SUPPORTING INFORMATION

ZIF-8 modified with 2-undecylimidazolate as filler for mixed matrix membranes for CO_2 separation

Marta Pérez-Miana[1,2], José Miguel Luque-Alled[1,2], Mohamed Yahia[1,2,3], Álvaro Mayoral[1], Joaquín Coronas[1,2*]

[1]Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza, 50018, Spain

[2]Chemical and Environmental Engineering Department, Universidad de Zaragoza, Zaragoza, 50018, Spain

[3]Chemistry Department, Faculty of Science, Helwan University, Cairo, 11795, Egypt

*Corresponding author: Joaquín Coronas (coronas@unizar.es)

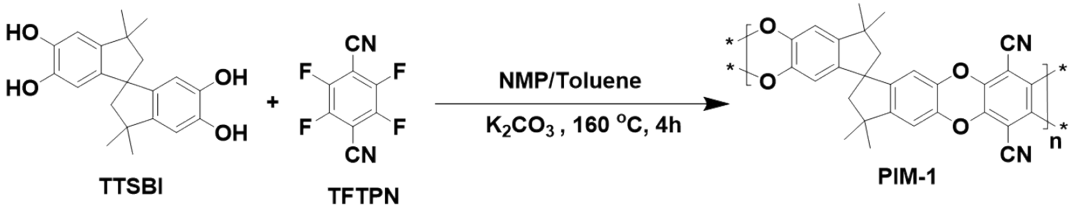

Figure S1. PIM-1 synthesizing procedure.

Characterization techniques

Thermogravimetry analyses (TGA) were carried out using Mettler Toledo TGA/STDA 851e. Samples were placed in 70 μL alumina pans and were heated under airflow from 35 to 700 °C at a heating rate of 10 °C min^{-1}.

X-ray diffraction (XRD) was performed in a Panalytical Empyrean equipment with CuKα radiation (λ = 0.154 nm), over the 2θ angle range of 5 - 40 ° at a scan rate of 0.03 ° s^{-1}.

Fourier transform infrared spectroscopy (FTIR-ATR) was carried out with a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector and a Golden Gate diamond ATR accessory. The spectra were recorded by averaging 16 scans in the wavenumber range of 4000–600 cm^{-1} at a resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM) images of the MOFs and membranes were obtained using an Inspect F50 model scanning electron microscope (FEI) operated at 10 kV and coating with Pd. Cross-sections of membranes were prepared by cutting after immersion in liquid N_2. The microscope is equipped with an energy-dispersive X-ray detector used for EDS analysis.

The N_2 adsorption–desorption isotherms were obtained using Micromeritics Tristar 3000 at 77 K. A previous degasification was performed before these measurements at 200 °C using a heating rate of 10 °C min^{-1} under vacuum during 8 h. Brunauer-Emmett-Teller (BET) analysis was used to calculate specific surface area of porous materials.

Solid-state NMR spectra for sample after SALE treatment were acquired with a Bruker Avance III 400 MHz Wide Bore spectrometer. Approximately 100 mg of product was packed in a 4 mm zirconium rotor and sealed with a Kel-F cap. The ^{13}C CP spectra were acquired with a MAS rate of 10 kHz, a ramp-CP contact time of 3 ms and a 7 s recycle delay.

Spherical aberration corrected (Cs-corrected) Scanning Transmission Electron Microscopy (STEM) coupled with an annular dark field detector (ADF) was used to gain information on the particle size, morphology and structure of the MOFs. Cs-corrected STEM experiments were carried out in a FEI Titan XFEG operated at 300 kV, fitted with a spherical aberration corrector for the electron probe. Prior experiments, the aberrations were minimized using a gold standard sample, assuring a spatial resolution of 0.8 Å. All data was collected using a Fischione dark field detector (30-180 mrad). The samples were prepared by dispersing the powder in ethanol absolute, then, few drops of the suspension were placed onto holey carbon copper grid and letting them to dry.

PIM-1 molecular weight (Mw) distributions were evaluated using Gel Permeation Chromatography (GPC) technique in conjunction with Multi Angle Light Scattering detection (MALS). The GPC-MALS setup comprised a Waters 2695 pump equipped with two in-line GPC columns (Phenogel linear (2) 5 μm, 300 x 8 mm from Phenomenex). Detection

was accomplished through a tandem of detectors, including a MALS detector (miniDAWN Treos) and a differential refractive index detector (Optilab Rex), both supplied by Wyatt Technology. The analysis was conducted at 35 °C, and the polymer was eluted using chloroform at a flow rate of 1.0 mL/min.

Water contact angle (WCA) was measured using a Krüss Drop Shape Analyzer 10 MK2 at room temperature and measuring in at least 6 areas of each membrane, with a volume drop of 4 μL.

Elemental analysis was carried out using a Perkin Elmer Series II 2400 CHNS/O Analyzer. It was measured using the CHNS method without optimizing the oxygen input; that is, without providing extra seconds of oxygen flow for enhanced combustion. Weighing was conducted at room temperature with exposure to air until it was encapsulated in tin capsules. The microbalance used is the Provectus 6500, also from Perkin Elmer, and it is connected to the analyzer.

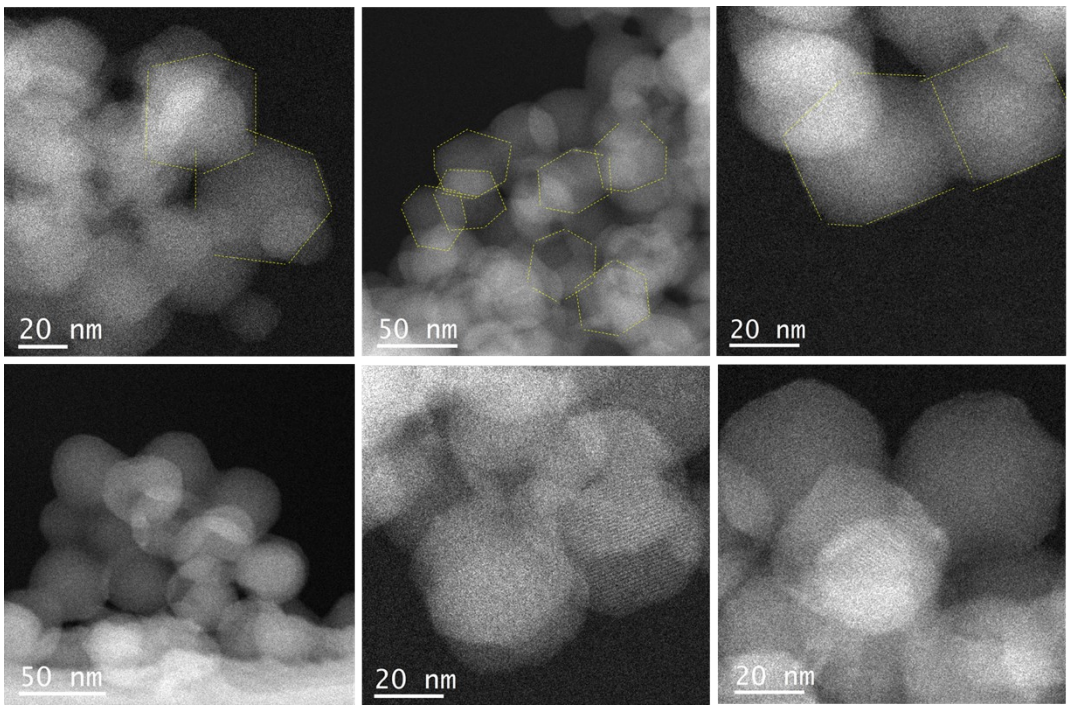

Figure S2. Cs-corrected STEM-ADF micrographs of ZIF-8–umIm from SALE at different magnifications, which evidence the faceted morphology of many nanoparticles. On the top row some of these facets are indicated by dashed yellow lines. While in the bottom one, we have omitted them for a clear visualization.

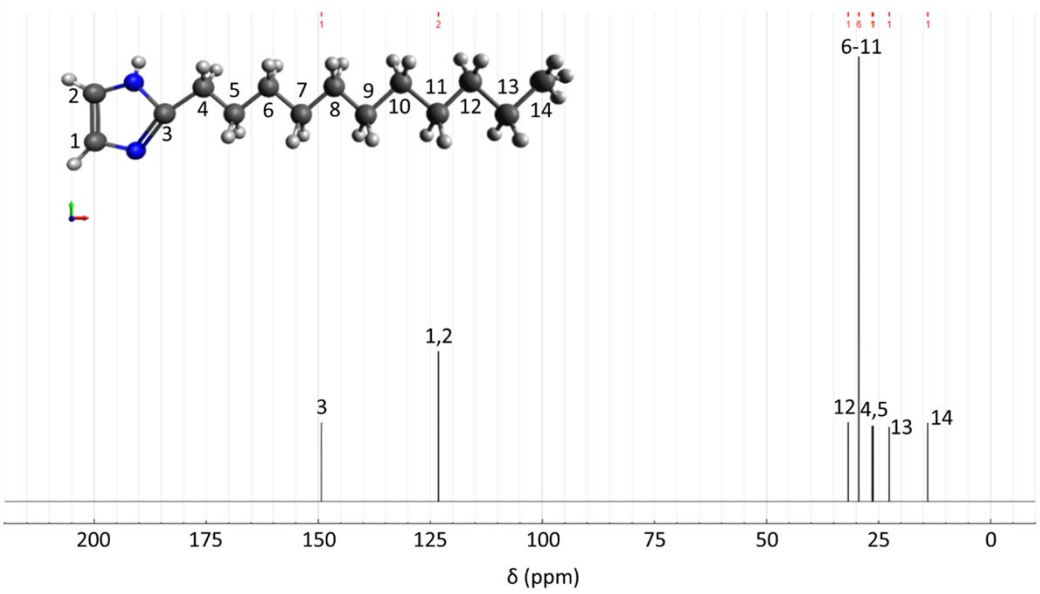

Figure S3. Simulated ^{13}C NMR spectra of umIm.

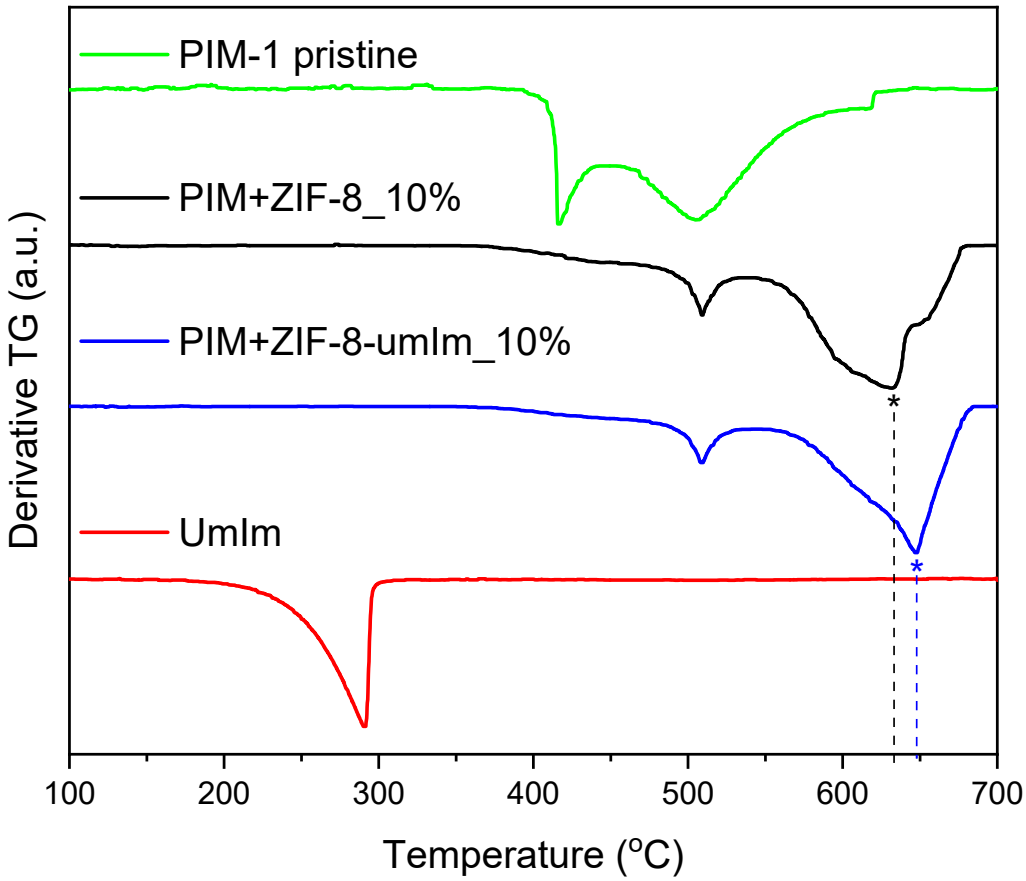

Figure S4. Derivative curves from TGA data of membranes of PIM-1 pristine (green), PIM with ZIF-8 (black), with ZIF-8-umIm (blue) and ligand umIm (red). Temperatures indicated with an asterisk (631.7 and 647.3 °C for ZIF-8 and ZIF-8-umIm, respectively) indicates thermal stability related to filler.

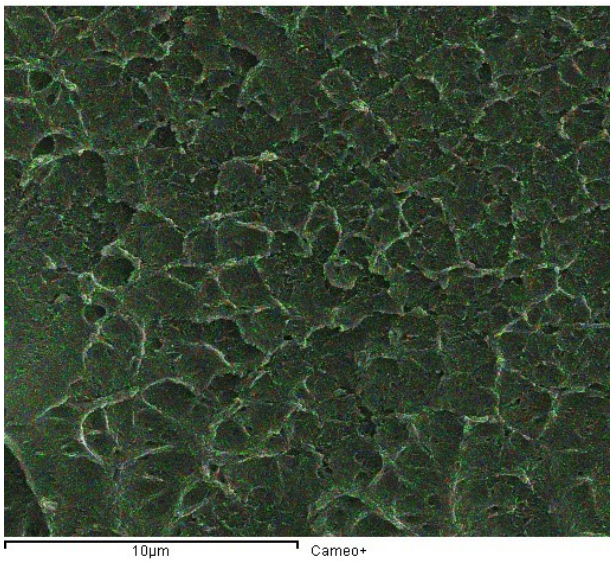

Figure S5. EDS mapping image with Zn (red), O (blue) and C (green).

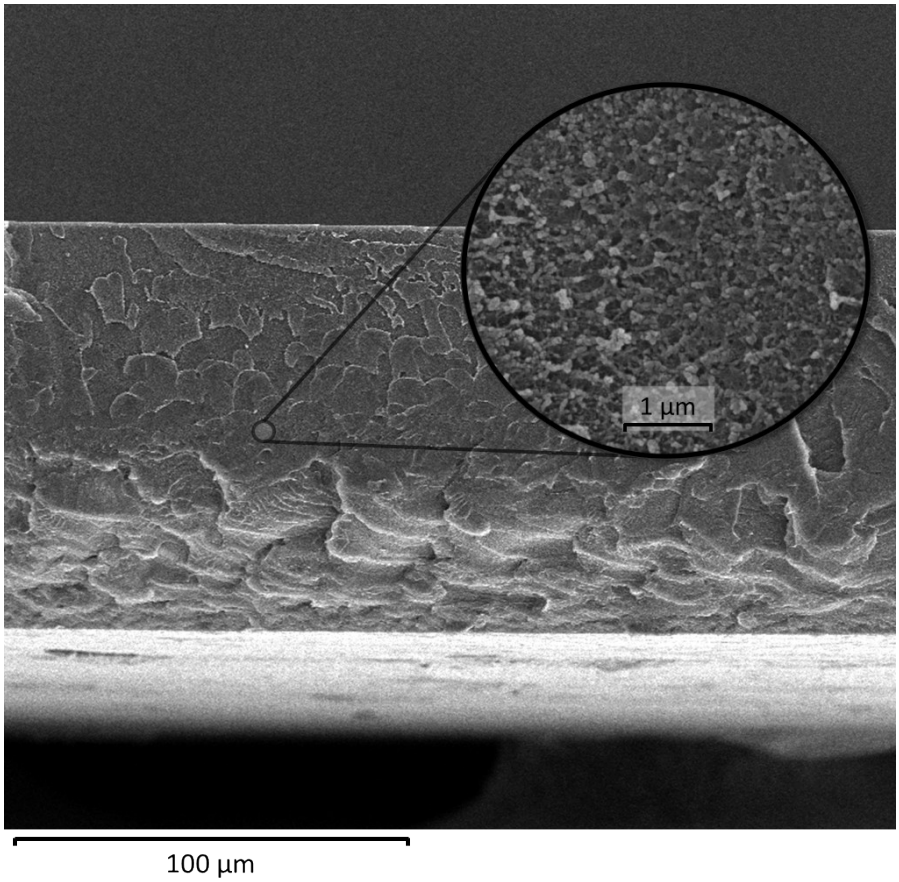

Figure S6. Cross-section image of a pristine PIM-1 membrane with a zoomed-up area.

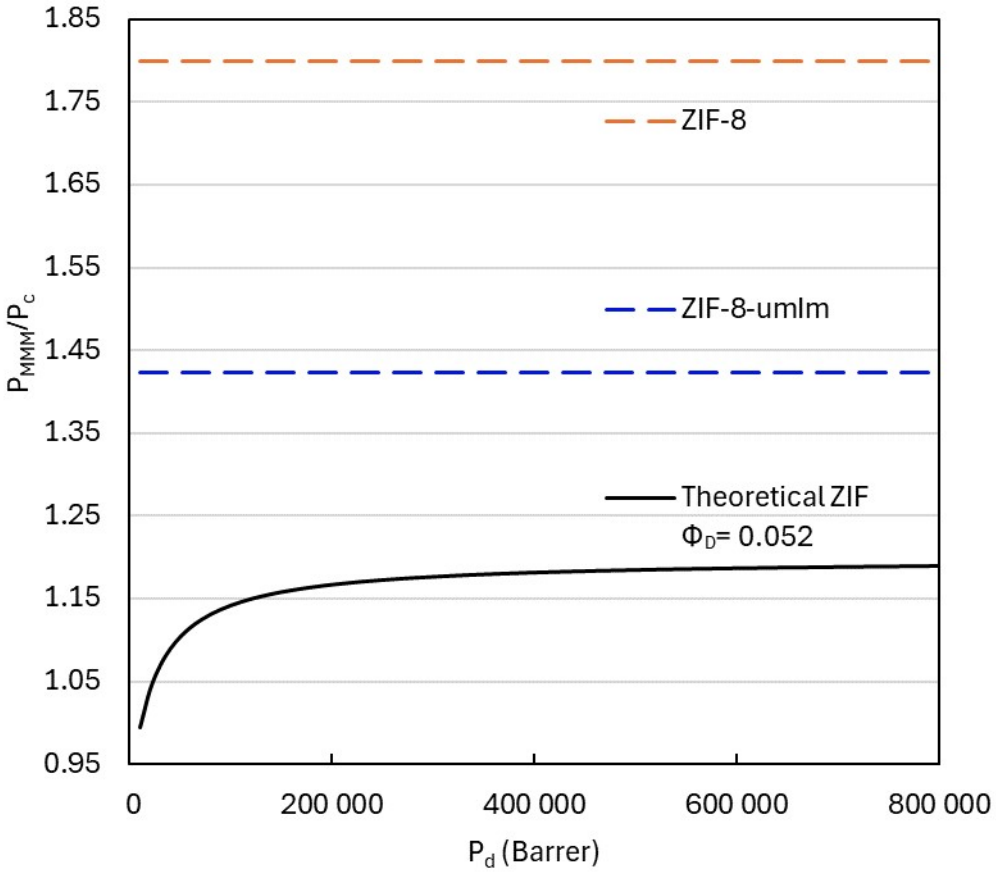

Figure S7. Maxwell model prediction of P_{MMM}/P_c vs. filler permeability (P_d) for a fraction volume (Φ_D) = 0.052 (black line) compared to experimental P_{MMM}/P_c values for MMMs with 5 wt.% of ZIF-8 (orange) and ZIF-8-umIm (blue).