Facile Synthesis of an Ultramicroporous MOF Tubular

Membrane with Selectivity towards CO_2

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Supporting Information

1.- Synthesis and characterization of SIM-1

Synthesis of SIM-1 powder

In a typical synthesis a solid mixture of 0.71 g (2.73 mmol) of $Zn(NO_3)_2 \cdot 4H_2O$ and 1.20 g (10.94 mmol) of 4-methyl-5-imidazolecarboxaldehyde is dissolved in 20 ml of DMF. Afterwards the solution is poured into a vial and heated in an oven at 358 K for 72 h. After the synthesis, the resulting powder is washed 3 times with DMF then with EtOH. The samples are dried at 358K for 3h and then overnight under vacuum at room temperature.

Characterization of SIM-1 powder
- Elemental analysis

Elemental analysis was carried out by Inductively Coupled Plasma ICP (Activa Horiba) after dissolution of the samples.

Elem. anal. calcd for $[C_{10}H_{10}N_4O_2Zn]$: C, 42.35; H, 3.55; N, 19.76; Zn, 23.06, found C, 42.29; H, 3.61; N, 19.71; Zn, 23.01.

- Liquid ^{1}H NMR

The ^{1}H NMR spectrum was recorded on a Brücker 250 MHz spectrometer at room temperature.

In a NMR tube, around 3mg of **SIM-1** were dissolved with a minimum of DCl/D_2O solution and then diluted in DMSO-d6 (c.a. 400µL). ^{1}H NMR δ (250 MHz, DMSO-d6, 294K) = 2.51 (s, 3H, CH_3), 8.81 (s, 1H, CH), 9.75 (s, 1H, CHO) ppm. Pics at 4.85 and 2.50 ppm correspond respectively to water (H_2O) and DMSO from the NMR solvent. No signal from DMF can be detected by NMR, thus showing the efficiency of the washing procedure.
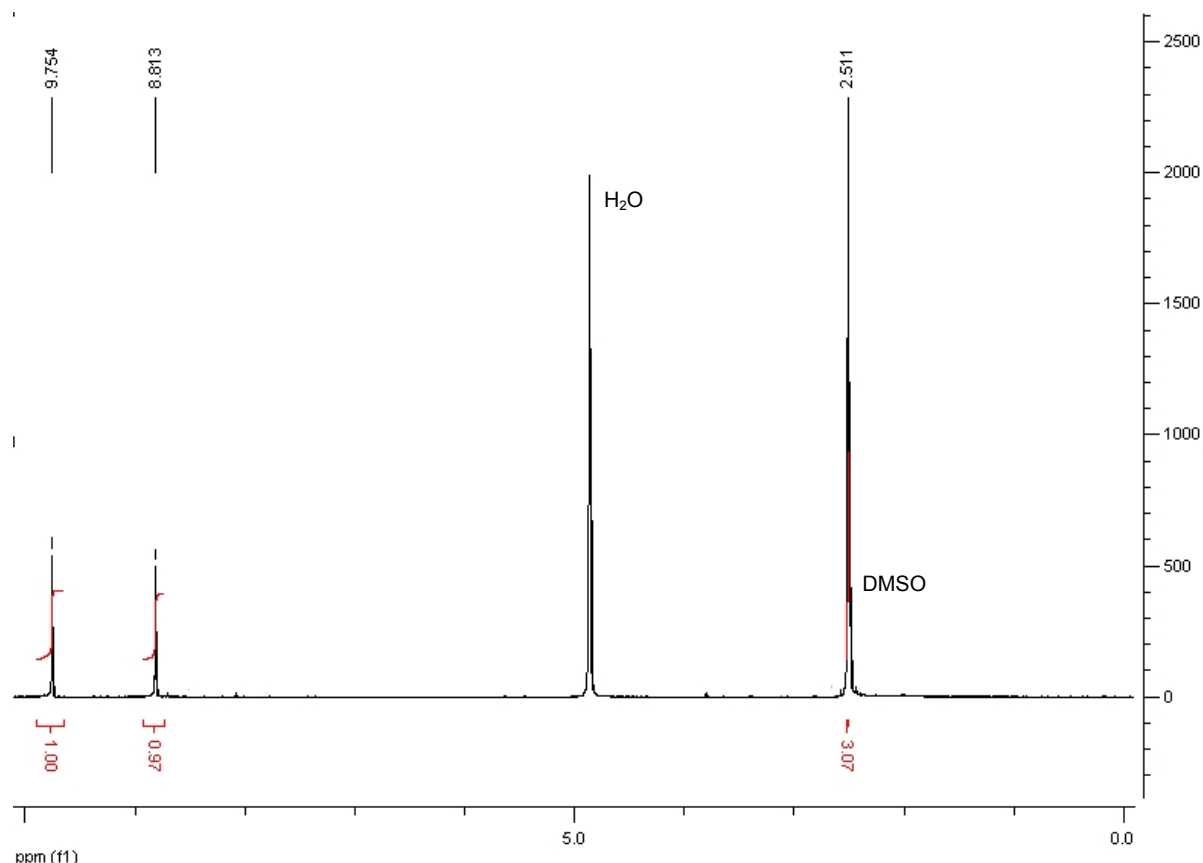

Figure S1: ^{1}H NMR of SIM-1.

2.- X-ray diffraction (XRD)

For indexing, high-quality powder diffraction data was obtained at room temperature employing a Panalytical X'Pert Pro diffractometer with Debye-Scherrer geometry. The pattern was scanned in the range $2\theta = 5\text{-}100°$ with a step length of $0.008°(2\theta)$ and a counting time of 2000 s per step. The X'Pert Pro system is equipped with a hybrid monochromator (combination of a parabolic multilayer mirror and a 2-crystal Ge(220) monochromator) producing a monochromatic Cu Kα_1 radiation ($\lambda = 1.5406$ Å), and a position sensitive detector (X'Celerator). Pattern indexing was performed with the program DICVOL91 [1] he Accelrys software suite, Materials Studio 5.0.
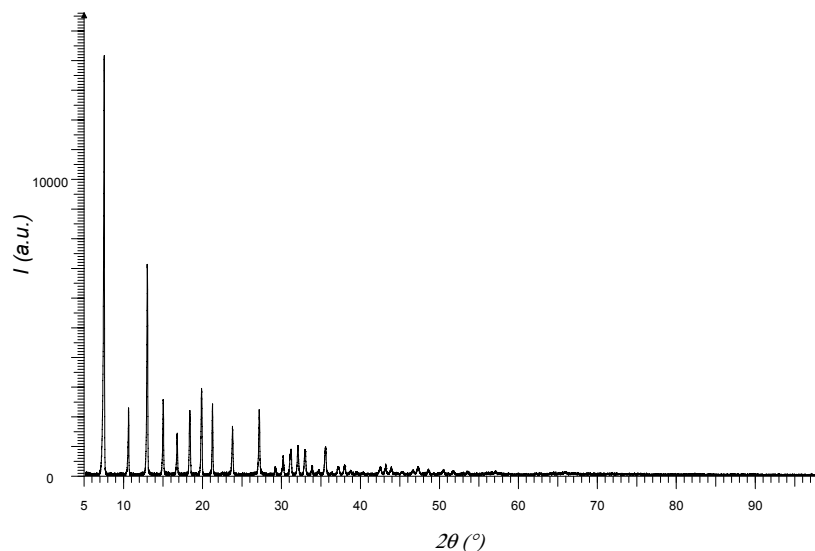

Figure S2: XRD pattern of SIM-1 powder.

For phase identification, XRD measurements were carried out at room temperature by powder X-Ray diffraction using a Bruker D5005 Diffractometer equipped with a secondary graphite monochromator (Cu Kα radiation, $\lambda = 1.5418$ Å) and a scintillation counter. The pattern was scanned in the range $2\theta = 5\text{-}50°$ with a step length of $0.02°(2\theta)$ and a counting time of 756 s per step.

[1] A. Boultif, D.J. Louër, *Appl. Crystallogr.* **1991**, *24*, 987.

3.- Structural analysis

The surface and cross-section morphology of the as-synthesized supported samples were examined by scanning electron microscopy (SEM) using a JSM 5800LV (JEOL), coupled to an analysis system by energy dispersion spectrometry (EDS) with a diode Si-Li (PGT). The tension range is 0.3-30 kV and the effective resolution is 0.5 nm at 30kV.

4.- TGA

The thermogravimetric analysis (TGA) was measured on a SETARAM (Setsys Evolution)TGA-DSC instrument, coupled with a mass spectrometer PFEIFFER (Omnistar) . For this purpose, ca.10 mg of sample were filled into alumina crucibles and heated in a flow of Ar (50 ml·min^{-1}) with a ramp of 5 K·min^{-1} from room temperature up to 973 K.
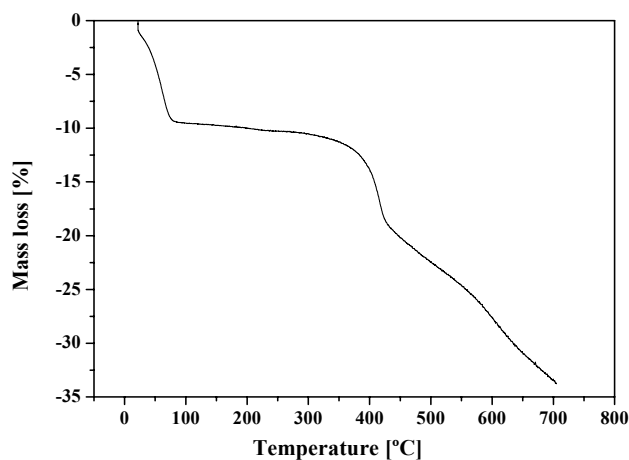

Figure S3: TG curve of SIM-1 powder.

5.- Gas sorption analysis

The N$_2$ adsorption/desorption isotherms at 77 K were measured on a BELSORP-MAX. The sample was outgassed under vacuum ($\sim 10^{-4}$ mbar) at 473K for 12 h before start of the measurements. The apparent specific surface area obtained by applying the BET method is 471 m^2·g^{-1}.
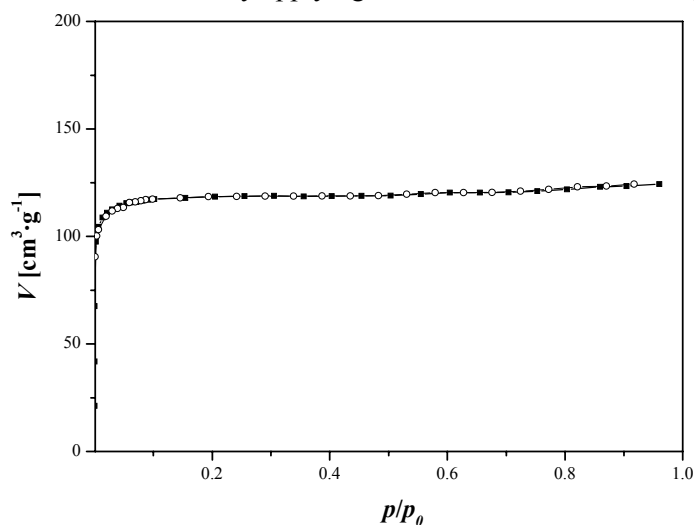

Figure S4: N$_2$ isotherm (77 K) of SIM-1. Close squares, adsorption. Open circles, desorption.

The CO$_2$ and N$_2$ adsorption/desorption isotherms at 303 K were measured on a BELSORP-HP. The sample was outgassed under vacuum ($\sim 10^{-4}$ mbar) at 473K for 12 h before start of the measurements.
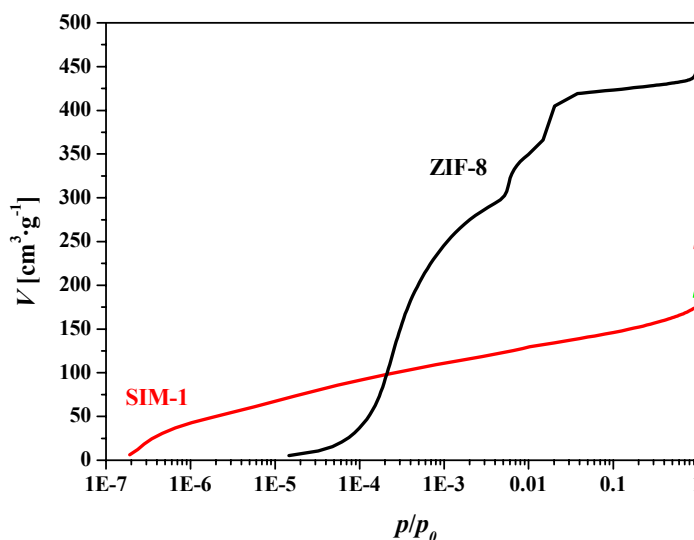
Figure S5: N_2 isotherm (77 K) of SIM-1 and ZIF-8, represented as linear-log diagrams.
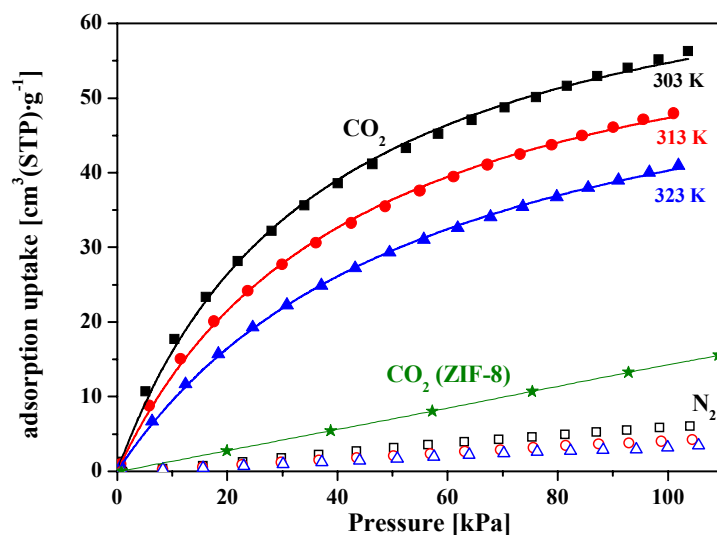

Figure S6: CO_2 and N_2 adsorption isotherms of SIM-1 at 303-323 K compared with ZIF-8 (CO_2 at 303 K). Black symbols, 303 K; red symbols, 313 K and blue symbols, 323 K.

The adsorption isotherm for ZIF-8 corresponds to previous reported results from other groups in which a linear profile is observed at low pressure. [2,3]

[2] A. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, R. R. Willis, *J. Am. Chem. Soc.* **2009**, *131*, 18198.
[3] S. Reyes, J. Santiesteban, Z. Ni, C. Paur, P. Kortunov, J. Zengel, H. Deckman, US Patent US 2009/0214407, **2009**.

For single gas permeation, the membranes were mounted in dead-end configuration module using flat gaskets pressed onto the enameled tube ending cross-section. Permeances were measured in dead-end configuration varying transmembrane pressure from 0.5 to 3 bar, and temperatures from room temperature to 120 ºC to evaluate the presence of defects or cracks.

Table S7: N_2 permeance of several membranes at 298 K and ΔP=100kPa

	N_2 permeance [mol·s^{-1}·m^{-2}·Pa^{-1}]	
	before EtOH washing	after EtOH washing
M1	0	$1.68 \cdot 10^{-8}$
M2	0	$2.12 \cdot 10^{-8}$
M3	0	$2.56 \cdot 10^{-8}$

7.- Binary permeation

For the mixed gas measurements feed was constant with a total volumetric flow rate of 300 ml min^{-1} with a composition 10 vol.% of CO_2 and 87 vol.% of N_2, with a 3 vol.% of water. The pressure in the feed was constant at 4 bar, and the pressure difference with the permeate side was 40 mbar. The measurements were made at room temperature (324 K).