Supporting Information

Two isostructural amine-functionalized 3D self-penetrating microporous MOFs exhibiting high sorption selectivity for CO_2

Bo Liu, Ruili Zhao, Guoping Yang, Lei Hou, Yao-Yu Wang* and Qi-Zhen Shi

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, College of Chemistry & Materials Science, Northwest University. Xi'an 710069 (P. R. China).
Email: wyaoyu@nwu.edu.cn, Tel: 86 29 88302604

Materials and Measurements. All reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained in KBr discs on a Nicolet Avatar 360 FTIR spectrometer in the 400−4000 cm^{-1} region. Elemental analyses (C, H and N) were performed with a Perkin Elmer 2400C Elemental Analyzer. Thermalgravimetric analyses (TGA) were carried out in nitrogen stream using a Netzsch TG209F3 equipment at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å), and the Variable-temperature PXRD patterns were recorded with a Rigaku D/MAX-3C diffractometer. All the gas sorption isotherms were measured by using a ASAP 2020M adsorption equipment.

Synthesis of $[Zn(atz)(bdc)_{0.5}]$ (1)

A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.1 mmol), H_2bdc (0.1 mmol) and Hatz (0.1 mmol) in DMF (2mL) and water (8 mL) was placed in a Teflon-lined stainless steel vessel (25 mL) and heated at 150 °C for 72 h, and then cooled to room temperature at a rate of 5 °C min^{-1}. The resulting colorless block crystals of **1** were isolated by washing with DMF/H_2O (1:4) and dried in air. The yield was 0.2038 g (88.4%, based on Hatz). Anal. Calcd for $C_6H_5N_4O_2Zn$: C, 31.24; H, 2.17; N, 24.29. Found: C, 31.23; H, 2.23; N, 24.17.

Synthesis of $[Co(atz)(bdc)_{0.5}]$ (2)

The procedure was similar to the preparation of **1**, except that the $Zn(NO_3)_2{\cdot}6H_2O$ was replaced by $Co(NO_3)_2{\cdot}6H_2O$. The resulting purple block crystals of **2** were isolated by washing with DMF/H_2O (1:4) and dried in air. The yield was 0.1831 g (81.7%, based on Hatz). Anal. Calcd for $C_6H_5N_4O_2Co$: C, 31.16; H, 2.25; N, 25.01. Found: C, 31.11; H, 2.31; N, 24.95.

Crystallography. Diffraction data were collected with a Mo Kα radiation (λ = 0.71073 Å) on a Bruker-AXS SMART CCD area detector diffractometer. Absorption corrections were carried out utilizing SADABS routine. The structure was solved by the direct methods and refined by full matrix least squares refinements based on F^2. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. A PLATON calculation that showed **1** and **2** had an effective solvent accessible volume of 27.5% and 28.2%, respectively. Though there were weak peaks with residual electron densities inside the channel, attempts to identify and further refine these peaks failed. The contribution of the disordered solvent molecules was subtracted from the reflection data by the SQUEEZE method as implemented in PLATON program. Crystal data as well as details of data collection and refinements for both **1** and **2** are summarized in Table S1.

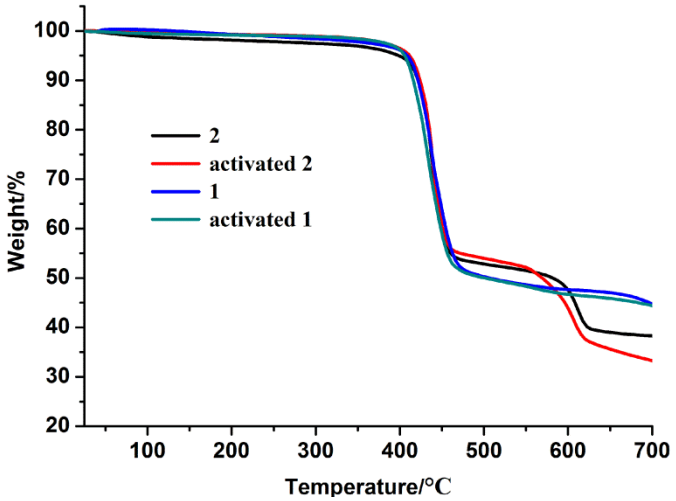

Fig. S1 TGA curves for **1, 2** and activated samples for both **1** and **2** measured under nitrogen.

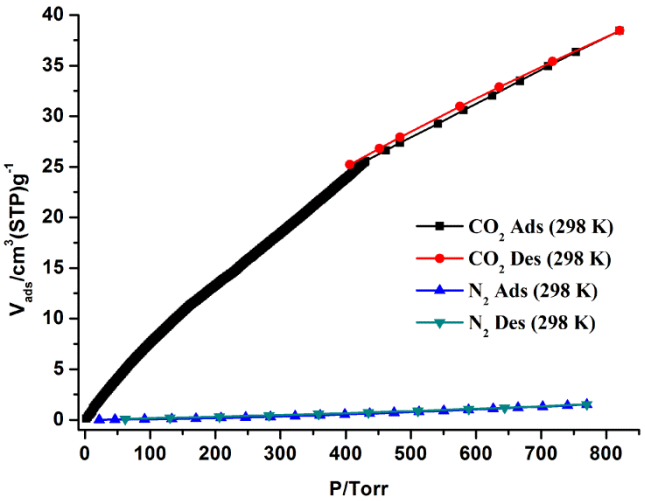

Fig. S2 N_2 and CO_2 gas sorption isotherms of **2** measured at 298 K and 1 atm.

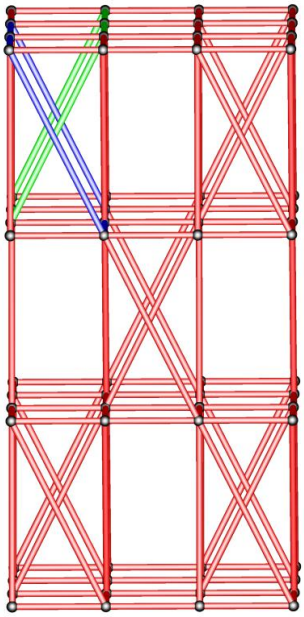

Fig. S3 View of the 6-connected network of **1** along the *b*-axis.

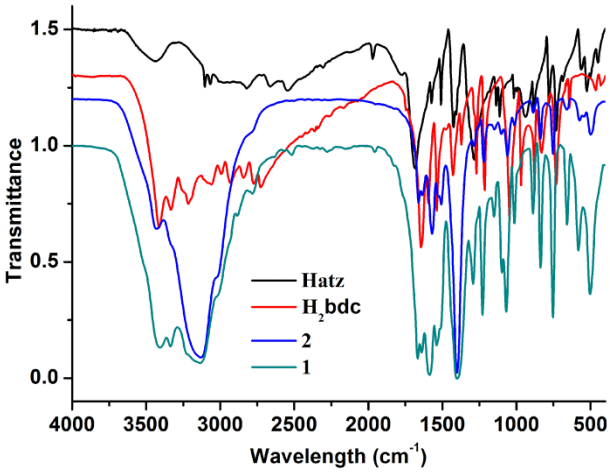

Fig. S4 IR spectra of **1**, **2**, H_2btc and Hatz ligands.

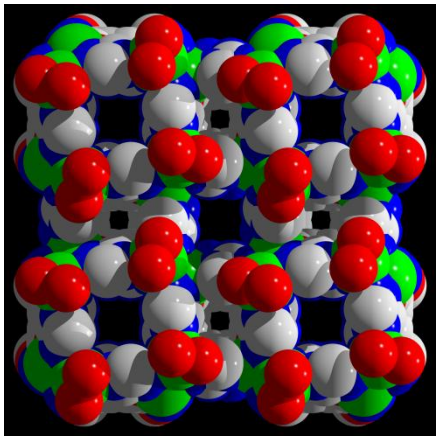

Fig. S5 The 3D framework in space filling mode along the *c*-axis.

Table S1. Crystal data and structure refinements for **1** and **2**.

Complex No.	**1**	**2**
Empirical formula	$C_6H_5N_4O_2Zn$	$C_6H_5N_4O_2Co$
Formula mass	230.51	224.07
Temperature [K]	296(2)	296(2)
Crystal system	Tetragonal	Tetragonal
Space group	P4/nnc	P4/nnc
a [Å]	12.6672(6)	12.5845(5)
b [Å]	12.6672(6)	12.5845(5)
c [Å]	25.4399(18)	25.4464(14)
β [deg]	90	90
V [Å^3]	4082.0(4)	4029.9(3)
Z	16	16
D_{calcd}.[g·cm^{-3}]	1.500	1.477
μ [mm^{-1}]	2.381	1.678
GOF on F^2	1.007	1.115
reflns collected/ unique	20221/2051	18513/1784
R_{int}	0.0553	0.0465
Final R[a]	R_1 = 0.0414	R_1 = 0.0579
indices [I>2 σ(I)]	wR_2 = 0.1153	wR_2 = 0.1564

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$