C under vacuum for 150 min. The absence of water molecules was checked by TGA and Nujol IR. Elemental analysis (%) calcd for $C_{42}H_{30}Mn_3O_{17}P_2$ (**2b**•3H_2O): C 48.81, H 2.93; found: C 48.83, H 3.00. The water molecules in the analytical data were present because water was readsorbed from air during measurement preparations.

Resolvated sample: The activated sample of **2b** was immersed in DMF/H_2O (2:1, v/v) for 24 h to produce the resolvated sample. The identical product was also obtained by soaking the MeOH-exchanged sample in DMF/H_2O.

Crystallographic Structure Determination. X-ray data for **1** were collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated MoKα radiation (λ = 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. For **2**, the diffraction data were measured with synchrotron radiation on a 6B MX-I ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210 ADX program (Ver. 1.92) was used for data collection and HKL2000 (Ver. 0.98.699) was used for cell refinement, reduction, and absorption correction. The structures of **1** and **2** were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program. Guest molecules in **2** 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. For **2**, the contributions of some 742 electrons were removed from the unit-cell contents, and as Z = 8 in this case, this could/might correspond with the removal of solvent such as 2DMF and H_2O [some 92 electrons] per asymmetric unit. All hydrogen atoms except for hydrogens bound to water oxygens were calculated at idealized positions and refined with the riding models. Crystal data of **1**: empirical formula = $C_{52}H_{54}Mg_2N_2O_{19}P_2$, Mr = 1121.53, T = 100 K, monoclinic, space group *C2/c*, a = 33.3495(12) Å, b = 10.5440(3) Å, c = 15.0994(6) Å, β = 103.703(2)°, V = 5158.4(3) Å^3, Z = 4, D_{calc} = 1.444 g cm^{-3}, μ = 0.189 mm^{-1}, 22195 reflections collected, 6418 unique (R_{int} = 0.0699), $R1$ = 0.0686, $wR2$ = 0.1657 [$I > 2\sigma(I)$]. **2**(squeezed): empirical formula = $C_{48}H_{50}Mn_3N_2O_{22}P_2$, Mr = 1233.66, T = 100 K, monoclinic, space group *C2/c*, a = 40.229(8) Å, b = 21.504(4) Å, c = 15.251(3) Å, β = 110.11(3)°, V = 12389(4) Å^3, Z = 8, D_{calc} = 1.323 g cm^{-3}, μ = 0.724 mm^{-1}, 43489 reflections collected, 11919 unique (R_{int} = 0.0570), $R1$ = 0.0617, $wR2$ = 0.1783 [$I > 2\sigma(I)$].

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Sogang University. Infrared spectra were obtained from KBr pellets with a Bomen MB-104 spectrometer. Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min in a N_2 flow using a Scinco TGA N-1000 instrument. PXRD data were recorded using Cu Kα (λ = 1.5406 Å) on a Rigaku Ultima III diffractometer with a scan speed of 2°/min and a step size of 0.01°.

Gas Sorption Measurements. Gas sorption isotherms of **2'** were measured using a BEL Belsorp mini II gas adsorption instrument up to 1 atm of gas pressure. The highly pure N_2 (99.999%), H_2 (99.999%), CH_4 (99.999 %), and CO_2 (99.999%) were used in the sorption experiments. N_2 and H_2 gas isotherms were measured at 77 K and CO_2 was measured at 195 K. The additional uptake isotherms for all the gases were obtained at 273 K. The CO_2 adsorption at 298 K was recorded to calculate heat of adsorption.

Table S1. Results of a BVS calculation for **1**.

Element1	Element2	Bond Length	Valence
Mg 2	O -2	2.024	0.409
Mg 2	O -2	2.042	0.389
Mg 2	O -2	2.080	0.351
Mg 2	O -2	2.091	0.341
Mg 2	O -2	2.096	0.336
Mg 2	O -2	2.144	0.296
		Sum	2.123

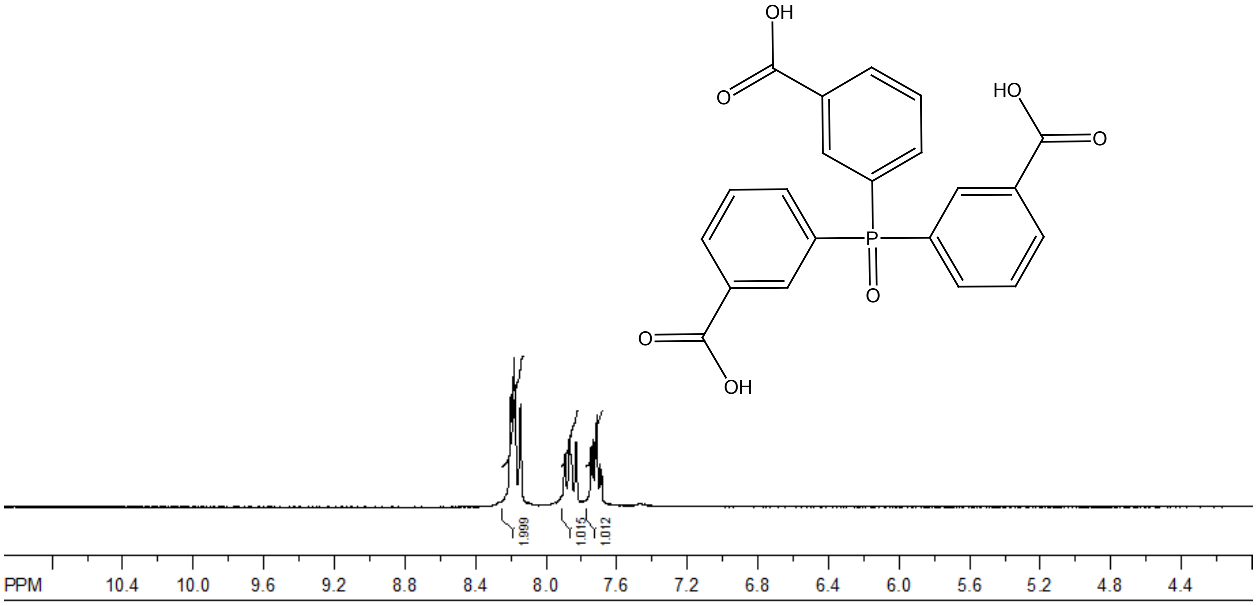


Fig. S1. ^{1}H NMR (DMSO-d_6) for H_3mTPO.

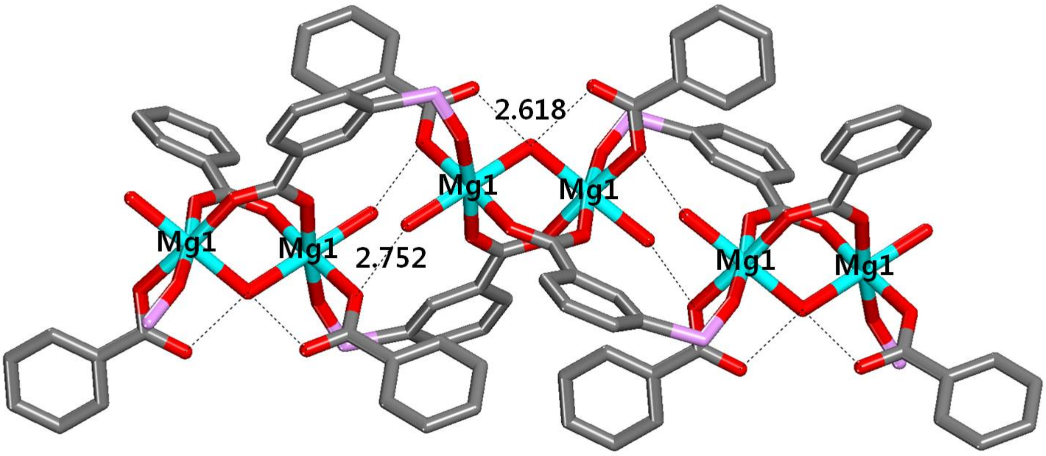


Fig. S2. Molecular structure of **1** showing the SBUs containing Mg atoms bridged by carboxylates and water molecules. The dotted lines represent hydrogen bonds.

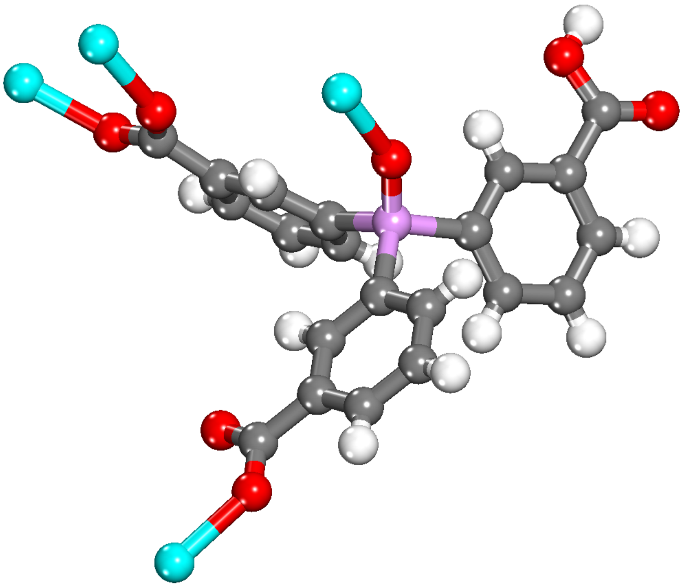


Fig. S3. The binding mode of HmTPO ligand to Mg atoms for **1**. Note that hydrogen atom of one carboxylic acid is retained.

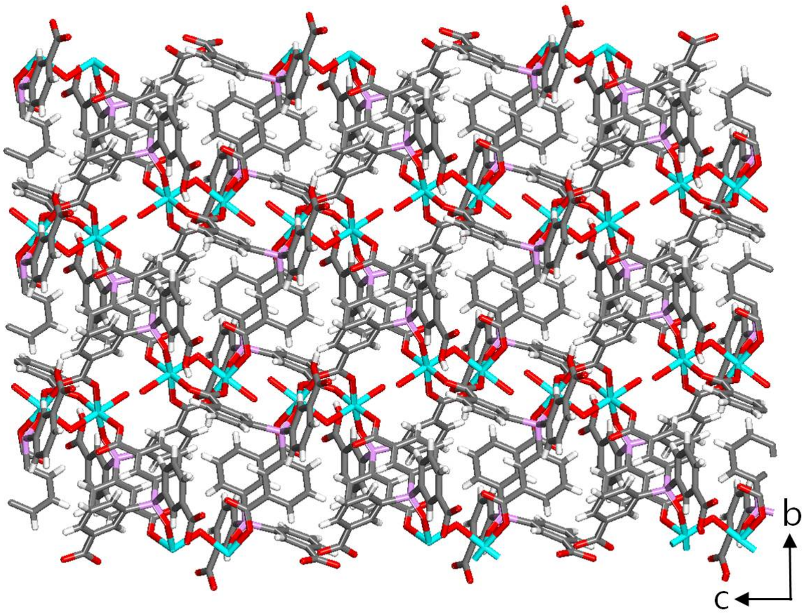


Fig. S4. 2D extended structure of **1** in the *bc* plane.

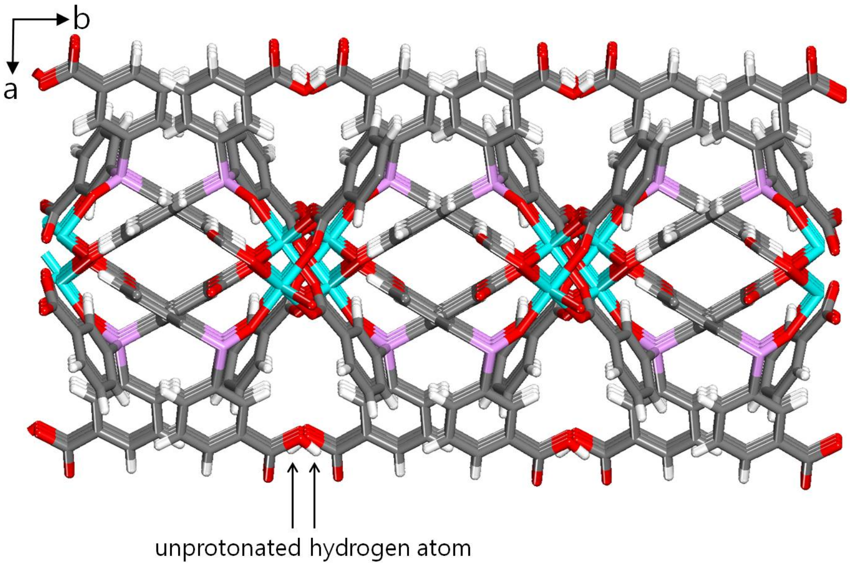


Fig. S5. 2D extended structure of **1** in the *ab* plane showing unprotonated hydrogen atoms.

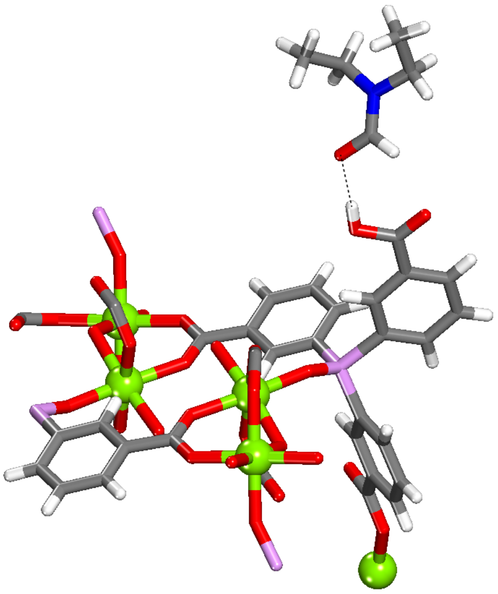


Fig. S6. Hydrogen bond (O---O = 2.562(5) Å) between unprotonated hydrogen atom of HmTPO and oxygen atom of DEF for **1**.

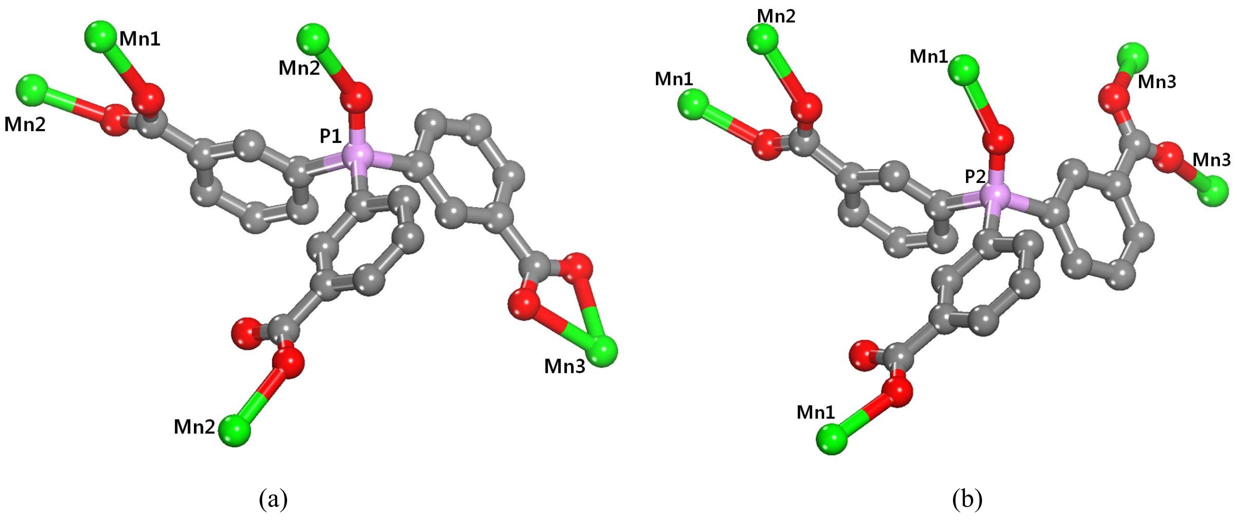


Fig. S7. The binding moded of $mTPO^{3-}$ ligand to Mn atoms for **2**.

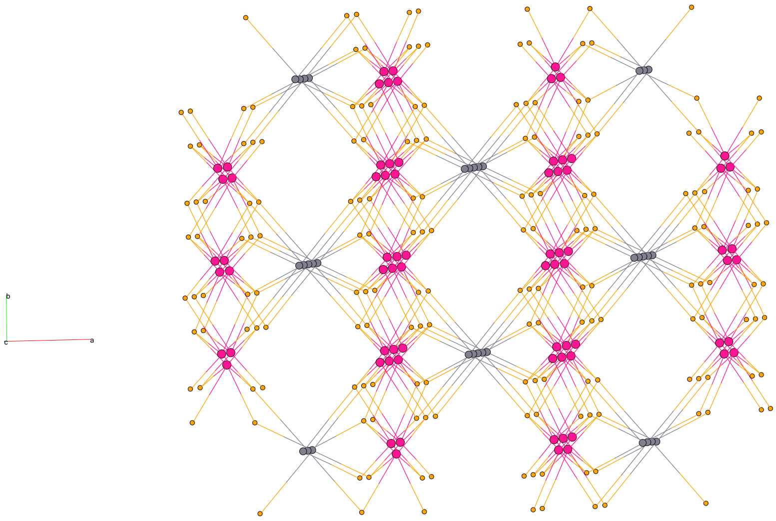


Fig. S8. Simplified net of **2**.

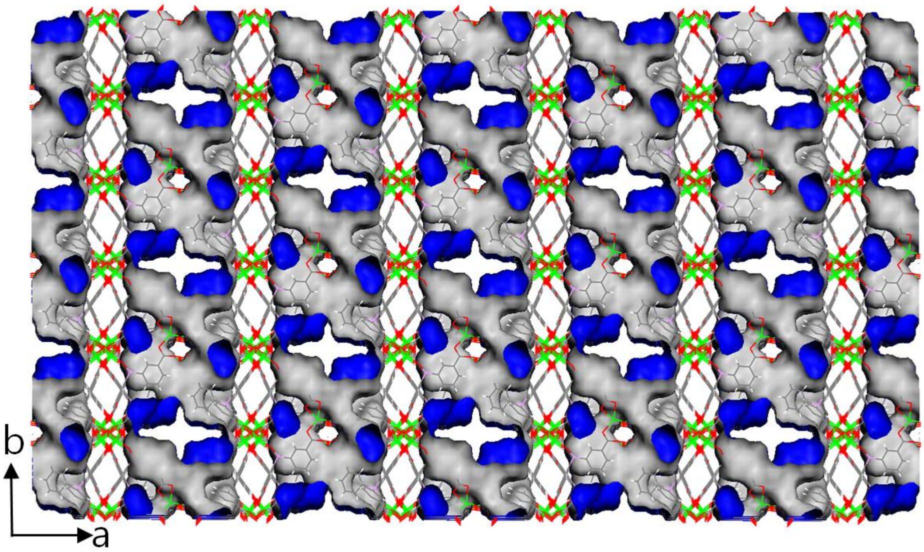


Fig. S9. Connolly surface diagram with 1D channels running down the c-axis.

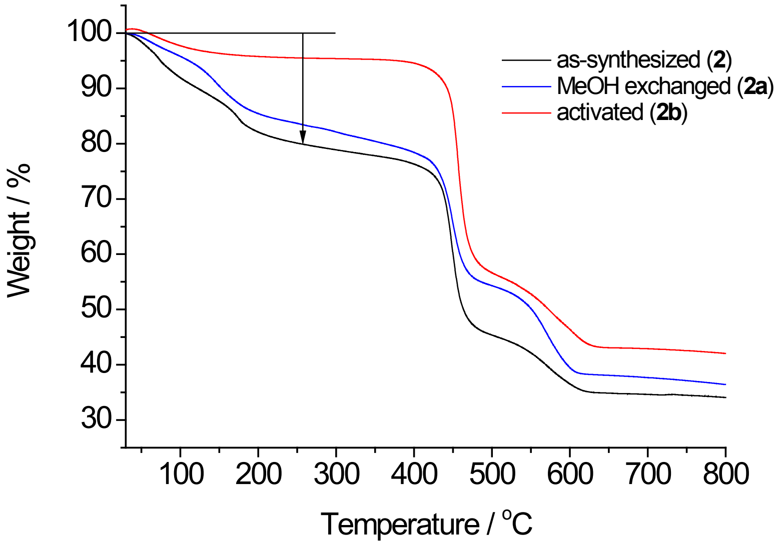


Fig. S10. TGA data for the as-synthesized (**2**), MeOH-exchanged (**2a**), and activated (**2b**) samples

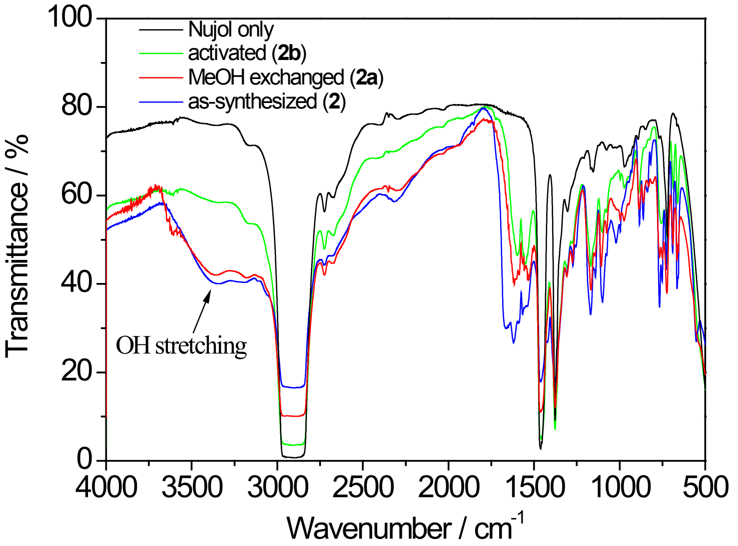


Fig. S11. Nujol IR data of as-synthesized, MeOH-exchanged, and activated samples.

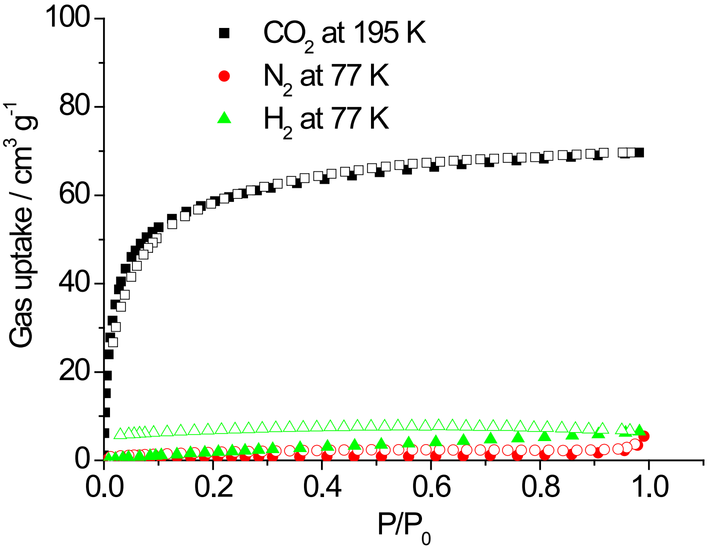
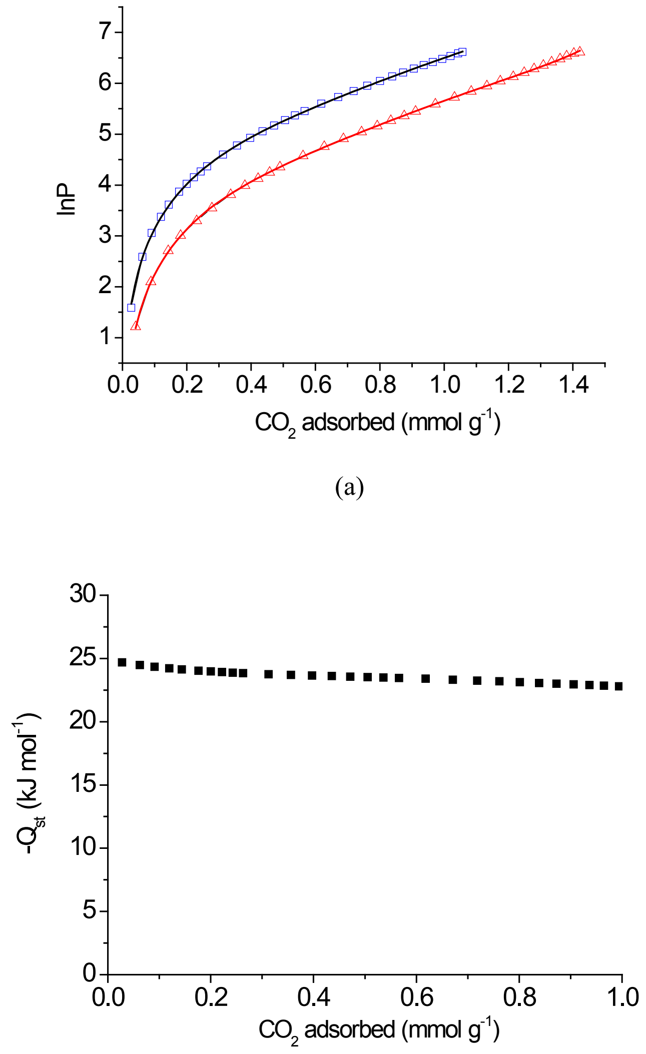


Fig. S12. N_2 ,H_2, and CO_2 sorption isotherms of desolvated **2b** at the indicated temperatures.



(b)

Fig. S13. (a) CO_2 isotherms at 273 K and 298 K, and virial equation fits for **2b**. (b) Plot of the isosteric heat of CO_2 adsorption for **2b**.

The CO_2 adsorption data at two temperatures were fitted using the virial-type equation with a_i and b_i parameters,

$$\ln P = \ln N + (1/T)\Sigma_{i=0}^{r}(a^{i}N^{i}) + \Sigma_{i=0}^{s}(b^{i}N^{i}) \qquad (1)$$

where P is the pressure in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and r and s are the number of coefficients required to express the isotherms. The fitted coefficients a_0 through a_r were then applied to estimate the isosteric heat of adsorption using the following expression

$$Q_{st} = -R\Sigma_{i=0}^{r}(a^{i}N^{i}) \qquad (2)$$

where Qst is the isosteric heat of adsorption depending on the coverage and R is the universal gas constant.

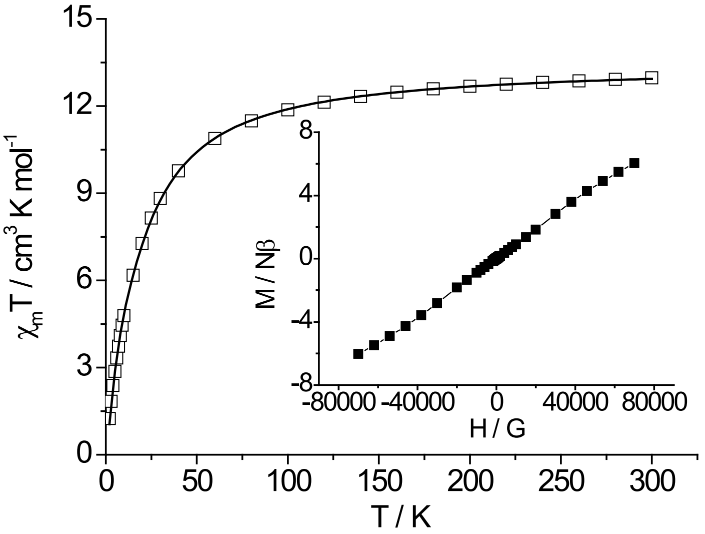


Fig. S14. Plot of χmT versus T of **2** at 1000 G. The inset shows the field dependence of the magnetization at 2 K.