Supporting information

A facile route for the recovery for the ligand of zeolitic imidazolate framework ZIF-94/SIM-1

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Materials

Methanol (HPLC grade, ≥99.9%) and hydrochloric acid (37%) were purchased from Panreac Applichem. 4-methyl-5-imidazolecarboxaldehyde (4-m-5-Imca, 97%) was obtained in Fluorochem. Sodium sulfide (synthesis grade) was purchased from Scharlau. Zinc acetate dehydrate (98%) and Tetrahydrofuran (99.85%) were purchased from Acros Organics. Sodium hydroxide (pellets) were purchased from Carlo Erba Reagents. Polyether-block-amide, Pebax® MH 1657 (comprising 60 wt% polyethylene oxide (PEO) and 40 wt% aliphatic polyamide (PA6)) in the form of pellets was kindly provided by Arkema, France. Absolute ethanol and distilled water were provided by Gilca, Spain. All gases used for the separation tests were of research grade (greater than 99.995 % of purity) and supplied by Abelló Linde S.A., Spain. All gases, reactants, polymers and solvents were used as received.

Characterization

X-ray diffraction (XRD) measurements were performed with an Empyrean PANalytical diffractometer with a Cu-K source (λ= 1.5406 Å). Data were collected in the 2θ range from 2.5^{o} to 40^{o} at a scanning rate of $0.01^{o}\cdot s^{-1}$.

Scanning electron microscope (SEM) images were obtained with a FEI-Inspect F50 microscope at a voltage of 10 kV. The samples were previously coated with Au/Pd under vacuum conditions.

Attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR) was carried out in a Bruker Vertex 70 FTIR spectrometer with a DTGS detector and a Golden Gate diamond ATR accessory in the 600-4000 cm^{-1} wavenumber range with a resolution of 4 cm^{-1}.

Thermogravimetric analyses (TGA) were carried out in a Mettler Toledo DSC-1 Star System at a heating rate of 10 °C·min^{-1} up to 700 °C under an air flow of 80 cm^3(STP)·min^{-1}.

The Brunauer-Emmett-Teller (BET) specific surface areas were obtained from N_2 adsorption data acquired at -196 °C using a Micromeritics Tristar 3000 after outgassing the samples at 200 °C for 9 h.

Carbon dioxide adsorption analysis have been performed in a Quantachrome Autosob iQ3 TPX acquired at 294K. The samples were previously degassed at 120 °C for 8 h.

Proton Nuclear Magnetic Resonance (^{1}H-NMR) and ^{1}H-^{13}C heteronuclear single quantum coherence (^{1}H-^{13}C HSCQ) spectra of the D_2O solutions (294 K) of the commercial and recovered 4-m-5-Imca were recorded on 500 MHz Bruker Advance spectrometer. Chemical shifts (δ) are given in ppm, coupling constants are reported in Hz.

For the gas separation performance tests, the membranes were cut and placed in a module consisting of two stainless steel pieces and a 316LSS macro-porous disk support (Mott Co.) with a 20 µm nominal pore size. Membranes, 12.57 cm^2 in area, were gripped inside with Viton O-rings. To control the temperature of the experiment (35 ^oC), the permeation module was placed in a UNE 200 Memmert oven. The gas separation measurements were carried out by feeding the post-combustion gaseous mixture CO_2/N_2 (15/85 cm^3(STP) min^{-1}) and the mixture CO_2/CH_4 (50/50 cm^3(STP) min^{-1}) to the feed side at an operating pressure of 3 bar to favor CO_2 permeation. Gas flows of the mixtures were controlled by mass-flow controllers (Alicat Scientific, MC-100CCM-D). The permeate side of the membrane was swept with a 50 cm^3(STP) min^{-1} of He, at atmospheric pressure (∼ 1 bar) (Alicat Scientific, MC-100CCM-D). Concentrations of CO_2, N_2 and CH_4 in the outgoing streams (permeate side) were analyzed online by an Agilent 990 MicroGC. Permeances of CO_2, N_2 and CH_4 were calculated in Barrer (1 Barrer = 10^{-10} cm^3(STP)·cm·cm^{-2}·s^{-1} $cmHg^{-1}$). The CO_2/N_2 and CO_2/CH_4 separation selectivities were calculated as the ratio of the corresponding permeabilities.

Time lag experiments were carried out at different temperatures using a constant volume/pressure instrument built by our group. In the time-lag method, dense membranes are placed in a stainless steel membrane cell with two separated compartments (feed and permeate side). The downstream reservoir (permeate side) consists of 3/8” stainless steel tubing to minimize resistance. Two membrane cells are available with different diameters: 3.2 and 4.5 cm. Circular membranes were inserted in the stainless steel module similar to the one described above. The inlet pressure of the feed gases can reach a value of up to 6 bar. The feed or upstream pressure is measured by a Wika A-10 pressure transducer (PT1, absolute pressure range of 0-10 bar). The downstream pressure is measured by a Pfeiffer TPR 271 Pirani gauge (PT2, pressure range of 5·10-4-103 mbar). The resolution of both pressure transducers is 1% of reading. The inlet tubing to the membrane module, the membrane module, and the downstream compartment are placed in an oven (Memmert UN55) to control the temperature. To ensure that the feed gas is at the desired temperature, a loop made of stainless steel tubing was mounted inside the oven before the membrane cell. Evacuation is performed by a rotary vane pump (vacuum level down to $5 \cdot 10^{-4}$ mbar).

Circular membranes with an effective area of 5.7 cm^2 (3.2 cm in diameter) were used. All the measurements were performed at 25, 35, and 50 ^{0}C with a feed pressure of 3 bar. The order of gases was 1) N_2 and 2) CO_2. The leak rate was determined for each membrane after the first measurement. The maximum leak rate was two orders of magnitude lower than the lowest permeation flux. Before every experiment, the membranes were evacuated (10^{-3} mbar) at both sides for at least 10 times the time lag (θd) to remove any gas traces from the membrane surface and from the rig. The experiments started when the membranes were exposed to the feed gas. The downstream pressure (pd) was recorded during all the test. Experiments were performed for 10 times the time lag at least. To fulfil the boundary conditions of the time lag method and obtain an effective stationary state of flux, the downstream pressure should be much lower than the upstream pressure, so that the maximum downstream pressure was fixed at 0.1% of the upstream pressure. Once this value was reached, the experiment was finished. Permeability (P) was calculated using the slope of the pd-t curve in the stationary region. The solubility coefficient (S) was obtained from P and D.

Supplementary Figures

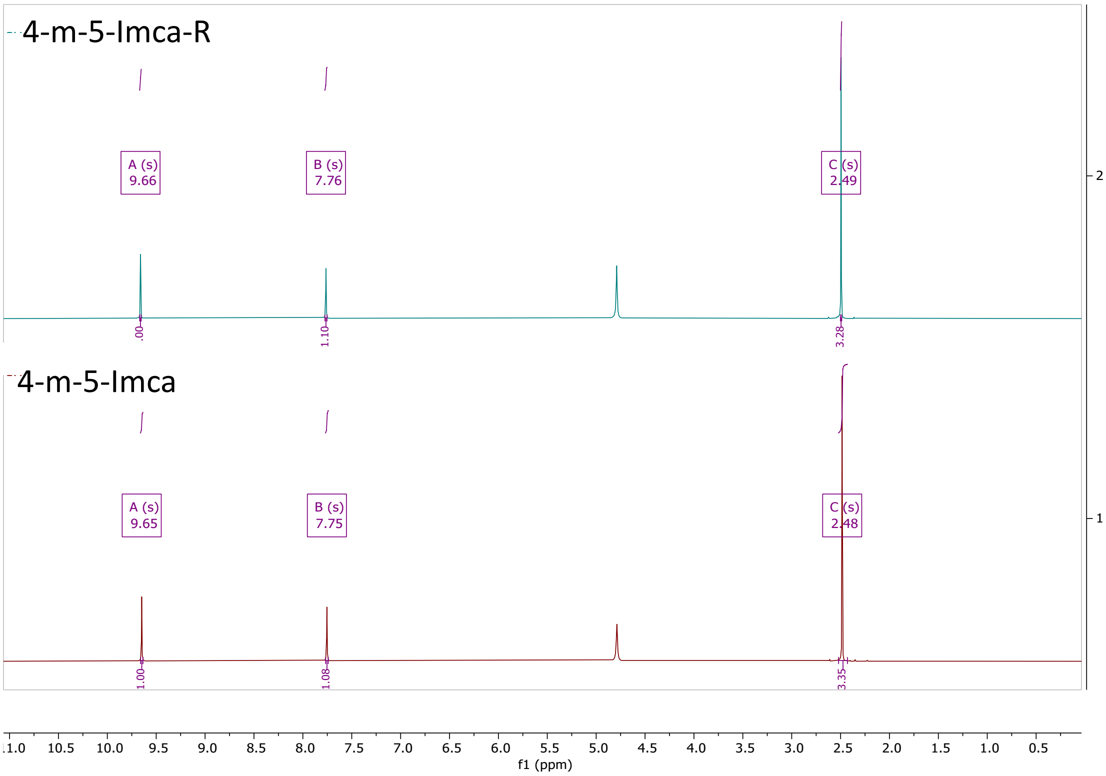

Fig. S1 ^{1}H NMR of both, commercial and recovered ligands.

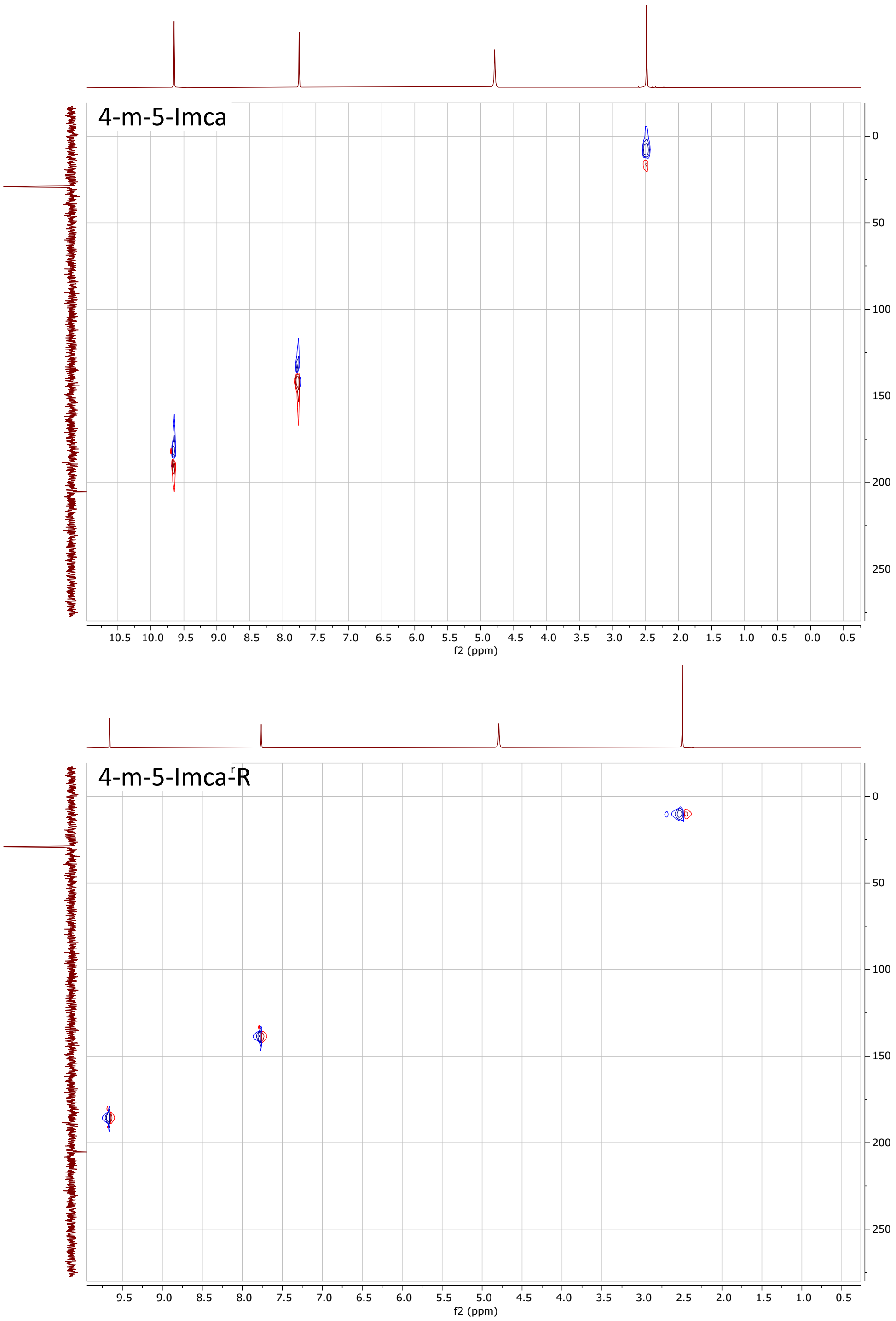

Fig. S2 ^{1}H-^{13}C HSCQ of both, commercial and recovered ligands.

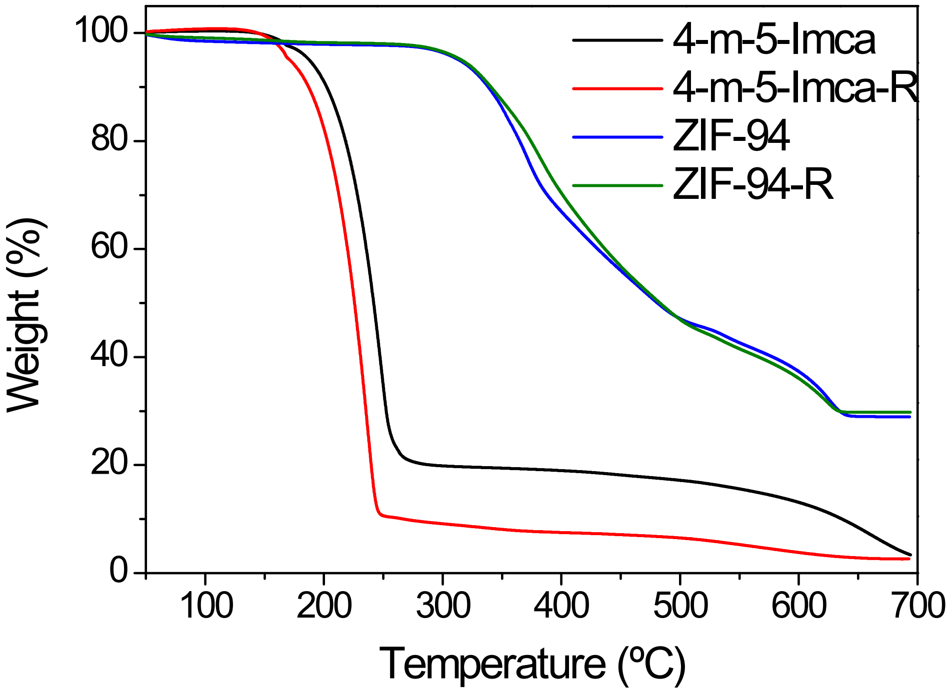

Fig. S3. TGA degradation curves of both, ligands and ZIFs.

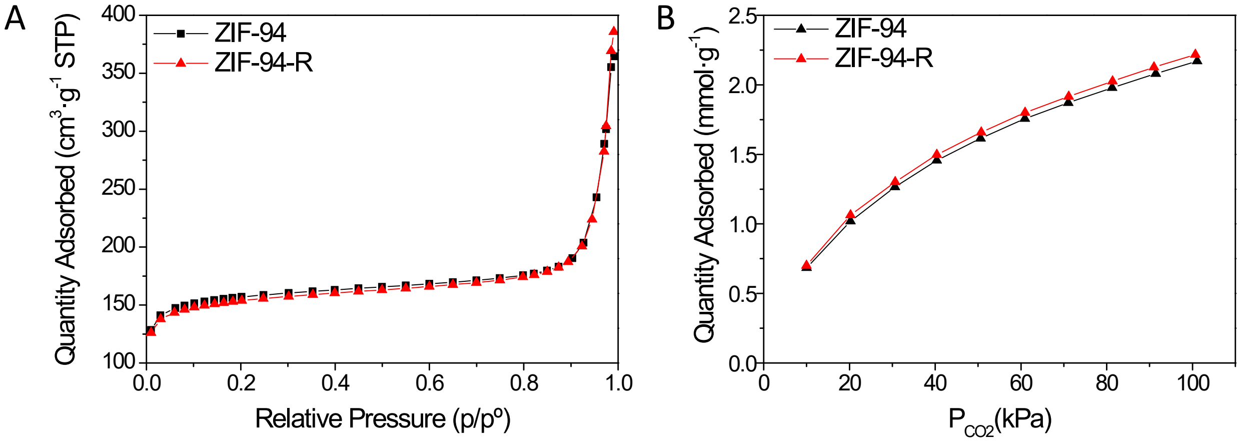

Fig. S4. Nitrogen adsorption isotherms at 77 K (A) and CO2 adsorption isotherms at 294 K (B) for both ZIF-94 materials.

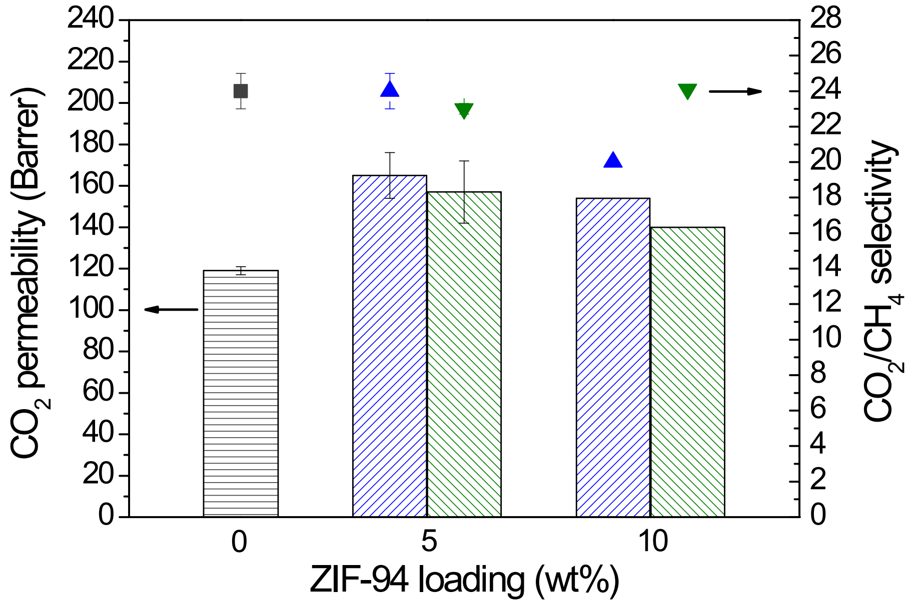

Fig. S5. Gas separation performance at 35 °C and 3 bar feed pressure for the MMMs prepared with ZIF-94 (blue) and ZIF-94-R (green) compared with the bare polymer (grey) for 50/50 CO_2/CH_4. Error bars come from the test of three different membranes.

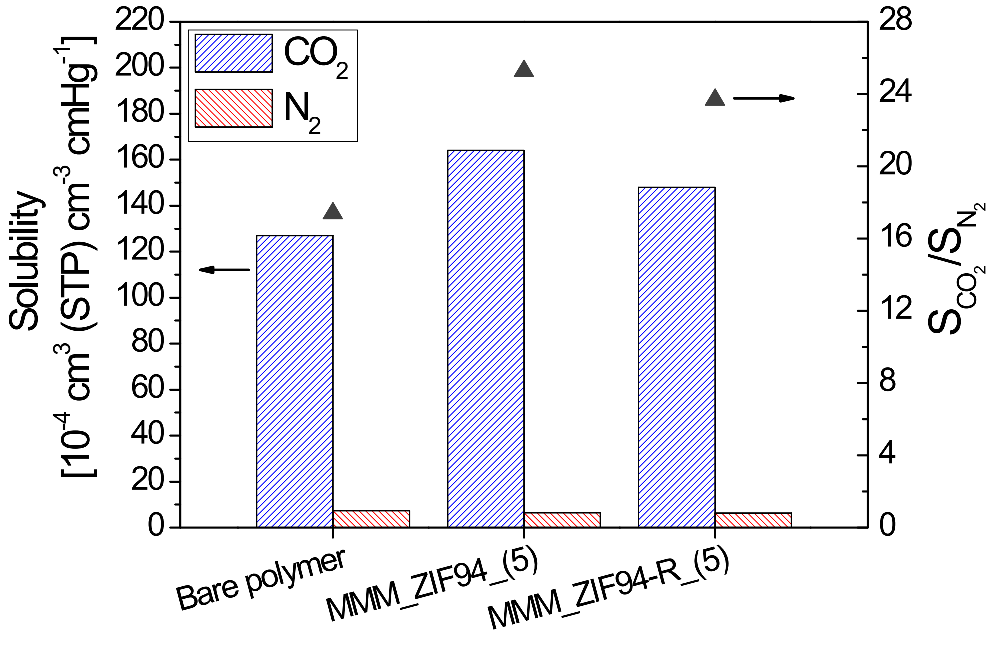

Fig. S6. Time-lag solubility experiments performed at 35°C and 3 bar pressure for CO_2 (blue) and N_2 (red)and their calculated selectivities for the bare Pebax®, MMMs with 5wt% of ZIF-94 (MMM_ZIF-94_(5)) and 5wt% of ZIF-94-R (MMM_ZIF94-R_(5)).