

Supporting Information for

CO₂/N₂ Separations with Mixed-Matrix Membranes Containing Mg₂(dobdc) Nanocrystals

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Experimental

Synthesis of Metal-Organic Framework Nanocrystals

Mg(NO₃)₂·6H₂O (5.46 mmol) and 2,5-dihydroxy-1,4-benzenedicarboxylic acid (1.70 mmol) were dissolved in 135 ml of dimethylformamide (DMF) in a round-bottom flask. To this solution, a mixture of ethanol/water/triethylamine (9, 9, and 1 ml, respectively) was quickly added while applying vigorous stirring and then the mixture was continuously stirred for additional 2 h at room temperature. After the synthesis, metal-organic framework crystals were collected by a centrifugation and redispersed in fresh DMF. The suspension was heated at 100 °C for 2 h to dissolve other non-crystalline impurities. Finally, the metal-organic framework crystals were purified and activated using the method described elsewhere. (Ref. 16 and 17) Ni- and Zn₂(dobdc) nanocrystals were synthesized by the same procedure using Ni(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O as metal sources, respectively.

Mixed-Matrix Membrane Fabrication

General: Membrane fabrication was performed in a N₂-filled glove bag in order for Mg₂(dobdc) crystals not to be exposed to air and moisture. Prior to gas adsorption and permeation measurements, membranes were thermally treated at 180 °C for 1 d under N₂ flow to remove any residual solvent or water in polymers as well as within pores of Mg₂(dobdc).

Polydimethylsiloxane (PDMS) membrane: Fully activated Mg₂(dobdc) nanocrystals were dispersed in anhydrous toluene by applying sonication and vigorous agitation. To this mixture, PDMS oligomer and crosslinker (Sylgard® 184) were added and then further agitated until the solution is homogenized. The gravimetric ratio of Mg₂(dobdc)/PDMS/toluene in the resulting solution was adjusted to 1/4/20, such that the filler loading in the mixed-matrix membrane was 20 wt%. Prior to the membrane casting, the solution was sonicated for 30 m to remove any gas bubble. The dope solution prepared was poured in a Teflon® dish and the solvent was evaporated at room temperature. Then, the nascent membrane was solidified by crosslinking PDMS oligomers at 150 °C for 4 h.

Crosslinked polyethylene oxide (XLPEO) membrane: The XLPEO membranes were synthesized by the procedure described in the previous work. (Ref. 25 and 26) Monomeric solution was prepared by mixing two PEO monomers, poly(ethylene glycol) methyl ether acrylate (PEGMEA, Mn=480), and poly(ethylene glycol) diacrylate (PEGDA, Mn=700). Next, fully activated Mg₂(dobdc) nanocrystals were directly dispersed in the monomeric solution and the mixture was agitated for at least 15 h. The gravimetric ratio of Mg₂(dobdc)/PEGMEA/PEGDA in the resulting solution was adjusted to 1/1.8/7.2, such that the filler loading in mixed-matrix membrane was 10 wt%. Next, the small amount of azobisisobutyronitrile (AIBN, about 0.5 wt% of PEGMEA) was added to the solution, which is then sonicated for 30 m to remove any gas bubble. The dope solution prepared was sandwiched in between two glass plates whose gap thickness was controlled by placing “spacers”. Finally, the membrane was solidified by polymerization of PEO monomers at 65 °C for 30 m.

Polyimide membrane: The polyimide (6FDA-TMPDA; 6FDA=2,2' bis(3,4'-dicarboxyphenyl)hexafluoropropane dianhydride and TMPDA=2,4,6-trimethyl-1,3-phenylenediamine) was synthesized based on the method described elsewhere. (Ref. 31) Polyimide mixed-matrix membranes were fabricated by the solution casting technique. After dispersing Mg₂(dobdc) crystals in anhydrous dichloromethane by applying sonication and vigorous agitation, the polyimide was added. The mixture was further agitated at room temperature until the solution is homogenized. Using that dope solution, the membrane was cast on a glass plate with the casting knife (Elcometer, US 3540) in a glove bag filled with N₂ and dichloromethane vapor that can prevent a rapid solvent evaporation from the nascent membrane.

Gas adsorption and permeation measurements

Gas adsorption properties of metal-organic framework crystals and membranes were measured by the custom-built high-throughput gas adsorption analyzer described in our previous work. (Ref. 24) The single-component CO₂ and N₂ permeation tests were performed using the isochoric (constant-volume, variable-pressure) technique. The scheme of permeation system containing a custom-built membrane cell is shown in Fig. S1. Prior to the permeation testing, all residual gases in the permeation system and membrane were removed using a turbo vacuum pump connected to both up- and downstream. During the measurement, the upstream pressure was precisely controlled using an electronic pressure controller (Tescom, ER3000) connected to a computer. The pressures in the feed and downstream collection volume were measured using pressure transducers (GE sensing, PTX7000), from which output were automatically recorded by the computer. Permeation tests were performed with three different samples for each mixed-matrix membrane and, the error bars were obtained from standard deviations.

Gas adsorption analysis

To evaluate the CO₂/N₂ adsorption properties for each metal-organic framework, recorded CO₂ and N₂ isotherms were fit with adsorption models. Simple adsorption models, such as the single-site Langmuir (SSL) model, often do not adequately describe CO₂ adsorption on materials containing strong binding sites. As such, in this work, a dual-site Langmuir (DSL) model was utilized to describe the CO₂ adsorption on our metal-organic frameworks:

$$q = \frac{q_{\text{sat},1} b_1 p}{1 + b_1 p} + \frac{q_{\text{sat},2} b_2 p}{1 + b_2 p} \quad (1)$$

Here, q is the quantity adsorbed, p is the pressure, $q_{\text{sat},1}$ and $q_{\text{sat},2}$ are the saturation loadings for sites 1 and 2, and b_1 and b_2 are the Langmuir parameters for sites 1 and 2, respectively. On the other hand, the N₂ adsorption could be described well using a SSL model:

$$q = \frac{q_{\text{sat}} b p}{1 + b p} \quad (2)$$

As we did in our previous work, (Ref. 24) the saturation loadings ($q_{\text{sat},1}$) for N₂ that are difficult to measure were assumed to be equal to the saturation capacities for CO₂ ($q_{\text{sat},1}$ plus $q_{\text{sat},2}$ in DSL model).

To quantify gas adsorption performance of metal-organic frameworks, Henry's coefficients (k_{H}) were also estimated using the mathematical descriptions of isotherms. For example, Henry's coefficients for the DSL model can be estimated by the following.

$$\begin{aligned} \lim_{p \rightarrow 0} q &= k_{\text{H}} p = (q_{\text{sat},1} b_1 + q_{\text{sat},2} b_2) p \\ k_{\text{H}} &= q_{\text{sat},1} b_1 + q_{\text{sat},2} b_2 \end{aligned} \quad (3)$$

Henry's coefficients for the SSL can be estimated using the same procedure.

$$k_{\text{H}} = q_{\text{sat}} b \quad (4)$$

In this work, the sorption selectivity of CO₂ over N₂ was defined as the ratio of Henry's coefficients for CO₂ and N₂.

$$\text{selectivity} = \frac{k_{\text{H,CO}_2}}{k_{\text{H,N}_2}} \quad (5)$$

Scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD)

The morphologies of both metal-organic framework crystals and mixed-matrix membranes were observed with a scanning electron microscope (Hitachi S-5000). The metal-organic framework nanocrystals were imaged after sputtering a gold layer on to the sample. To observe the morphologies of cross-sections, the mixed-matrix membrane samples were sputtered with gold after being cryogenically fractured in liquid nitrogen.

Powder X-ray diffraction (PXRD) data were collected using a Bruker D8-Advance θ - 2θ diffractometer in reflectance Bragg-Brentano geometry employing Ni filtered Cu K $\alpha_{1,2}$ lines focused radiation (1.54059 Å, 1.54439 Å) at 1600 W (40 kV, 40 mA) power and equipped with a Na(Tl) scintillation detector fitted at 0.2 mm radiation entrance slit. To estimate the size of crystallites, the following Scherrer equation was applied to the initial two strong peaks in XRD patterns.

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (6)$$

Here, τ is the size of crystallites, K is the dimensionless shape factor (here, 0.94 for spheres), λ is the X-ray wavelength, β is the peak width at half the maximum intensity in radians and the θ is the Bragg angle.

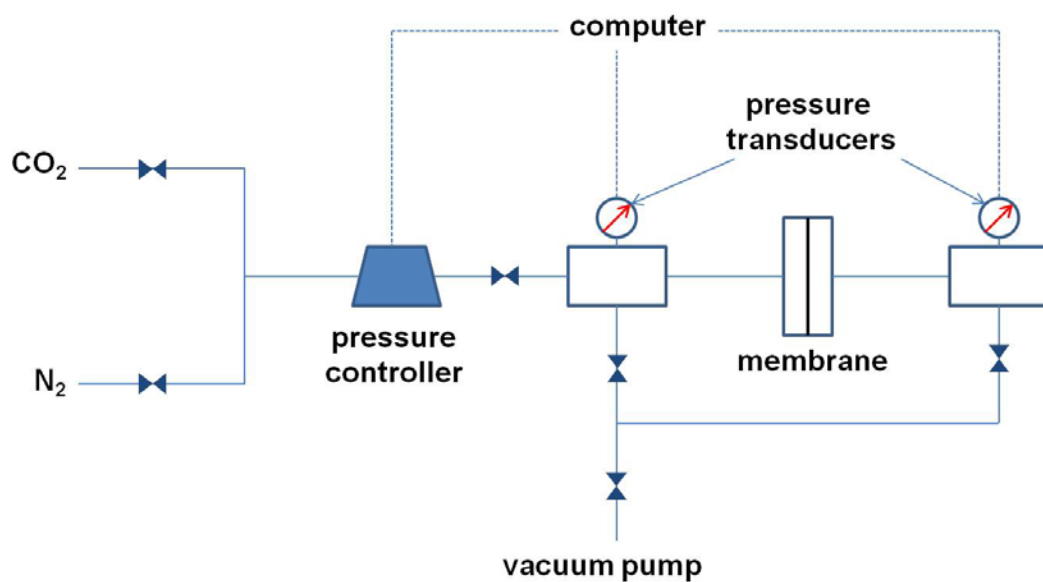


Figure S1. Scheme of the gas permeation testing system.

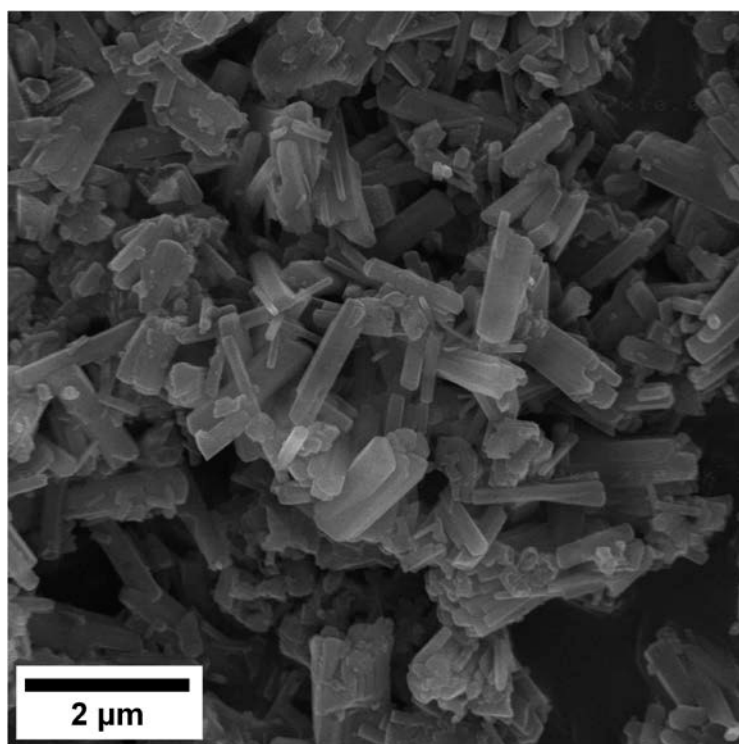


Figure S2. Morphology of Mg₂(dobdc) crystals solvothermally synthesized using the method in Ref 16.

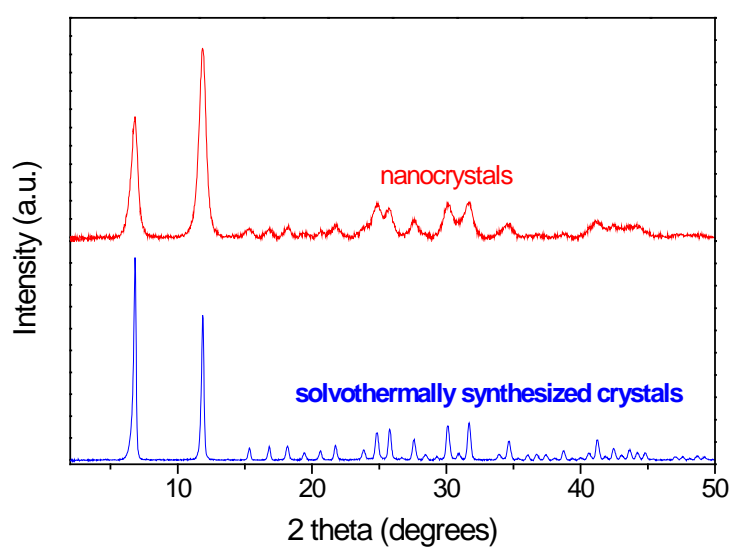


Figure S3. Powder X-ray diffraction patterns of $Mg_2(dobdc)$ crystals.

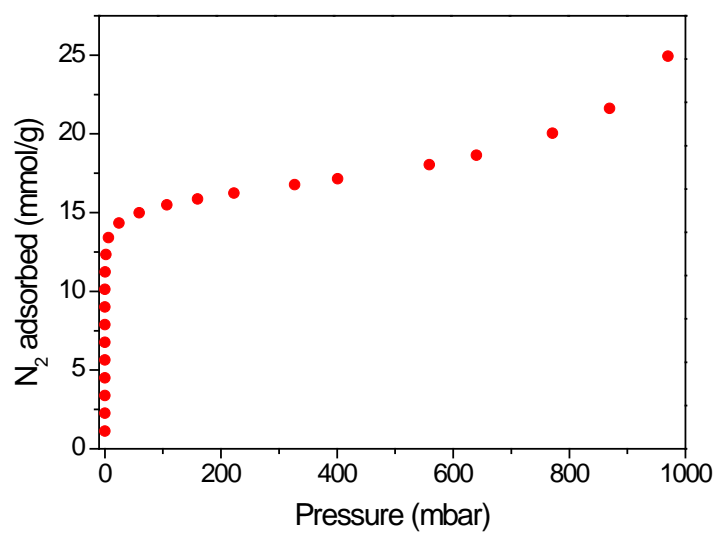


Figure S4. Nitrogen adsorption of Mg₂(dobdc) nanocrystals measured at 77 K. Langmuir and BET surface areas calculated are 1820 and 1380 m²/g, respectively.

Table S1. Fitting parameters for CO₂ adsorptions at 25 °C.

	q_1 (mmol/g)	b_1 (bar ⁻¹)	q_2 (mmol/g)	b_2 (bar ⁻¹)
Mg ₂ (dobdc)	5.31	36.5	10.2	0.290
Ni ₂ (dobdc)	3.99	8.43	7.95	0.168
Zn ₂ (dobdc)	3.57	1.83	7.62	0.402

Table S2. Fitting parameters for N₂ adsorptions at 25 °C.

	q (mmol/g)	b (bar ⁻¹)
Mg ₂ (dobdc)	15.5	0.0688
Ni ₂ (dobdc)	11.9	0.0353
Zn ₂ (dobdc)	11.2	0.0273

Table S3. Henry's coefficients and CO₂/N₂ sorption selectivities of metal-organic framework nanocrystals.

	k_{H, CO_2} (mmol/g·bar)	k_{H, N_2} (mmol/g·bar)	CO ₂ /N ₂ selectivity
Mg ₂ (dobdc)	197	1.07	184
Ni ₂ (dobdc)	36.0	0.421	83.0
Zn ₂ (dobdc)	9.60	0.305	31.4

Table S4. Pure component CO₂ and N₂ permeation properties of membranes measured at 2 bar upstream pressure and 25 °C.

membranes	CO ₂ permeability (barrers)	N ₂ permeability (barrers)	CO ₂ /N ₂ selectivity
pure PDMS	3100	330	9.5
Mg ₂ (dobdc)/PDMS	2100 ± 500	180 ± 40	12 ± 0.4
pure XLPEO	380	17	22
Mg ₂ (dobdc)/XLPEO	250 ± 20	10 ± 1	25 ± 2
pure PI	650	46	14
Mg ₂ (dobdc)/PI	850 ± 50	38 ± 5	23 ± 2

Table S5. CO₂ permeabilities, diffusivities, and solubilities in membranes at 2 bar upstream pressure and 25 °C. CO₂ solubilities in membranes were estimated by the fitting CO₂ adsorption isotherms in Figure 5 with mathematical models. Linear, single-site Langmuir, and dual-site Langmuir models were used for pure PDMS and XLPEO, pure PI, and all mixed matrix membranes, respectively. Then, CO₂ diffusivities were calculated using the following relationship.

Diffusivity = Permeability/Solubility

membrane	permeability mol·m/m ² ·s·bar	solubility mol/m ³ ·bar	diffusivity m ² /s
pure PDMS	1.0×10^{-7}	180	5.7×10^{-10}
Mg ₂ (dobdc)/PDMS	7.0×10^{-8}	390	1.8×10^{-10}
pure XLPEO	1.3×10^{-8}	140	8.9×10^{-11}
Mg ₂ (dobdc)/XLPEO	8.5×10^{-9}	220	3.80×10^{-11}
pure PI	2.2×10^{-8}	760	2.90×10^{-11}
Mg ₂ (dobdc)/PI	2.8×10^{-8}	1100	2.60×10^{-11}

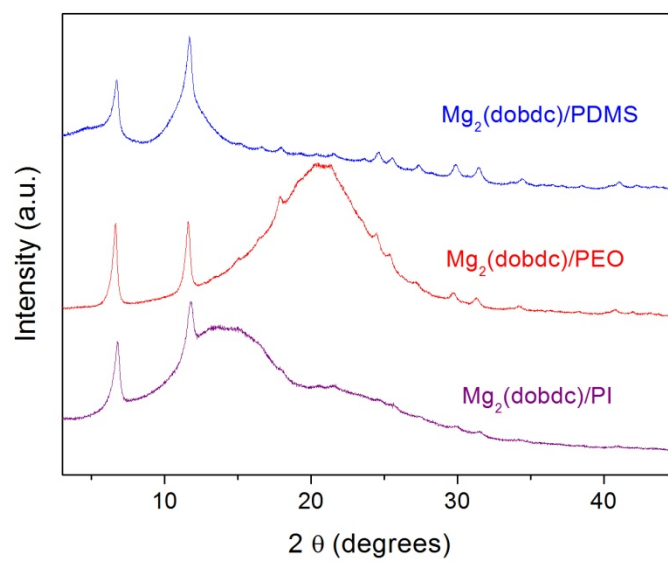


Figure S5. X-ray diffraction patterns of mixed-matrix membranes containing Mg₂(dobdc) nanocrystals.

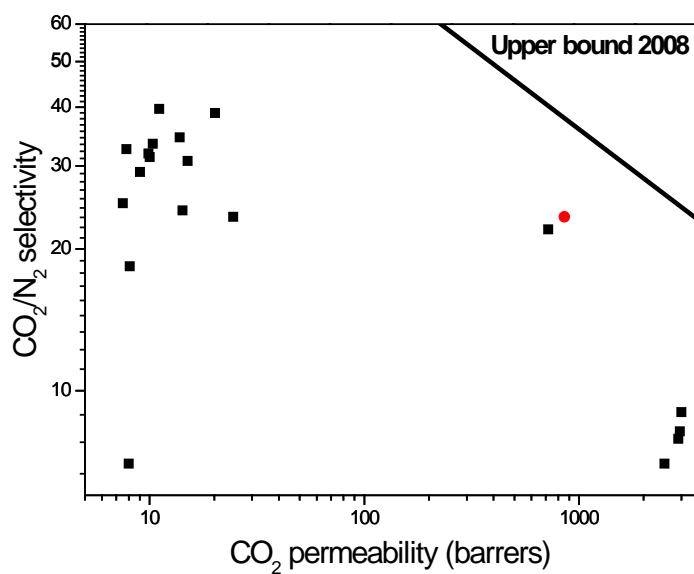


Figure S6. CO₂/N₂ separation performance of the present Mg₂(dobdc)/PI mixed-matrix membrane (red circle), compared with the compiled data on metal-organic framework-containing mixed-matrix membranes (black squares) in Ref 7.