

## Electronic Supporting Information

# Enhanced permeation arising from dual transport pathways in hybrid polymer-MOF membranes

Norman C. Su<sup>a,b</sup>, Daniel T. Sun<sup>b,c</sup>, Christine M. Beavers<sup>d</sup>, David K. Britt<sup>b</sup>, Wendy L. Queen<sup>b,c</sup>,  
and Jeffrey J. Urban<sup>\*,b</sup>

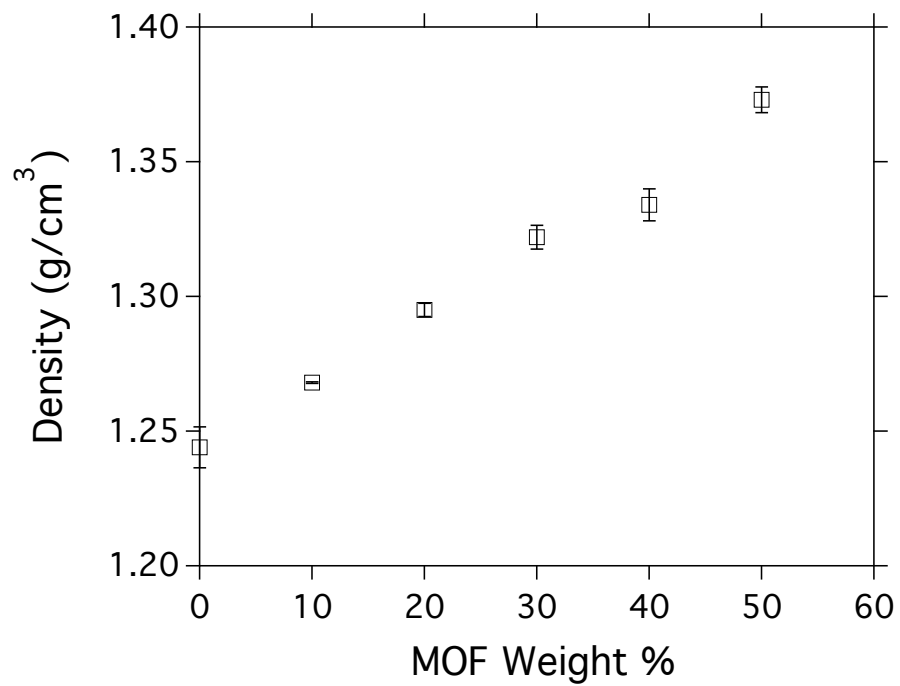
<sup>a</sup>Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States

<sup>b</sup>The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

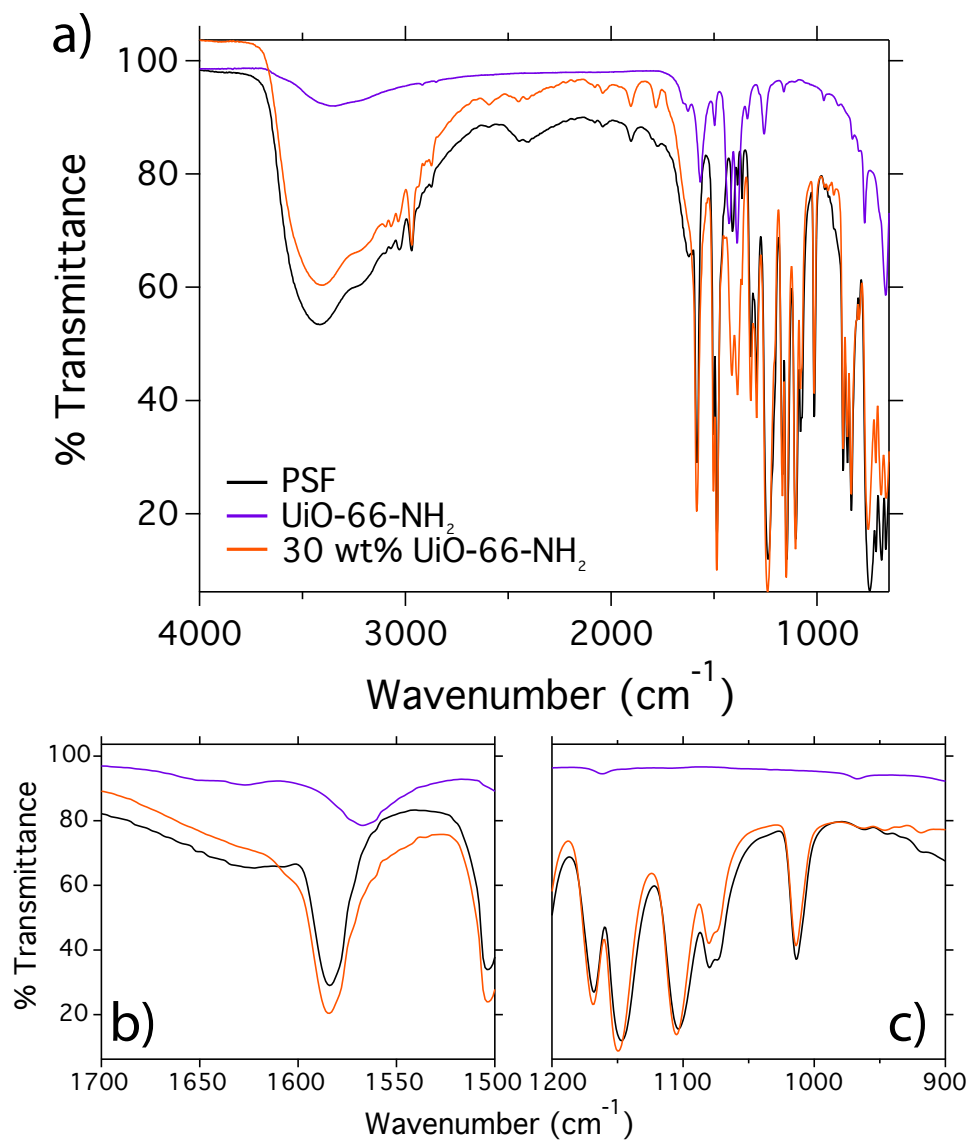
<sup>c</sup>Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL) CH 1051 Sion, Switzerland

<sup>d</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

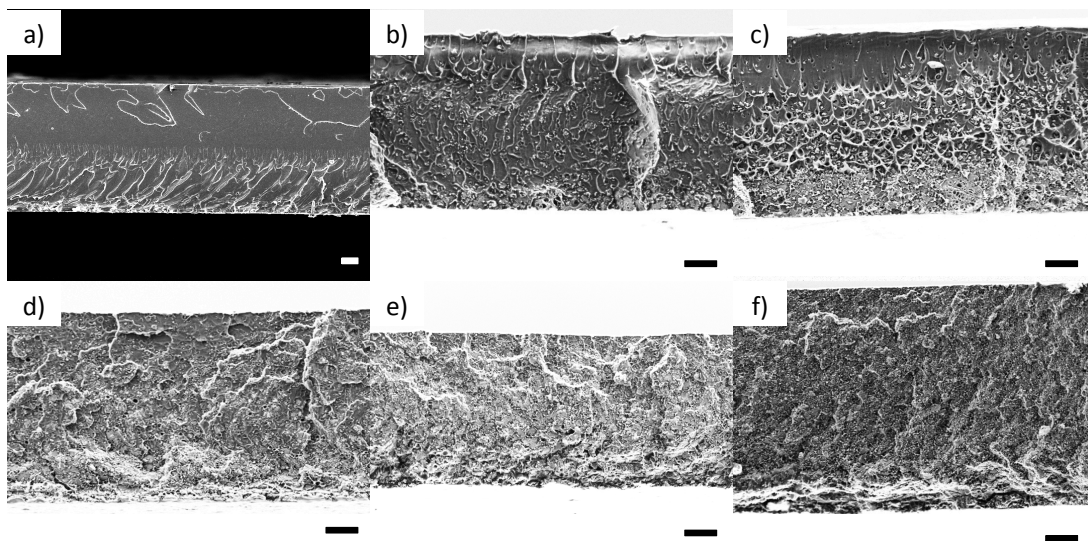
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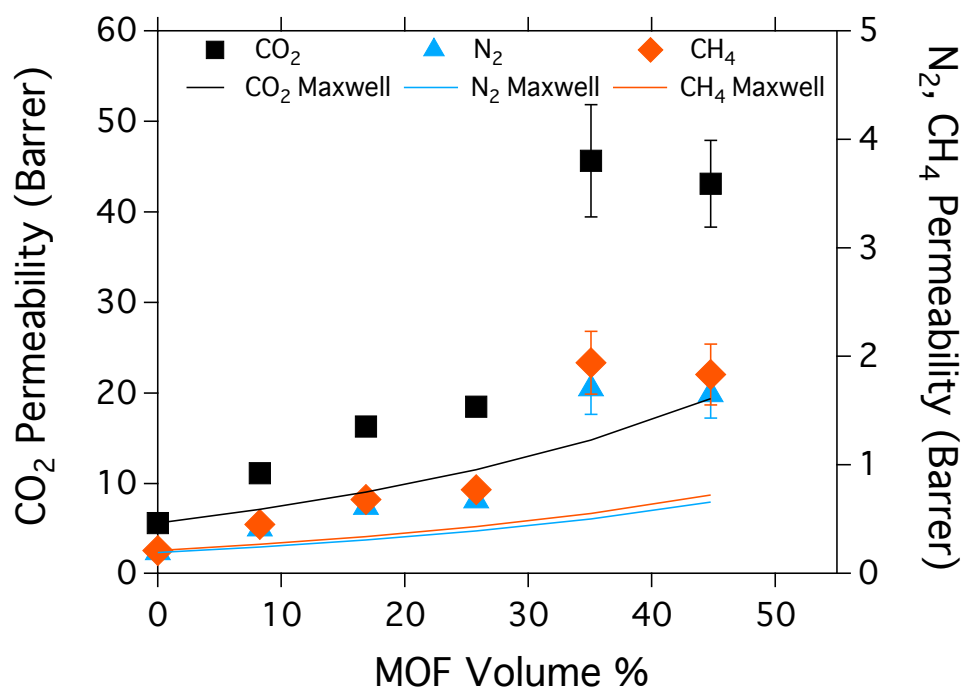
**Fig. S1.** Hydrostatic density measurement of UiO-66-NH<sub>2</sub> PSF hybrid membranes. Density follows a linear trend, indicating good interphase interaction.



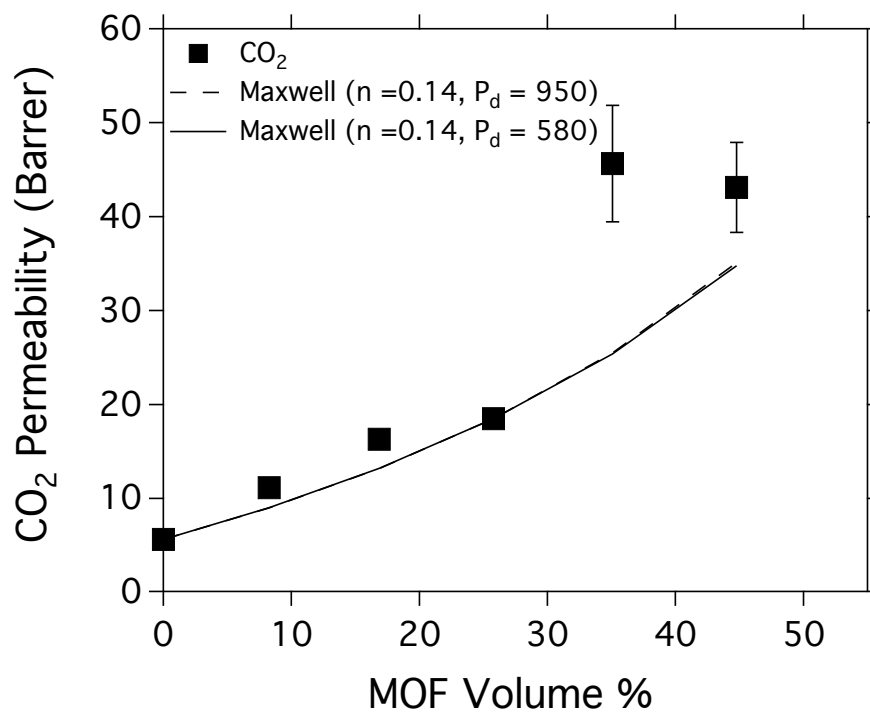
**Fig. S2.** a) FT-IR spectra of UiO-66-NH<sub>2</sub>, PSF, and 30 wt% UiO-66-NH<sub>2</sub>/PSF. b) Primary amine peak of UiO-66-NH<sub>2</sub> at 1567  $\text{cm}^{-1}$  becomes less apparent upon incorporation with PSF at 30 wt% indicating possible hydrogen-bonding interactions. c) Sulfonyl peak at 1150 and 1170  $\text{cm}^{-1}$  does not shift with addition of UiO-66-NH<sub>2</sub>



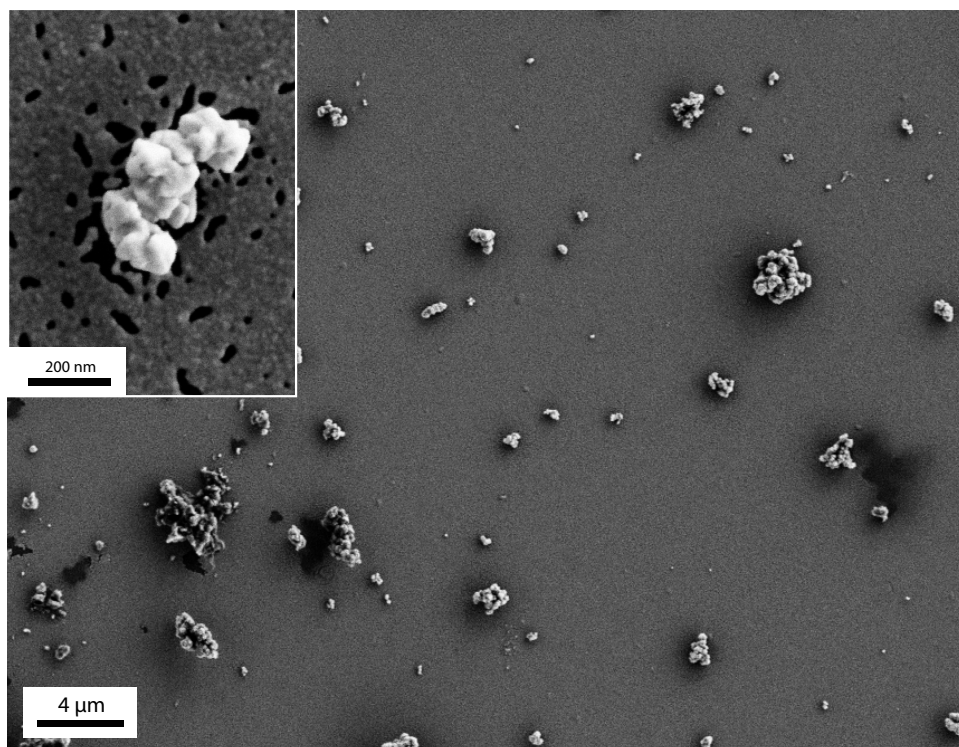
**Fig. S3.** Thickness of hybrid membranes. a) PSF, b) 10 wt% UiO-66-NH<sub>2</sub>, c) 20 wt% UiO-66-NH<sub>2</sub>, d) 30 wt% UiO-66-NH<sub>2</sub>, e) 40 wt% UiO-66-NH<sub>2</sub>, f) 50 wt% UiO-66-NH<sub>2</sub>. All scale bars represent 10  $\mu\text{m}$ .



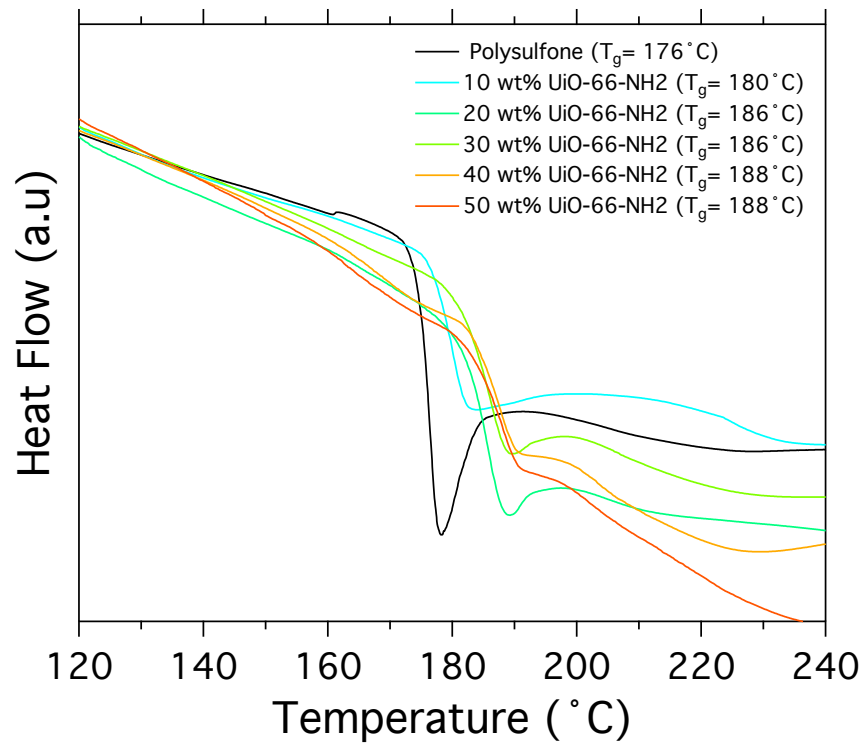
**Fig. S4.** Comparing Maxwell's predicted permeability with a spherical shape factor of  $n = 1/3$  and  $P_d = \infty$  to experimental permeability. Maxwell's permeability consistently underestimates permeability for CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>; this breakdown in the predictive value of the model is accentuated for high MOF loadings



**Fig. S5.** Comparing Maxwell's permeability with an adjustable shape factor.  $n$  converges to 0.14. Permeability of UiO-66-NH<sub>2</sub> ranges from 500-1000 barrers. Maxwell permeability trends shown for 580 and 950 barrer. Excellent correlation with experimental permeability below 30 wt%.



**Fig. S6.** SEM image of UiO-66-NH<sub>2</sub> nanoparticles. We observe partial aggregation of smaller domains of UiO-66-NH<sub>2</sub>, which results in presence of elongated UiO-66-NH<sub>2</sub> ellipsoids (inset) consistent with percolation theory.



**Fig. S7.** DSC thermograms of UiO-66-NH<sub>2</sub> PSF hybrid membranes. Scan rate 20 °C/min. T<sub>g</sub> increases with increasing MOF loading.

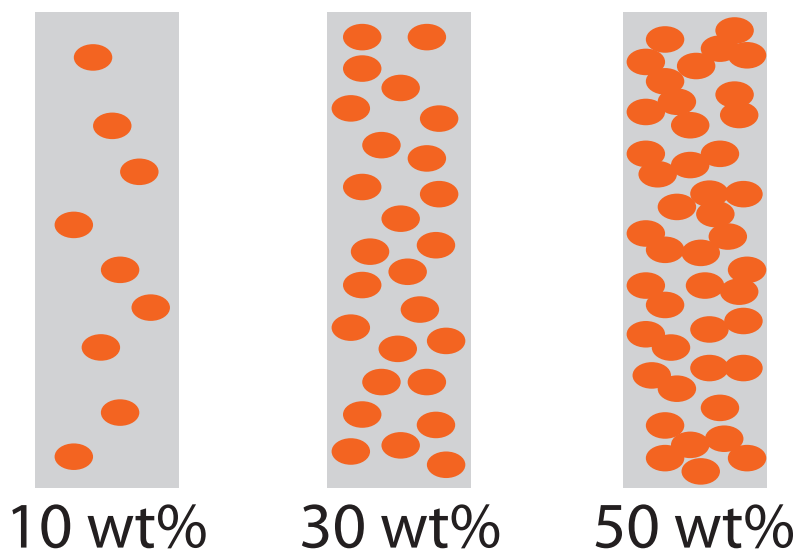


**Table S1.** CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> permeabilities in barrers for UiO-66-NH<sub>2</sub> at 3 bar and 35 °C

MOF Weight %	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
0%	0.19 ± 0.011	0.21 ± 0.017	5.6 ± 0.32
10%	0.41 ± 0.012	0.45 ± 0.013	11 ± 0.32
20%	0.61 ± 0.032	0.68 ± 0.036	16 ± 0.86
30%	0.67 ± 0.017	0.77 ± 0.02	19 ± 0.47
40%	1.7 ± 0.024	1.9 ± 0.28	46 ± 6.2
50%	1.65 ± 0.022	1.8 ± 0.28	43 ± 4.8

**Table S2.** CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities for UiO-66-NH<sub>2</sub> at 3 bar and 35 °C

MOF Weight %	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
0%	27	30
10%	25	27
20%	24	27
30%	24	28
40%	24	27
50%	24	26

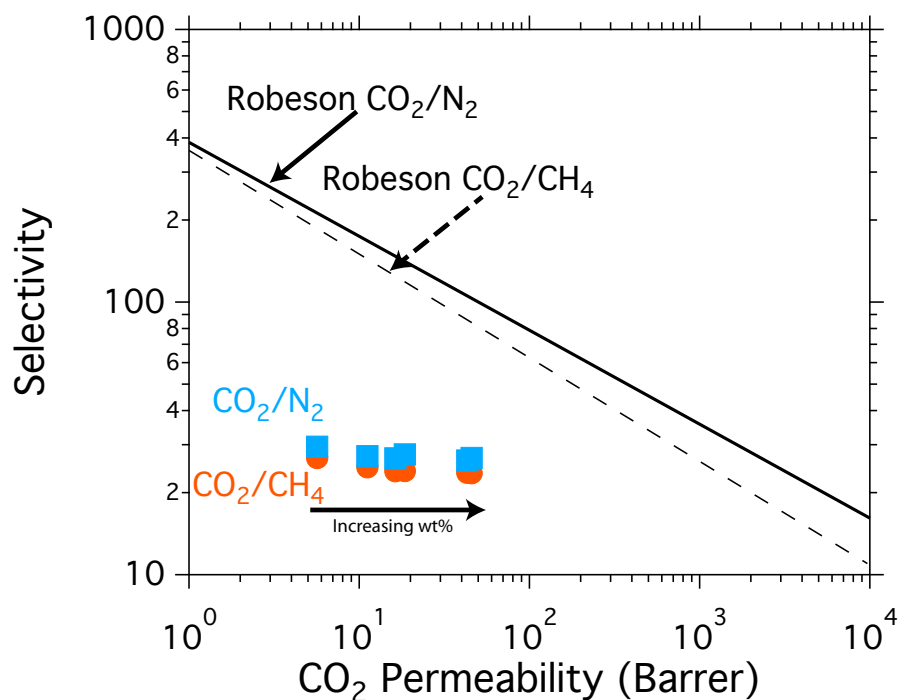


**Fig. S8.** Schematic of formation of percolative interconnected network of MOF crystals with ellipsoid geometry. Interconnected network of MOF crystals is formed when percolation threshold is reached.

Gas transport above the percolation threshold can be understood by the following equation:<sup>1,2</sup>

$$P_{\text{Hybrid}} = P_{\text{cluster}}\phi_{\text{cluster}} + P_{\text{polymer}}(1 - \phi_{\text{cluster}})$$

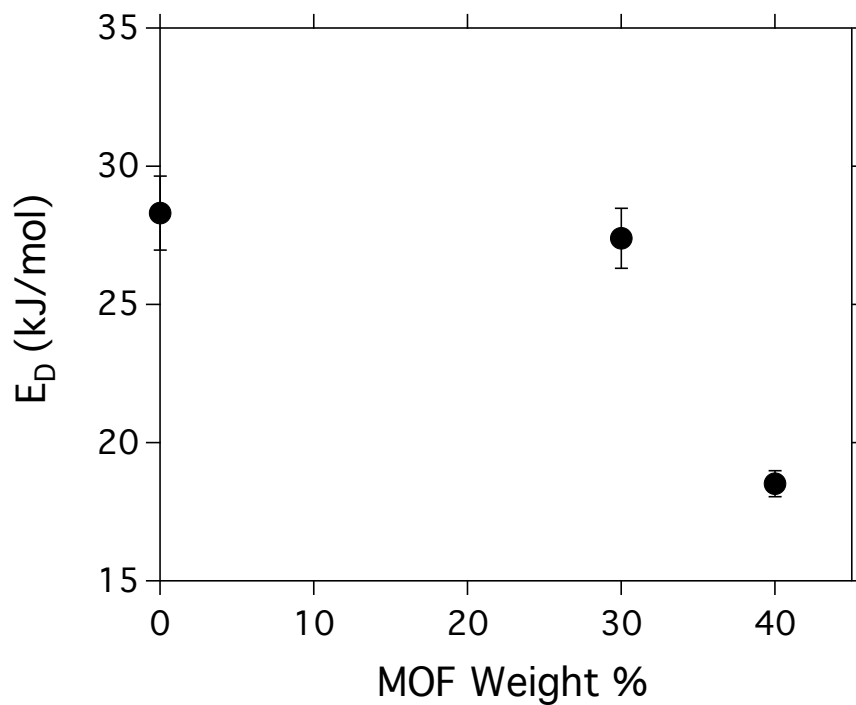
where  $P_{\text{Hybrid}}$  is the permeability of the hybrid membrane,  $P_{\text{cluster}}$  is the permeability of the percolation cluster,  $\phi_{\text{cluster}}$  is the volume fraction of the percolation cluster, and  $P_{\text{polymer}}$  is the permeability of the polymer. We were not able to quantify the volume fraction of the MOF that participated as a percolation cluster but we believe it to be only a small fraction of the total MOF available for transport.



**Fig. S9.** Robeson upper bound plot of UiO-66-NH<sub>2</sub> PSF hybrid membranes for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>. In both cases, the addition of MOF moves the transport performance of the hybrid membrane closer to the upper bound line.

**Table S3.** Diffusivity, Solubility, and Gas Uptake Values for UiO-66-NH<sub>2</sub> membranes at 3 bar and 35 °C

MOF wt%	Diffusion*10 <sup>8</sup> (cm <sup>2</sup> /s)			Solubility (cm <sup>3</sup> (STP)/(cm <sup>3</sup> atm))			Gas Uptake(cm <sup>3</sup> /(cm <sup>3</sup> atm))		
	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO <sub>2</sub>
0%	0.72	0.18	1.1	0.20	0.90	4.0	0.63	2.8	12.5
10%	1	0.27	1.5	0.30	1.2	5.8	0.92	3.9	17.9
20%	1.3	0.42	1.9	0.35	1.2	6.4	1.1	3.8	19.8
30%	1.2	0.39	1.7	0.44	1.5	8.1	1.4	4.7	25.5
40%	1.5	0.7	3.1	0.92	2.3	11.6	2.8	7.2	36.0
50%	1.7	0.69	2.9	0.88	2.4	12.3	2.7	7.6	38.2



**Fig. S10.** CO<sub>2</sub> activation energy for diffusion,  $E_D$  as a function of MOF weight %. Under the percolation threshold (up to 30 wt% MOF), the activation energy shows no significant decrease. Over the percolation threshold (over 40 wt% MOF),  $E_D$  drops significantly due to the formation of dual transport pathways.

References:

1. Bakhtin, D., Eremin, Y. S., Grekhov, a. M. & Volkov, V. V. Gas Permeability of PVTMS/CNT Mixed Matrix Membranes. *Phys. Procedia* **72**, 166–170 (2015).
2. Eremin, Y. S. & Grekhov, a. M. Calculation of Percolating Clusters Characteristics in Mixed Matrix Membrane with CNT. *Phys. Procedia* **72**, 37–41 (2015).