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Type 3 Porous Liquid Design Based on Pore Accessibility and Framework Stability

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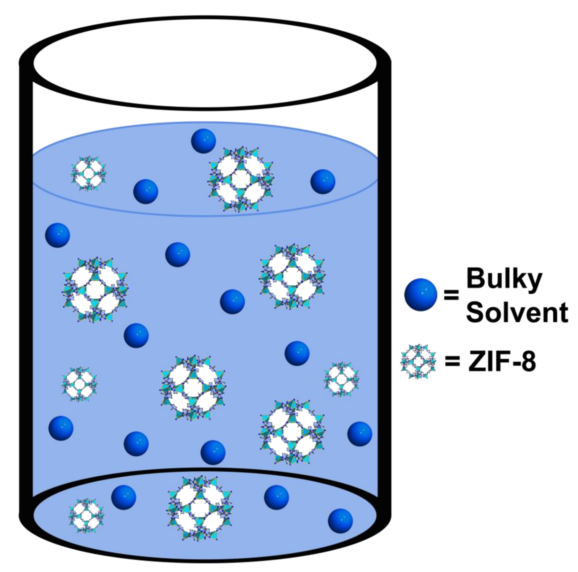
Introduction

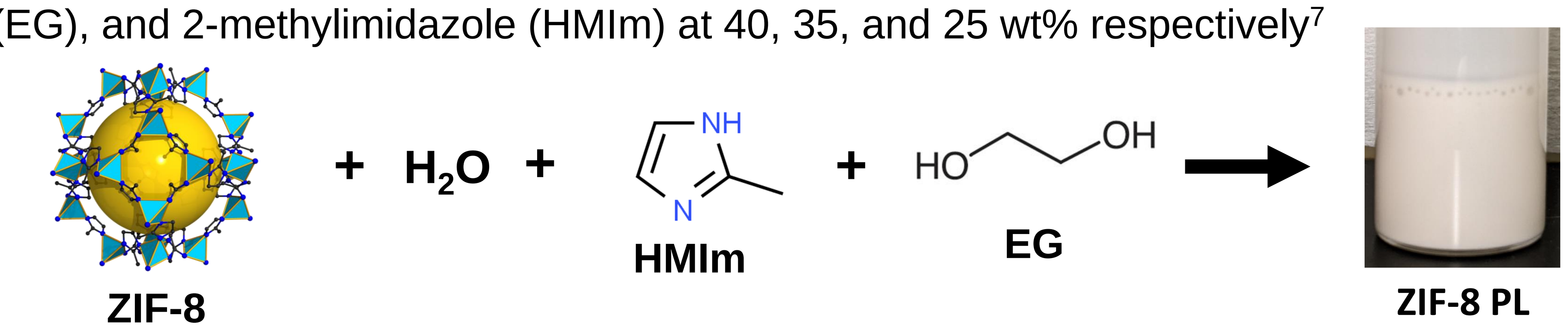
- There is an immediate need for sorbent materials capable of selectively capturing carbon dioxide (CO_2) directly from the atmosphere
- Porous liquids (PLs), a new sorbent material being evaluated for carbon capture, combine features of both solid and liquid sorbents[1,2]
- Metal-organic frameworks (MOFs) offer additional tunability of PL properties, as shown with the exemplar MOF ZIF-8[3,4]
- However, interactions within these complex systems, including solvent-sorbent and CO_2-sorbent interactions, are not well understood
- Simulated aging was used to probe the interactions of CO_2 with an aqueous ZIF-8 based PL system and its effect on long-term stability[5]
- Density analysis was used to determine solvent adsorption in ZIF-based PLs, to ultimately understand the effects of host porosity on CO_2 capture[6]
- This joint experimental and computational effort, involving multiple UNCAGE-ME PIs, has resulted in our recent publication (5) and presentations at both Spring and Fall national ACS conferences

ZIF-based Type 3 Porous Liquid



Experimental and Simulated Aging of ZIF-8 PLs

- An exemplar ZIF-8 PL was formed using previously reported solvent mixture of water, ethylene glycol (EG), and 2-methylimidazole (HMIm) at 40, 35, and 25 wt% respectively[7]

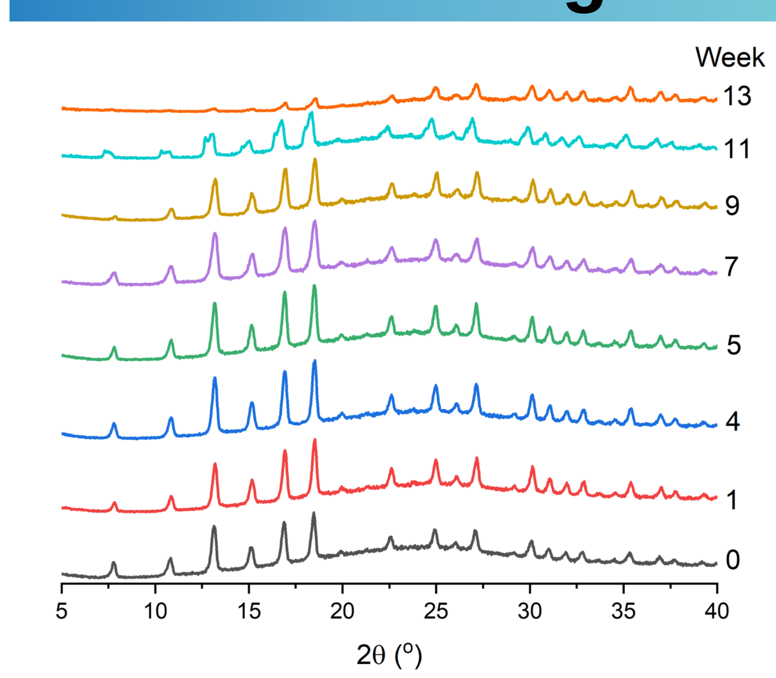


- ZIF-8 PLs were experimentally aged under air (350 ppm CO_2), N_2, or CO_2 through modification of a previously reported aging procedure[8]
- Effects of aging on both ZIF-8 and ZIF-8 based PLs were examined with X-ray diffraction, FTIR, and N_2 gas adsorption
- CO_2 uptake by PLs was monitored by changes in pH and mass

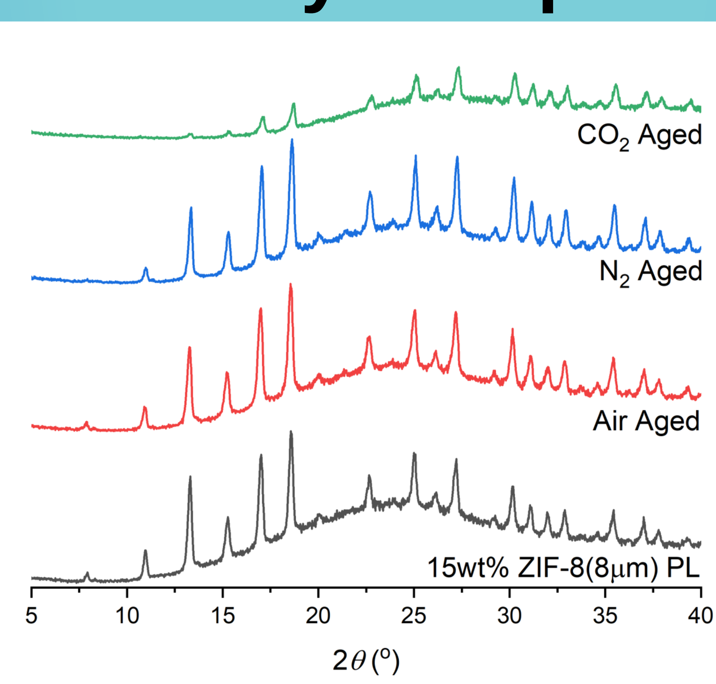
Aging Gas	Aging Time (days)	Mass Change of Aged PL (mg)	pH Change Aged PL
CO_2	7	17 ± 5	-1.48 ± 0.10
N_2	7	-16 ± 1	-0.16 ± 0.09
Air	7	-13 ± 1	-0.18 ± 0.08

- Density functional theory (DFT) was used to calculate formation enthalpies of possible CO_2 speciation within PLs
- ^{13}C NMR spectroscopy of CO_2 exposed PLs was used to validate DFT results

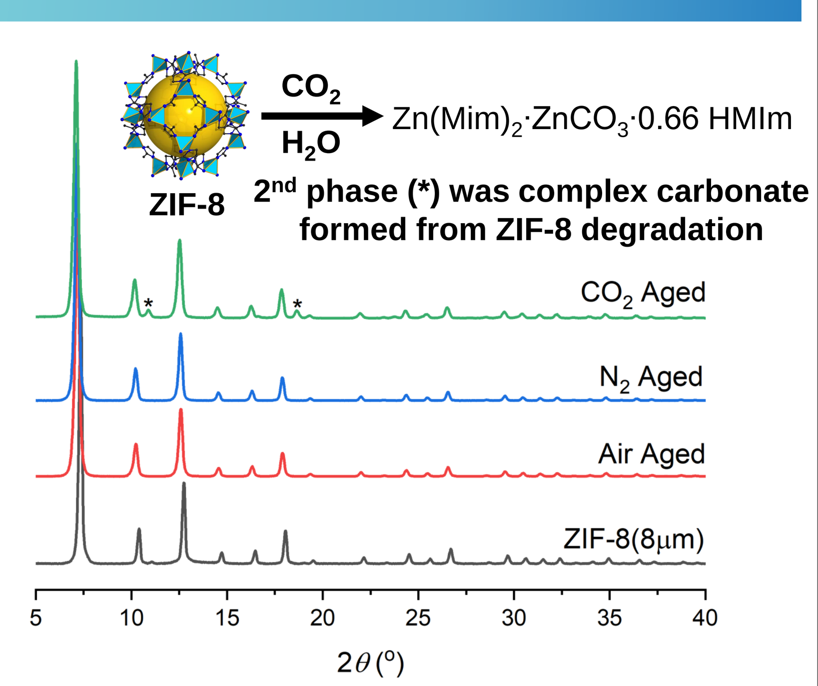
Long-Term Stability of Aqueous ZIF-8 PLs



PXRD of PL over 13 week period



PXRD of PLs after aging



Recovered ZIF-8 from aged PLs

- PLs stable in air for 9 weeks, changes at 11 weeks due to solvent evaporation not ZIF-8 degradation
- CO_2 aging caused PL and ZIF-8 degradation due to formation of carbonate species

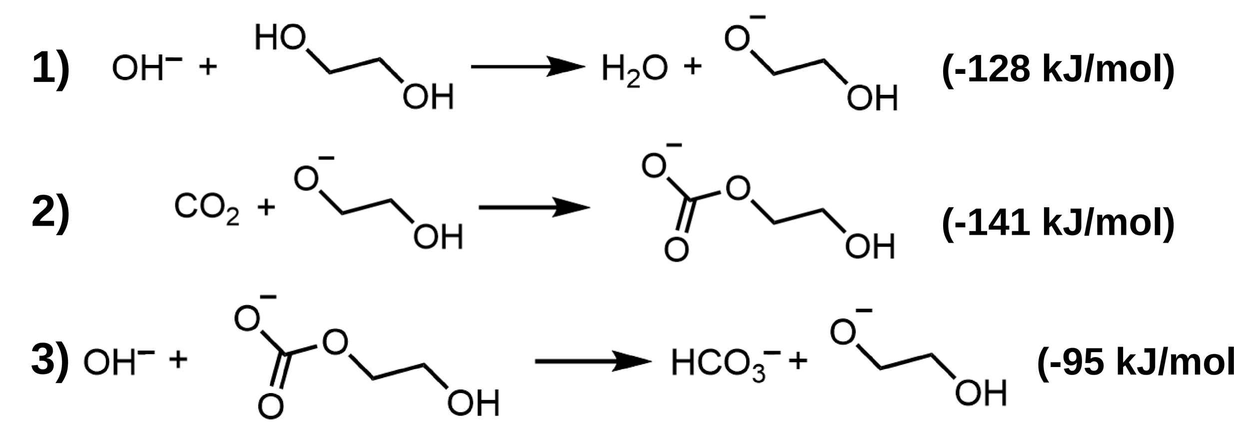
References

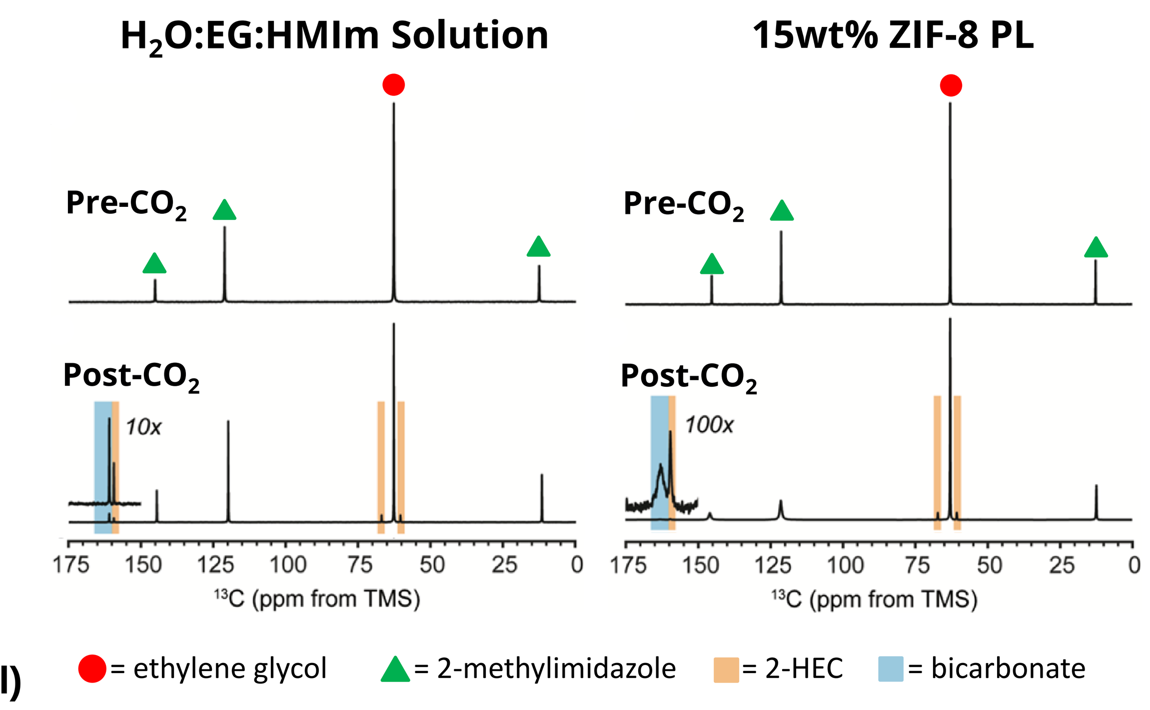
(1) Ahmad, M. Z. & Fuoco, A. *CRGSC* **2021**, *4*, 100070 **(2)** Rimsza, J. M. & Nenoff, T. M. *ACS Appl. Mater. Interfaces* **2022**, *14* (16), 18005 **(3)** Cahir, J.; *et. al. Chem. Sci.*, **2020**,*11*, 2077 **(4)** Erdosy, D. P.; *et. al Nature, **2022**, 608*, 712 **(5)** **Hurlock, M. J.**; *et. al. ACS Appl. Mater. Interfaces* **2023,** 15 (27), 32792 (**6)** **Hurlock, M. J.**; *et. al. ACS Mater. Au,* **2023,** *In Preparation* **(7)** Li, H.; *et. al.* **2018**, *182*, 189 **(8)** Mottillo, C. & Friščić, T. *Angew. Chem. Int. Ed.* **2014**, *53* (29), 189. (**9)** Zhao, Y. H.; *et. al. J. Org. Chem.* **2003**, *68* (19), 7368

Mechanism of Solvent Evolution Upon CO_2 Adsorption

- DFT calculations demonstrated that deprotonated EG favorably reacts with CO_2
- OH^- is the only species capable of EG deprotonation
- NMR studies confirmed the presence of carbonate species

Reaction Mechanism of EG with CO_2



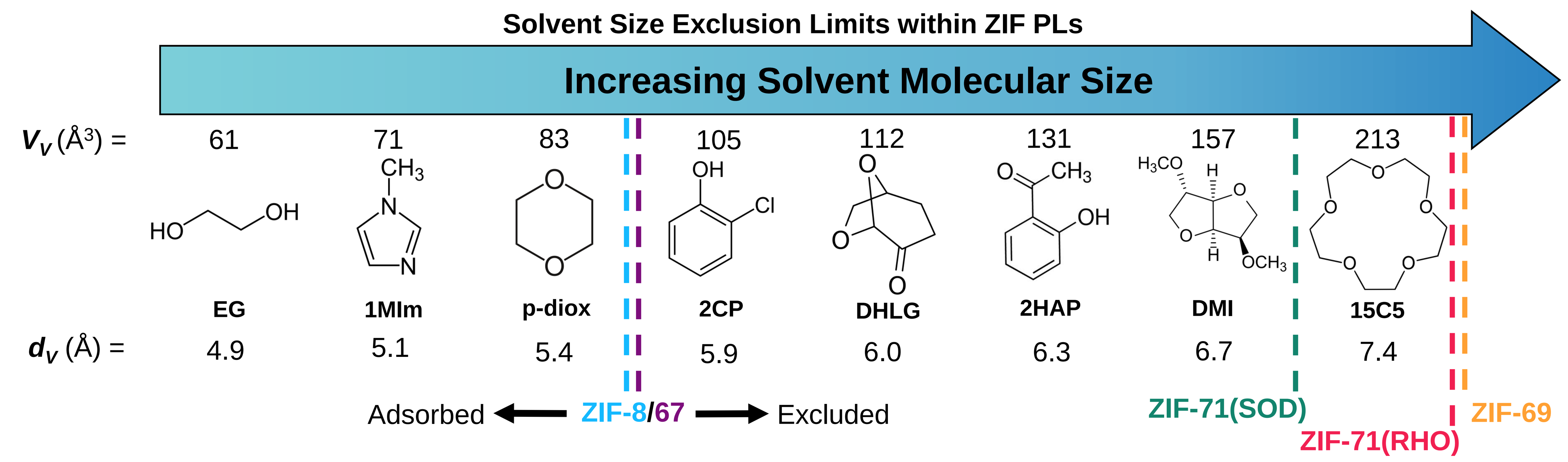


ZIF-8 did not effect the reactivity of the solvent components

Solvent Size Exclusion Limits within ZIF-Based PLs

- Density measurements were used to determine the solvent exclusion size of each ZIF through comparison to theoretical calculated densities[4]
- Solvent molecular diameters (d_V) were calculated from van der Waals volumes (V_V)[9]

Solvent Size Exclusion Limits within ZIF PLs



Pore apertures: ZIF-8/67 = 3.4 Å < ZIF-71(SOD) = 3.8 Å < ZIF-71(RHO) = 4.2 Å < ZIF-69 = 4.4 Å

- Pore aperture expansion occurred for all ZIFs, irrespective of metal node identity or framework topology
- Water (d_V = 3.2 Å) was excluded based on hydrophobicity of the ZIF frameworks

Conclusions

- ZIF-8 based PLs are stable in air for long periods of time, though solvent compositional changes caused by evaporation and CO_2 exposure lead to decreased PL stability
- Combine computational modeling and NMR spectroscopy showed the formation of multiple carbonate species within aqueous PLs upon CO_2 exposure
- Excess ligand within the PL solvent system was not sufficient to stop framework degradation and influenced the reactivity and stability of PL components over prolonged CO_2 exposure
- Density analysis of ZIF dispersions showed framework flexibility increased expected solvent exclusion limits
- This work will inform the design of next generation Type 3 PLs that maintain porosity of the solid host and possess improved long-term stabilities

Next Steps and On-Going Work:

- Utilize the solvent exclusion limit data to determine the effects of porosity on CO_2 adsorption within ZIF-based PLs
- Perform neutron diffraction studies using deuterated-ZIF-8 to determine the binding of solvent and CO_2 within aqueous ZIF-8 PLs, in collaboration with ORNL and the NOMAD beamline

Acknowledgements

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