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(NO₃)₂·4H₂O 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 [C₁₀H₁₀N₄O₂Zn]: 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 ¹H NMR
The ¹H 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/D₂O solution and then diluted in DMSO-d₆ (c.a. 400μL). ¹H NMR δ (250 MHz, DMSO-d₆, 294K) = 2.51 (s, 3H, CH₃), 8.81 (s, 1H, CH), 9.75 (s, 1H, CHO) ppm. Pics at 4.85 and 2.50 ppm correspond respectively to water (H₂O) 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: ¹H 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 $2\theta = 5-100^\circ$ 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.](image)

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 $2\theta = 5-50^\circ$ with a step length of 0.02°($2\theta$) and a counting time of 756 s per step.


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.](image)

5.- Gas sorption analysis
The N₂ adsorption/desorption isotherms at 77 K were measured on a BELSORP-MAX. The sample was outgassed under vacuum (~ 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 m²·g⁻¹.

![Figure S4: N₂ isotherm (77 K) of SIM-1. Close squares, adsorption. Open circles, desorption.](image)

The CO₂ and N₂ adsorption/desorption isotherms at 303 K were measured on a BELSORP-HP. The sample was outgassed under vacuum (~ 10⁻⁷ 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]


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 °C to evaluate the presence of defects or cracks.

**Table S7:** N₂ permeance of several membranes at 298 K and ΔP=100kPa

<table>
<thead>
<tr>
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<th>N₂ permeance [mol·s⁻¹·m⁻²·Pa⁻¹]</th>
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<tbody>
<tr>
<td></td>
<td>before EtOH washing</td>
</tr>
<tr>
<td>M1</td>
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</tr>
<tr>
<td>M2</td>
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<td>M3</td>
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**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 CO₂ and 87 vol.% of N₂, 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).