

## SUPPORTING INFORMATION

*for*

### Investigation of storage environments on aminopolymer stabilization within UiO-67(Zr) for CO<sub>2</sub> capture

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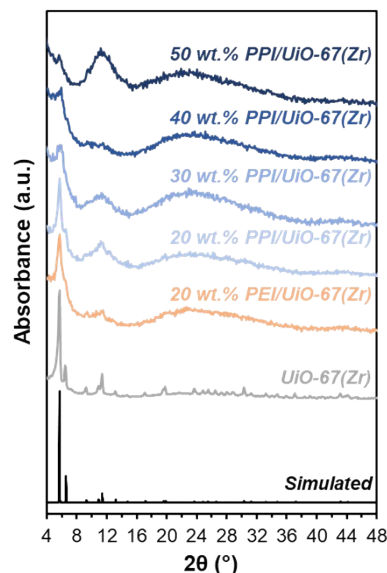
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**Keywords:** carbon capture, metal-organic frameworks, aminopolymer, storage stability, adsorption

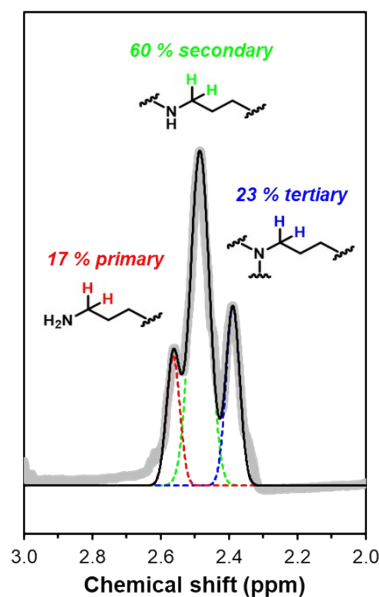
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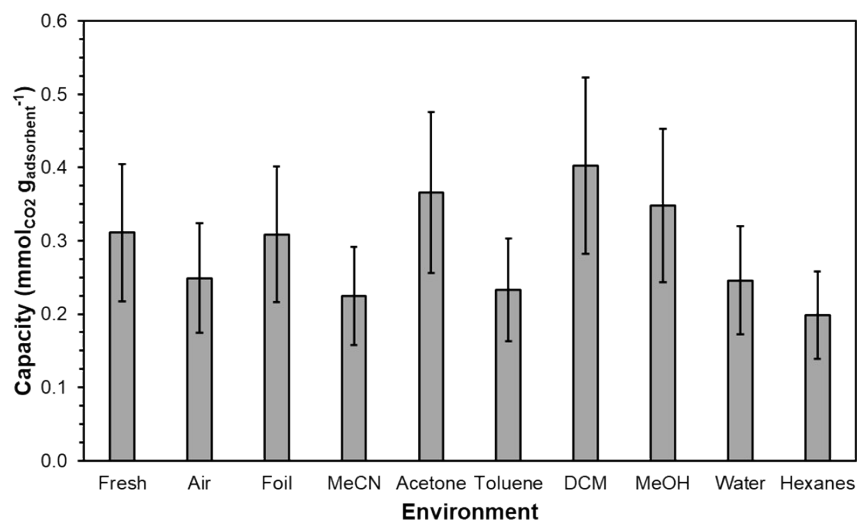


**Figure S1.** XRD patterns for simulated UiO-67(Zr) and fresh UiO-67(Zr), 20 wt.% PEI/UiO-67(Zr), and 20-50 wt.% PPI/UiO-67(Zr).

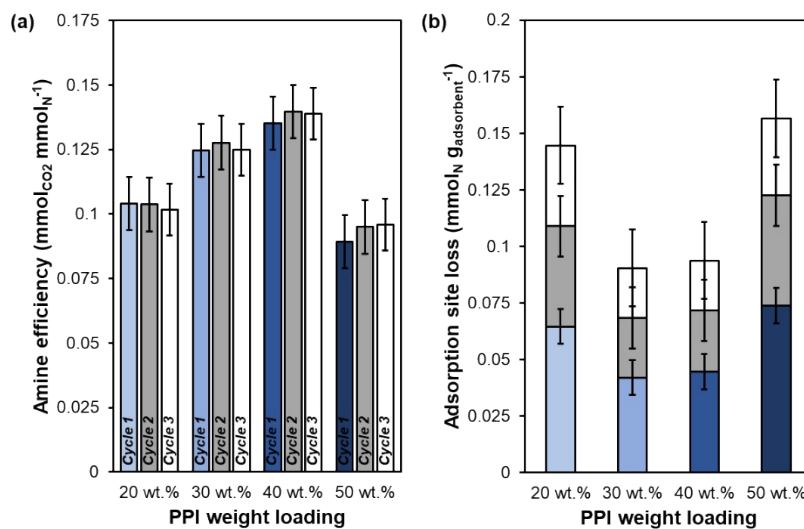
All samples (~30 mg) were mounted on an amorphous glass slide utilizing vacuum grease as a powder adhesive. Powder samples were gently hand pressed to form a smooth, thin film and mounted vertically on the Bruker D8 Discover stage with a piece of double-sided (XRD amorphous) Scotch tape. Broad peaks observed at 24 ° in the 20 wt.% PEI/UiO-67(Zr), 20 wt.% PPI/UiO-67(Zr), 30 wt.% PPI/UiO-67(Zr), 40 wt.% PPI/UiO-67(Zr), and 50 wt.% PPI/UiO-67(Zr) patterns are due to the amorphous silica glass slide since lower amounts of sample were available for analysis compared to bulk UiO-67(Zr). The broad peak at 11.5 ° likely corresponds to amorphous aminopolymer.



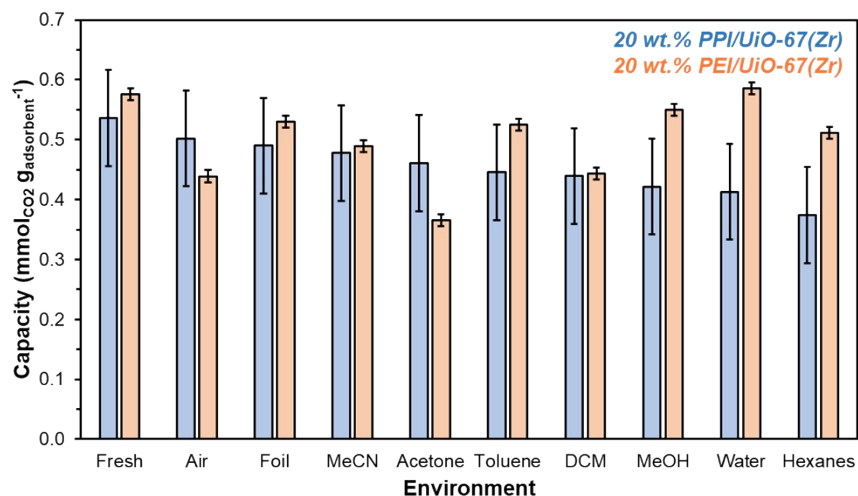
**Figure S2.**  $^1\text{H}$  NMR spectrum of as-synthesized poly(propylene imine) in  $\text{D}_2\text{O}$  solvent. Primary (red), secondary (green), and tertiary (blue) distributions are fitted Gaussian distributions.



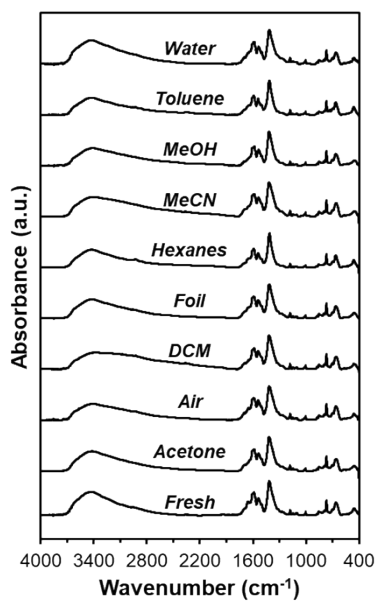
**Figure S3.** Mass-normalized CO<sub>2</sub> capacities for UiO-67(Zr) after exposure to different solvent environments for 7 days. All uptake measurements are under 40 mL min<sup>-1</sup> 10% CO<sub>2</sub> in He for 1 h at 308 K after volatile solvent removal at 383 K under 40 mL min<sup>-1</sup> Ar for 3 h. Errors are from duplicate UiO-67(Zr) measurements from 2 batches.



**Figure S4.** (a) Amine efficiencies for varying weight percentages (20-50 wt.%) of PPI supported on UiO-67(Zr) for three 1 h uptake cycles at 308 K with 2 h regeneration steps at 383 K under 40 mL min<sup>-1</sup> Ar flow in between cycles. (b) Amine site losses (normalized by adsorbent mass) after cycle 1 (blues), cycle 2 (grey), and cycle 3 (white) are based on 400 g mol<sup>-1</sup> PPI molecular weight.



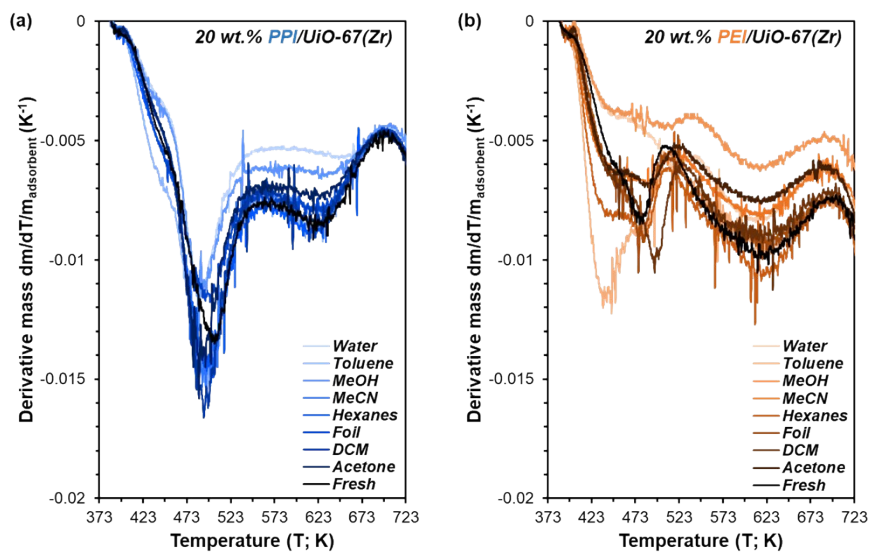
**Figure S5.** Mass-normalized 1 h CO<sub>2</sub> capacities at 308 K for 20 wt.% PPI/Uio-67(Zr) (blue) and 20 wt.% PEI/Uio-67(Zr) (orange) after 7 days of exposure to each solvent environment.



**Figure S6.** Ex-situ FTIR spectra of UiO-67(Zr) after 7 days in each solvent environment. All samples are 2 wt.% in KBr diluent.

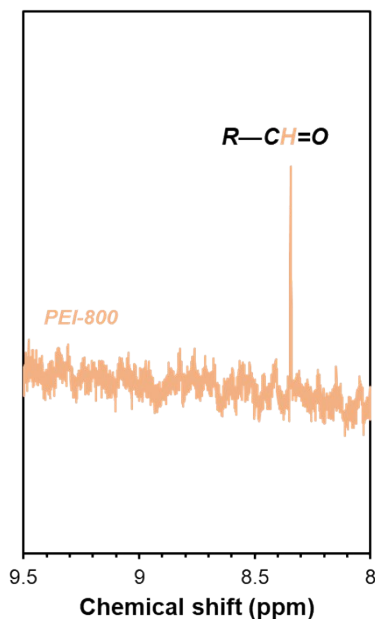


**Figure S7.** Images of (a) PEI and (b) PPI in liquid solvents after 7 days of storage at ambient temperature and pressure.

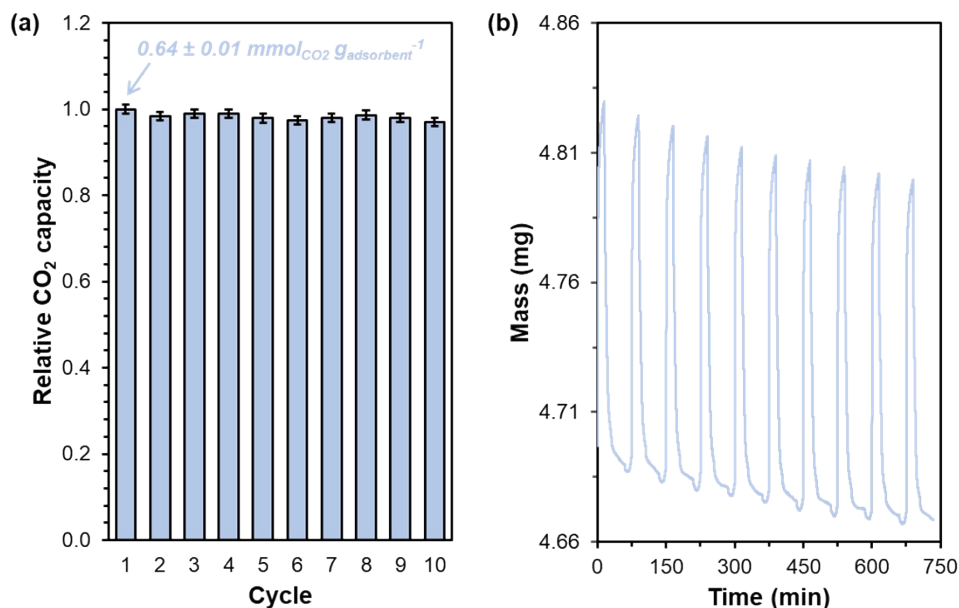


**Figure S8.** Derivative mass losses normalized by dried adsorbent composite masses determined from TGA for (a) 20 wt.% PPI/UiO-67(Zr) and (b) 20 wt.% PEI/UiO-67(Zr) after 7 days in each storage environment.

Aminopolymer (PPI, PEI) loadings are determined via thermogravimetric analysis (TGA). Samples (typically 3-10 mg) were loaded onto tared ceramic pans, heated ( $5 \text{ K min}^{-1}$ ) to 383 K under  $40 \text{ mL min}^{-1}$  Ar, and held for 3 h under flow to remove water and other volatiles. Afterwards, gas flow was changed to  $90 \text{ mL min}^{-1}$  zero air and samples were heated from 383 K to 1173 K at  $10 \text{ K min}^{-1}$  to determine organic loadings. Finally, samples were cooled ( $10 \text{ K min}^{-1}$ ) to 303 K under  $40 \text{ mL min}^{-1}$  Ar and disposed of. Resulting derivative mass losses as a function of temperature are integrated to determine aminopolymer loadings used in amine efficiency calculations (**Figure 4**).



**Figure S9.**  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ; 500 MHz) spectra for commercial PEI-800 after 24 h exposure to air at ambient temperature and pressure.



**Figure S10.** (a) Mass-normalized  $\text{CO}_2$  capacities for 20 wt.% PPI/UiO-67(Zr) normalized by fresh  $\text{CO}_2$  capacity ( $0.64 \text{ mmol}_{\text{CO}_2} \text{ g}_{\text{adsorbent}}^{-1}$ ) in cycle 1 and (b) accompanying raw TGA mass measurements for ten rapid 15 min uptake cycles at 308 K with 30 min desorption steps at 383 K under  $40 \text{ mL min}^{-1}$  Ar flow in between cycles.

Cyclic stability was assessed utilizing TGA. After thermal treatment (383 K) at 3 h under  $40 \text{ mL min}^{-1}$  Ar, 20 wt.% PPI/UiO-67(Zr) was subjected to  $40 \text{ mL min}^{-1}$  10 %  $\text{CO}_2$  in He for 15 min at 308 K, heated to 383 K at  $5 \text{ K min}^{-1}$  under  $40 \text{ mL min}^{-1}$  Ar, held at 383 K for 30 min under  $40 \text{ mL min}^{-1}$  Ar, cooled to 308 K at  $5 \text{ K min}^{-1}$  under  $40 \text{ mL min}^{-1}$  Ar, and repeated for 10 cycles.