Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information for :

Plasticization-resistant Ni_2(dobdc)/polyimide composite membranes for CO_2 removal from natural gas

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Methods

Synthesis of Ni_2(dobdc) nanocrystals

Solid 2,5-dihydroxyterephthalic acid (1.0 g, 5.0 mmol; H_4(dobdc)) and 16 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ were added to a mixture of 400 mL of DMF, 27 mL of ethanol, and 27 mL of water in a 500-mL round bottom flask. 5 mL of triethylamine was added rapidly while stirring under an N_2 atmosphere. The Ni_2(dobdc) nanocrystals precipitated within minutes, but was allowed to continue for 2 hours. The dispersed Ni_2(dobdc) nanoparticles were immediately collected by centrifugation, the solid was redispersed in 250 mL of DMF, and the suspension was heated at 120 °C for 6 h. The Ni_2(dobdc) undergoes a color change from green to brown upon heating. The centrifugation and DMF washing steps were repeated five times in order to remove unreacted ligand. The nanocrystals were then collected by centrifugation and redispersed in 250 mL of methanol and the suspension was heated at 60 °C for 2-5 h. The centrifugation and methanol washing steps were repeated six times in order to exchange all of the DMF for methanol, including those molecules coordinated to the metal sites. Full removal of DMF was confirmed by infrared spectroscopy. Nanocrystals were then stored in methanol until membrane casting, or dried under reduced pressure at 180 °C for 24 h prior to gas adsorption measurements.

Polymer Synthesis

6FDA-DAT, 6FDA-DAM, and 6FDA-durene were formed from 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and either 2,4,6-trimethyl-1,3-phenylenediamine (DAM), 2,6-diaminotoluene (DAT) or 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene) using standard chemical imidization techniques.[1,2] The random 1:1 copolymer **6FDA-DAT:DAM** was synthesized in a similar manner, according to reported techniques.[3] The dianhydride and diamines were purchased from TCI. Before use, 6FDA was purified once by vacuum sublimation, DAM and DAT were purified three times by vacuum sublimation, and durene was purified by recrystallization in methanol. N-methyl-2-pyrrolidone (NMP) was purchased from Spectrum Chemicals and vacuum distilled immediately before use. Triethylamine and acetic anhydride were purchased from EMD and Sigma-Aldrich, respectively, and were used as received. A dry atmosphere was maintained within the reaction glassware by flowing house nitrogen through a Drierite column (W.A. Hammond Drierite Co., Ltd., Xenia, OH) upstream of the reaction vessel. All glassware was attached to flowing, dry nitrogen after being flame dried. **Cellulose acetate** and **Matrimid®** were kindly provided by Membrane Technology and Research (MTR) Inc.

Membrane casting and activation

Concentration of Ni_2(dobdc) in methanol were determined by sonicating a stock solution and reducing a 1-mL aliquot to dryness to find the mass of activated nanocrystals, and resulting stock solutions were found to be ~30 mg/ml. For composite membranes, an aliquot from the Ni_2(dobdc) stock solution in methanol was taken and redispersed in 10 mL of the casting solvent in a 20 mL vial. The Ni_2(dobdc) was then centrifuged and redispersed in 10 mL of casting solvent in order to ensure no residual methanol was present during membrane casting. Dichloromethane was used as the casting solvent for all polymers except cellulose acetate, for which acetone was used. The nanocrystal suspension was then sonicated using a horn sonicator for 1 min with addition of casting solvent in order to maintain a total volume of 10 mL. The polymer was then dissolved into the Ni_2(dobdc) suspension and the mixture was sonicated for another 1 min. The mixture was cast onto a glass plate and the solvent was allowed to evaporate over the course of ~24 h, and the resulting films were found to be 40-70 μm thick. The freestanding film was then dried in a vacuum oven at 120 °C for 24 h in order to remove residual casting solvent.

The loading of Ni_2(dobdc) nanocrystals in the composite film was determined by a thermogravimetric analysis method. For reference, the Ni_2(dobdc) powder was first activated under flowing N_2 at 180 °C for 1.5 h to ensure activation, and then the samples were heated to 600 °C under flowing O_2. The remaining oxide mass was compared to the initial activated mass of the metal-organic framework. The same procedure was conducted for the Ni_2(dobdc)/6FDA-DAM films. The percentage of mass remaining after the ramp to 600 °C under O_2 is attributable to metal oxide, and from this the amount of activated M_2(dobdc) present in the film was obtained.

Gas permeability measurements

Single component gas permeation experiments were conducted on an instrument constructed in-house. The procedure for membrane sample preparation is described in our previous work.[4] For multicomponent permeation experiments, an equimolar mixture of CO_2/CH_4 was swept over the feed side of the membrane at a rate > 100x the permeation rate, in order to ensure no concentration polarization. The composition of the permeate, $p_{CO2}/(p_{CO2}+p_{CH4})$, was determined by collecting the permeate, and then expanding it to a mass spectrometer (MKS Microvision 2). The mass fraction of (mass 44)/[(mass 44) + (mass 15)] in the collected permeate was used to determine the mixed-gas selectivity. A calibration of the mass fraction was determined using standards with 10%, 50%, and 90% CO_2 in methane. Standard error of the CO_2/CH_4 mole fraction calibration is 0.79%. The uncertainty in the downstream mole ratio, as well as uncertainty in mixed-gas selectivities, is a propagation of uncertainty from the standard error in the mole ratio calibration.

Gas adsorption measurements

Low-pressure gas adsorption data between 0 and 1.1 bar were measured using a high throughput gas-adsorption analyzer constructed by Wildcat Discovery Technologies, using a method described previously.[5] Samples consisting of 50-100 mg of Ni_2(dobdc) powder, polymer film, or mixed-matrix film were loaded into a preweighed 4 mL, and heated at 180 °C for 24 h. The mass of the activated sample was then used as the basis for the adsorption measurements. After an adsorption isotherm was measured, the sample was reactivated at 180 °C for 6 h before measuring a subsequent adsorption isotherm.

Determination of glass transition temperatures

The glass transition temperatures (T_g) were determined by differential scanning calorimetry using a TA Q200 instrument. Temperature scans were conducted at 10 °C/min starting at 50 ˚C and ending at a temperature that varied depending on the polymer, which was ~20 ˚C above the observed T_g. Multiple temperature cycles were run, and the reported T_g was taken from either the second or third cycle.

Calculating permeability

In order to ensure steady-state permeation rates were attained, permeability measurements were run for at least 6× the time lag, where the time lag is defined as the intercept on the time-axis on the pressure vs. time plot where a line is drawn fitting the linear region.[6] The time $t = 0$ corresponds to when the downstream volume is closed to vacuum and the gas is allowed to begin accumulating. At the end of 6× the time lag, the slope of the line fitting the last 20% of the data was used to determine the steady-state permeation rate. In the case that the time lag was not detectable, i.e., for CO_2 permeation in Ni_2(dobdc)/6FDA-durene, the permeation at each pressure point was allowed to proceed for three minutes.

The pressure-based permeability is calculated using Eqn. 1, where *P* is the permeability, *l* is the thickness of the film, V_{cell} is the volume downstream of the membrane where gas is allowed to accumulate during a permeation test, *A* is the area of the membrane exposed to permeation, P_f is the upstream pressure, *R* is the gas constant, *T* is the temperature in *K*, $\left({}^{dp}/_{dt}\right)_{SS}$ is the steady-state permeation rate, and $\left({}^{dp}/_{dt}\right)_{leak}$ is the leak rate. We report permeabilities in the unit of Barrer (1 Barrer = $10^{-10}\,\frac{cm^3(STP)*cm}{cm^2*s*cmHg}$).

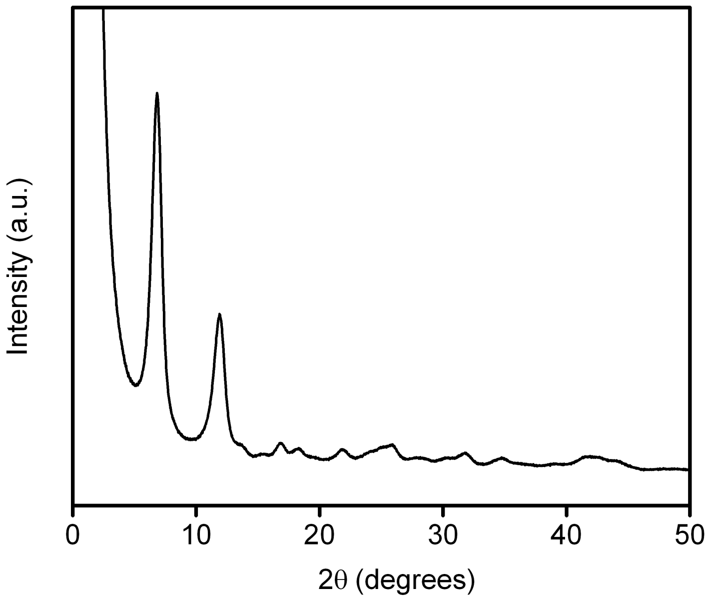
$$P = \frac{l*V_{cell}}{A*p_f*R*T}\left[\left({}^{dp}/_{dt}\right)_{SS} - \left({}^{dp}/_{dt}\right)_{leak}\right] \tag{1}$$

Uncertainty in the permeability was propagated from uncertainty in the film thickness, film area, upstream pressure transducer, temperature, and downstream volume.

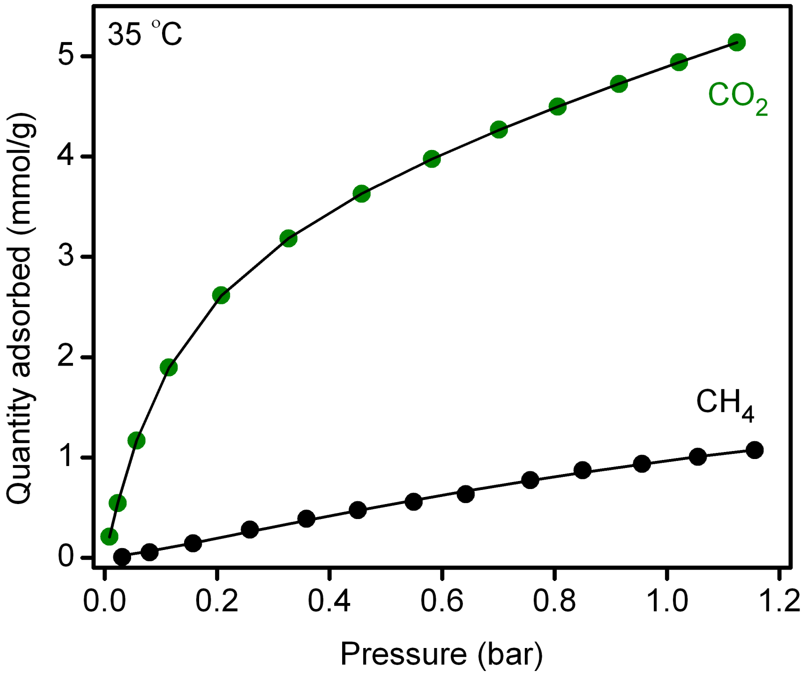
GPC

Molecular weights were determined using a Viscotek TDA 302 size exclusion chromatography (SEC) system calibrated relative to polystyrene and using tetrahydrofuran (THF) as the solvent. Supplementary Table 1 presents the weight-averaged molecular weight, number-averaged molecular weight, and polydispersity index for the samples considered in this study.

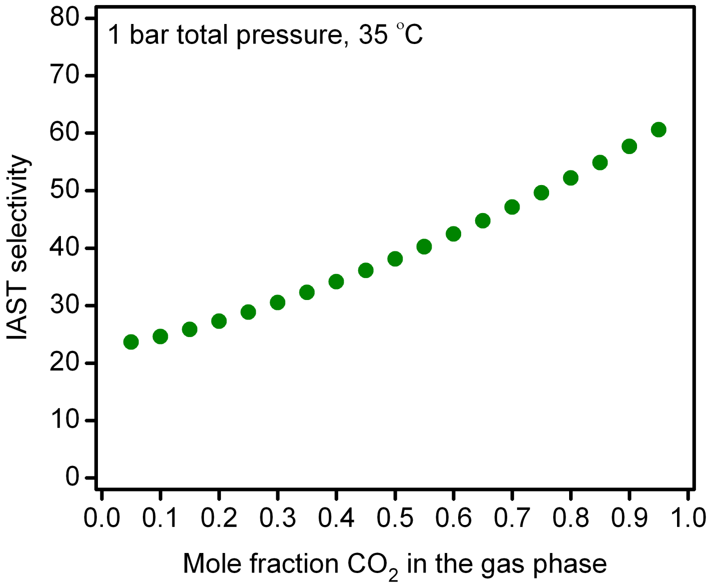
Figures



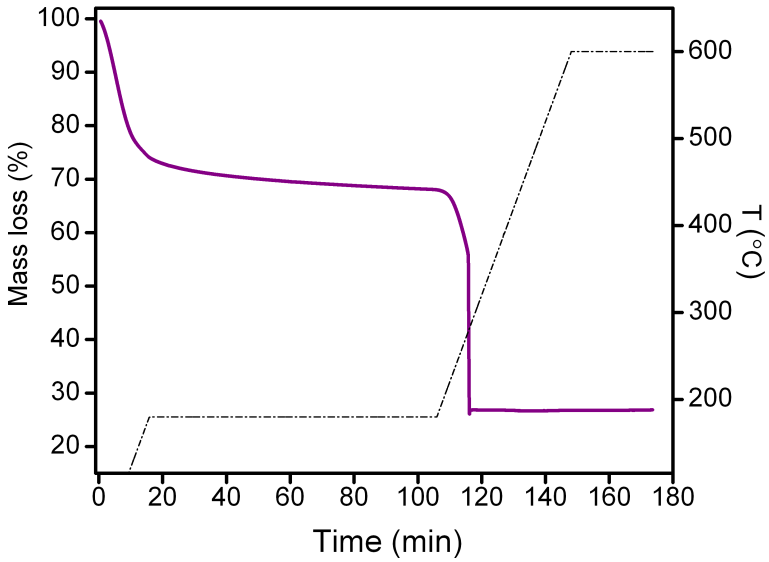
Supplementary Figure 1 | Powder X-ray diffraction pattern for Ni_2(dobdc) nanocrystals.



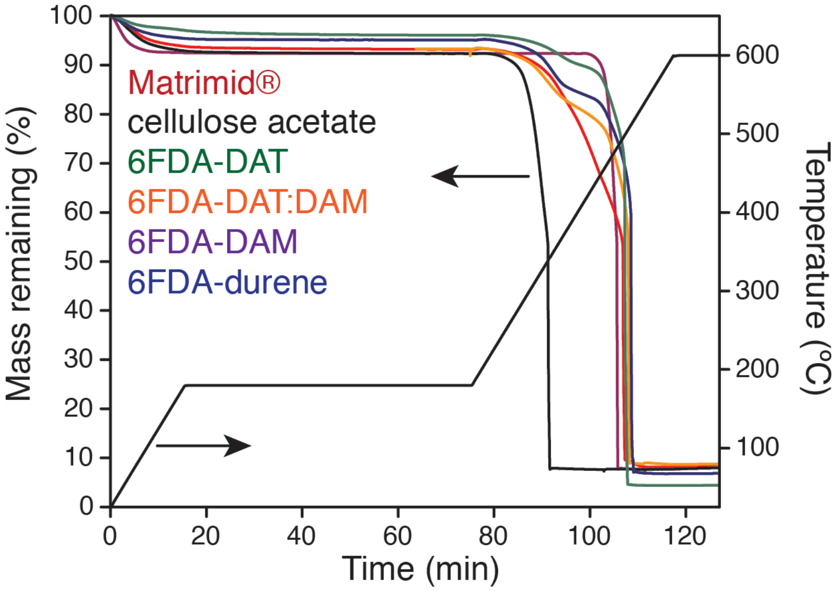
Supplementary Figure 2 | Equilibrium adsorption isotherms of CO_2 (green) and CH_4 (black) in neat Ni_2(dobdc) at 35 ˚C. Black lines correspond to dual-site and single-site Langmuir-Freundlich fits for CO_2 and CH_4, respectively.



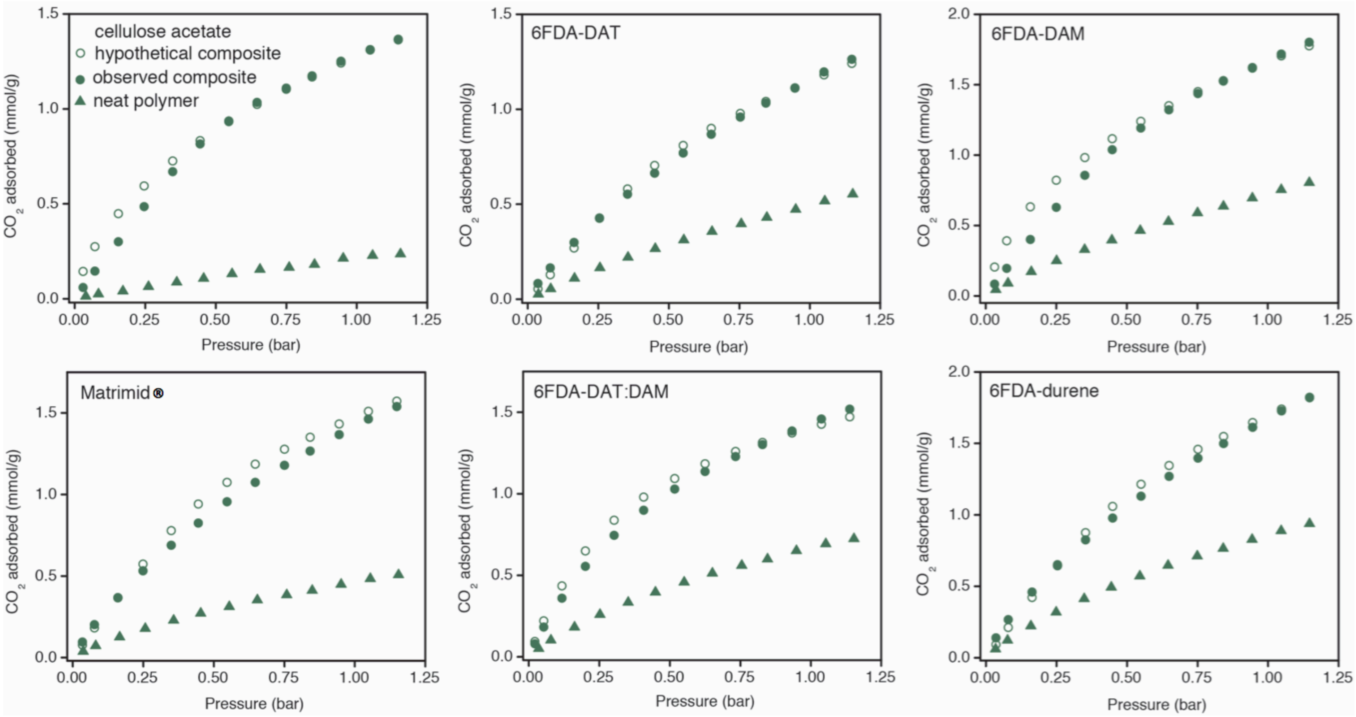
Supplementary Figure 3 | CO_2/CH_4 adsorptive selectivities in neat Ni_2(dobdc) as predicted from Ideal Adsorbed Solution Theory (IAST), with adsorption data taken at 35 ˚C and calculated at 1 bar total gas pressure.



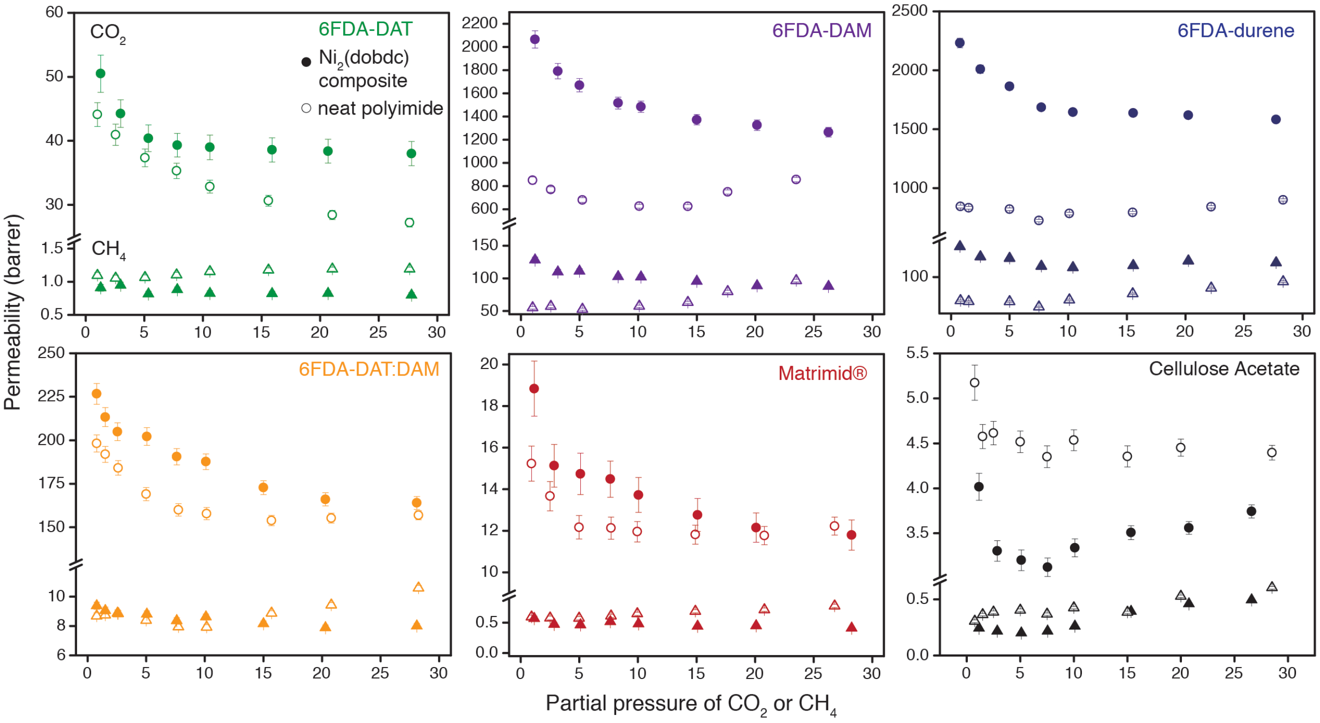
Supplementary Figure 4 | Thermogravimetric analysis curve for the decomposition of Ni_2(dobdc). From 0-110 minutes, the sample was activated at 180 ˚C under flowing N_2, and then was heated to 600 ˚C under flowing O_2. The difference between the activated mass and final mass was used to calculate the loading of Ni_2(dobdc) in the composite films.



Supplementary Figure 5 | Thermogravimetric analysis curve for composite membranes. Films were first activated under flowing N_2 at 180 ˚C and then heated to 600 ˚C under flowing O_2. The difference in mass between the activated film and remaining metal-oxide was used to calculate the amount of Ni_2(dobdc) in the composite.



Supplementary Figure 6| CO_2 adsorption isotherms in the neat polymer (closed triangles) and composite (closed circles) membranes. Open circles correspond to the weighted average of CO_2 adsorbed between the neat polymer and Ni_2(dobdc) powder. Amounts adsorbed at 1 bar were used for the calculation of pure component solubility parameters, S_{CO2}.



Supplementary Figure 7 | CO_2 (circles) and CH_4 (triangles) permeability data for neat (open) and composite (closed) membranes under an equimolar feed of CO_2 and CH_4. Uncertainties were propagated from the standard error in the calibration curve which determined the CO_2/CH_4 ratio in the permeate.

Supplementary Table 1 |Size exlusion chromatography characterization for each polymer tested. Mw and Mn refer to weight average and number average molecular weight, respectively. PDI is the polydispersity index.

Polymer	Mn	Mw	PDI
6FDA-durene	7,300	24,800	3.3
6FDA-DAM	69,500	166,000	2.4
6FDA-DAT:DAM	74,200	129,400	1.7
6FDA-DAT	15,700	37,000	2.3
Matrimid®	34,800	79,500	2.3
Cellulose acetate	62,600	166,000	2.7

References

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