SAND2024-09109C

Plenary PL7

Sandia National Laboratories

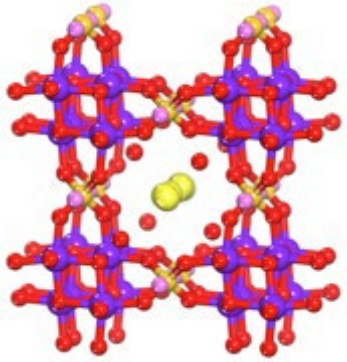
Exceptional service in the national interest

Elucidating Design Principles of Type 3 Porous Liquids for Selective Carbon Capture

Tina M. Nenoff, Jessica Rimsza, Matthew J. Hurlock, Matthew S. Christian, Dennis Robinson Brown

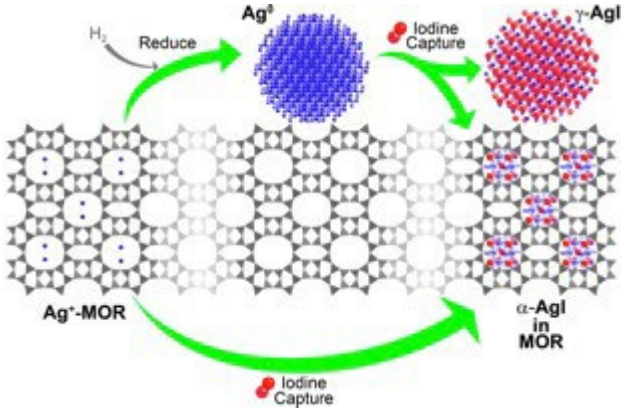
ZMPC2024
International Symposium on Zeolites and Microporous Crystals 2024, Osaka, Japan
July 24, 2024

Background: Nanoscale Materials for bulk scale applications



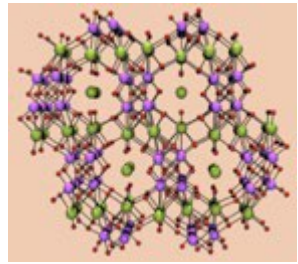
R&D100 1996
JACerS, **2009**, *92(9),* 2144
JACerS, **2011**, *94(9),* 3053
Solvent Extr. & Ion Exch, **2012**, *30*, 33

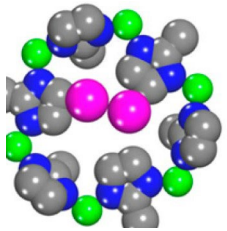
CST, Cs^+ removal from water to Pollucite Waste Form
US Patents *6,479,427; 6,110,378*

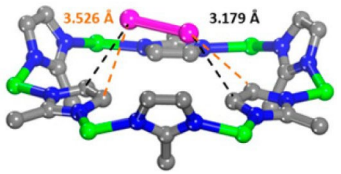


Ag-MOR I_2(g) capture & mechanisms
JACS, **2010**, *132*(26), 8897
J Phys Chem Lett, **2011**, *2*,2742
I&ECR **2017,** *56*(8), 2331

SOMS, Sr^{2+} getter, 1-step to Perovksite WF
JACS, **2002**,*124(3),*1704
US Patent 7,122,164; 2006

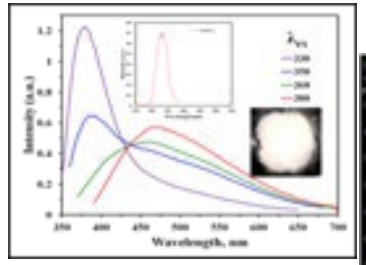


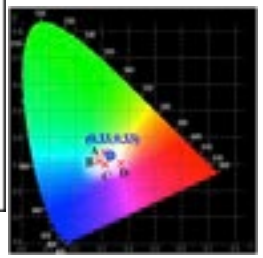




I_2/ZIF-8, Isolation to Waste Form
JACS, **2011**,*133(32),*12398
US Patent 9,117,560; 2015
JACS **2013**, *135*, 16256

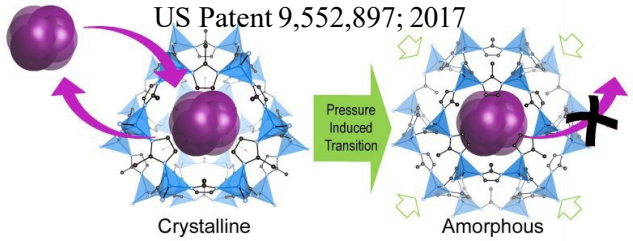
Design on the nanoscale of the Separation Material to optimize on the bulk scale



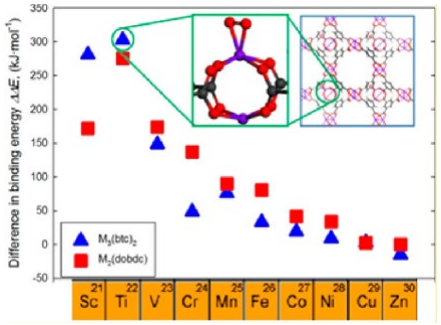


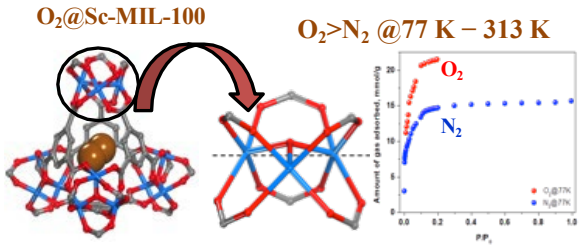
MOFs, White Light PL
JACS, **2012**,*134*(9), 3983
Chem Mater, **2014**, *26* (9), 2943
Adv. Opt. Mater., **2022**, 202200058

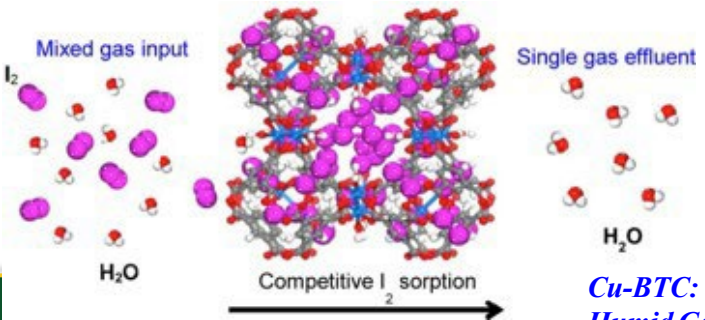
MOF Amorphization for Gas Storage
JACS, **2011**,*133*(46),18583
US Patent 9,552,897; 2017



O_2 Separations with MOFs for Energy Efficient Oxyfuel Combustion
Chem. Mater. **2016**, 28(10), 3327-3336
Chemical Science **2016**, *18*, 11528
J. Phys. Chem. C, **2015**, *119,* 6556
Chem. Mater. **2015**, *27*(6), 2018
US Patent 10,549,261; 2020

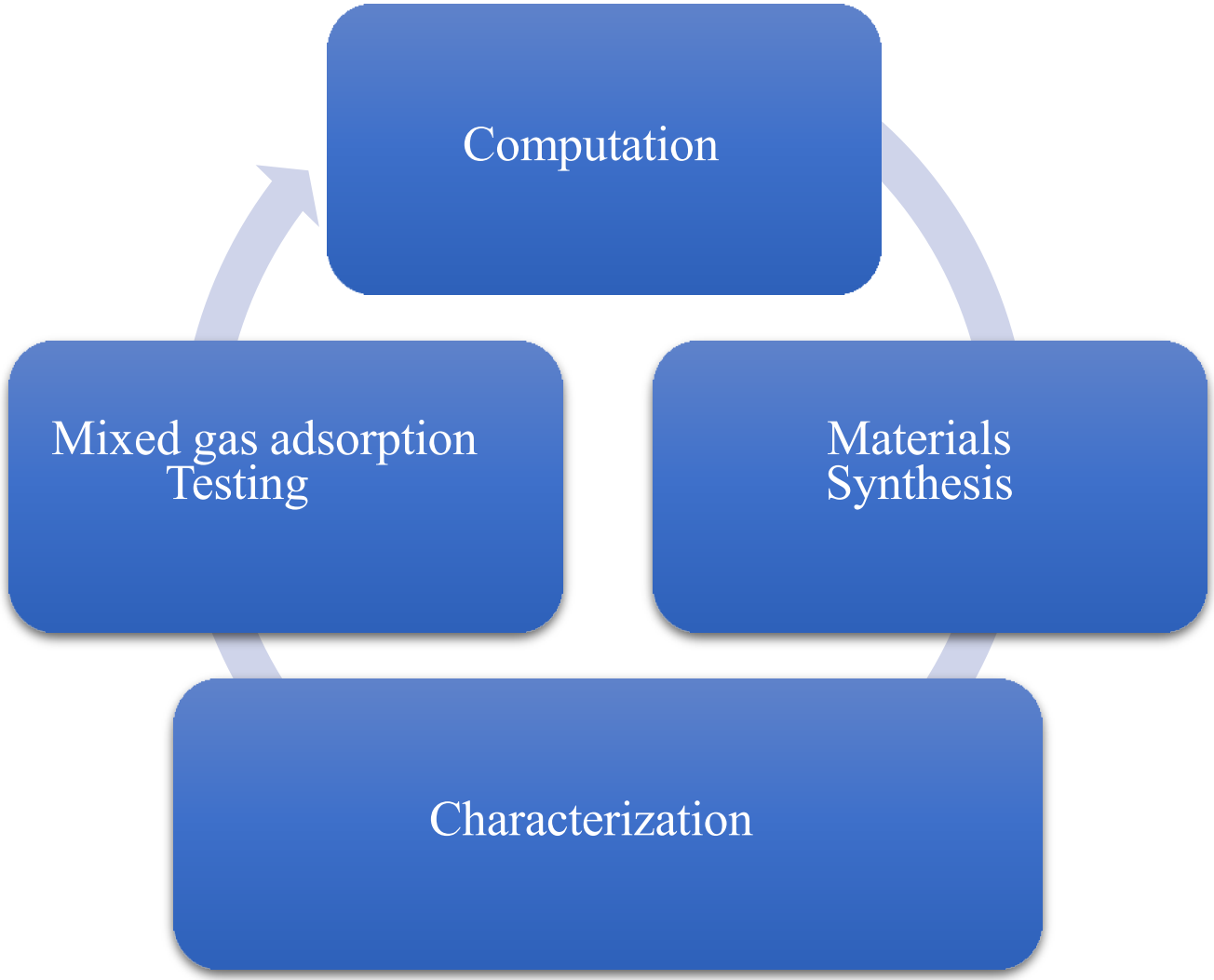






Cu-BTC: I_2 from Humid Gas Stream
Chem. Mater. **2013**, *25*(13), 2591

Multidisciplinary approach enables Rapid Materials Discovery



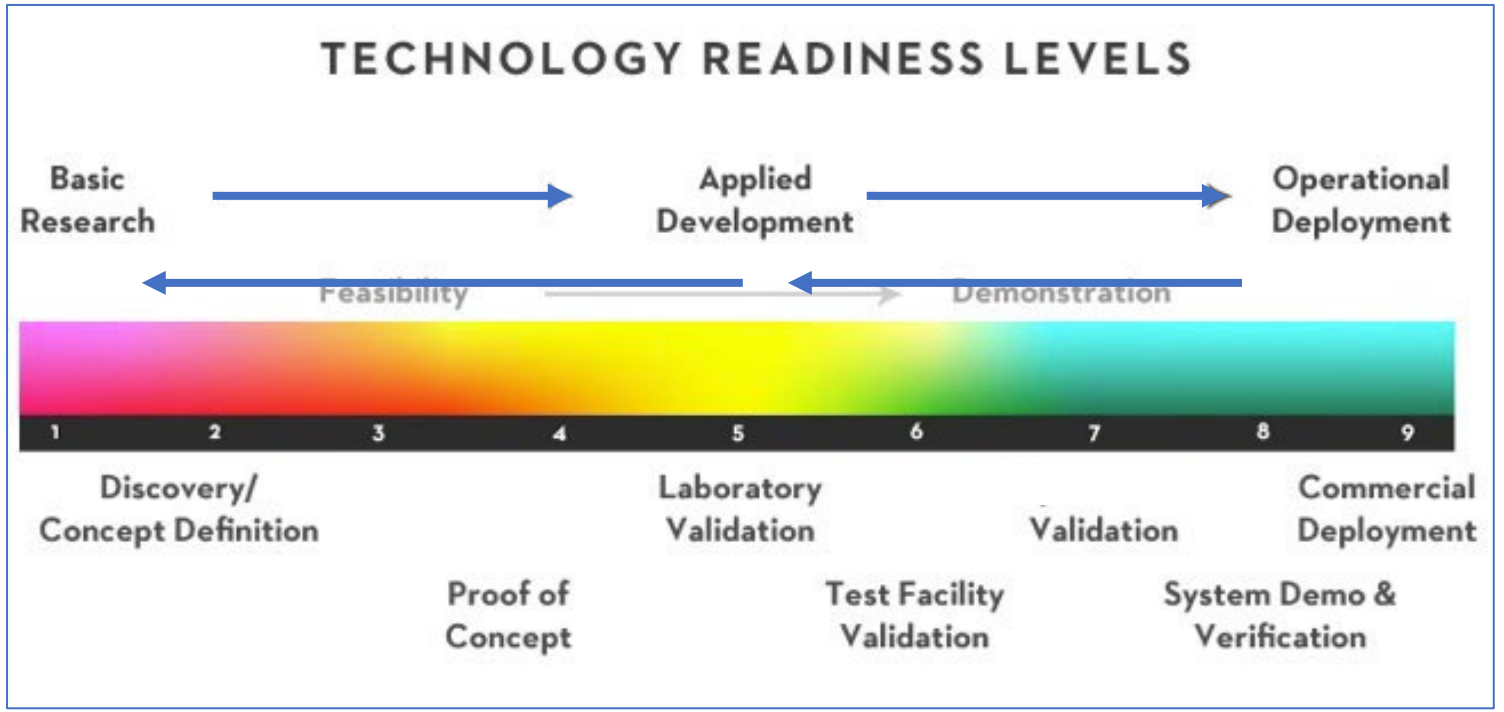
Current engagement with the Technical Community

Basic to Applied to Commercialization: fundamental research with an eye to application

Use-Inspired

My research moves **up and down** the TRL scale when opportunity arises

Enables excellent collaborations inside SNL and outside with the world

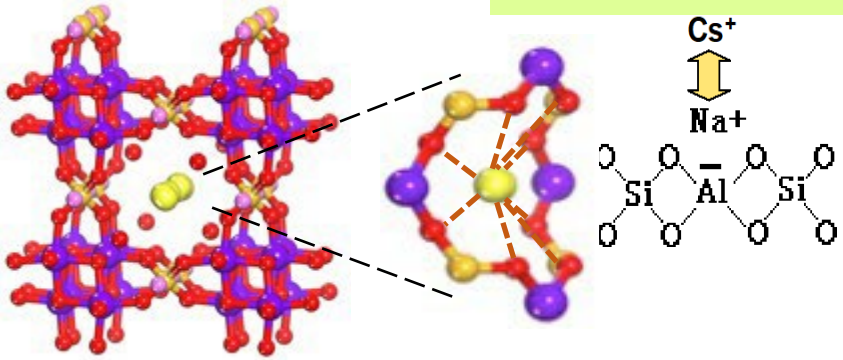


Edited from:
https://snmrec.fau.edu/ocean-energy/ocean-energy-industry.html

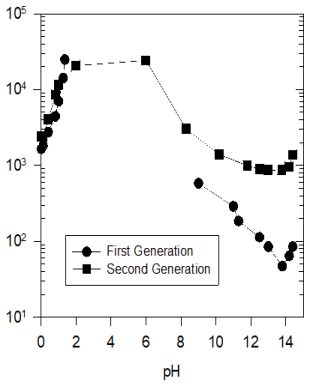
1990-2000s Geo-Inspired: Rad Ion, Highly Selective Separations & Capture TRL 1 (LDRD) - 5 (DOE/EM) - 9 (UOP LLC)

CSTs: Crystalline Silico-titanates

Research (1993): Sandia LDRD project – gram reactors
Development: DOE/EM – 1-5 gallon reactors
Commercialization: CRADA with UOP Corp.,
IONSIV™ IE-910 & IE-911 (Dec 1995)
1800 lb lots produced



^{137}Cs 30.7 y
^{135}Cs 2.3 x 10^6 y



Sandia: Distribution Coefficient of Cs on CST

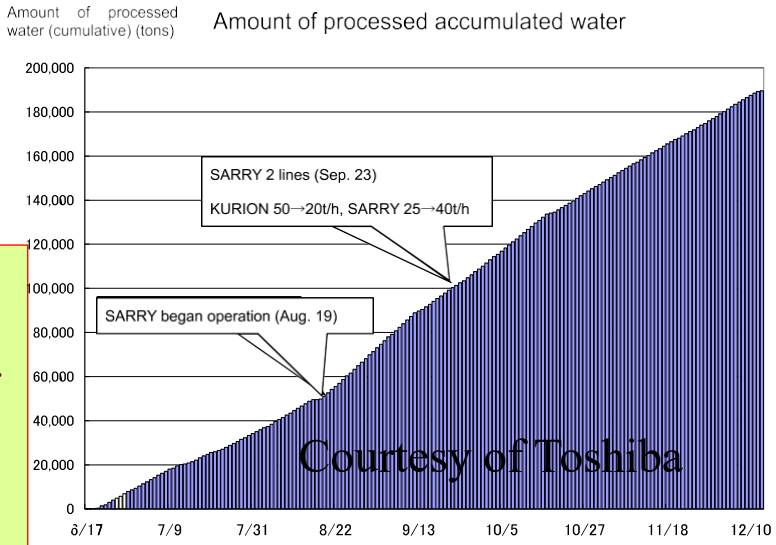
UOP IONSIV™ IE-911

Fukushima Daiichi Nuclear Power Plant Accident, March 2011
- 2011 SNL re-licensed CST IP to (Honeywell) UOP LLC who coordinated with Toshiba for implementation in the SARRY™ Process at Fukushima

SARRY™: Simplified Active Water Retrieve and Recovery System augmentation of Accumulated Water processing Facility

2011: UOP re-licensed CST IP, in production of 40K+ lots within 2 months of Fukushima accident

SARRY was installed August 2011, decontamination factors of Cs SARRY process is 5 x 10^5

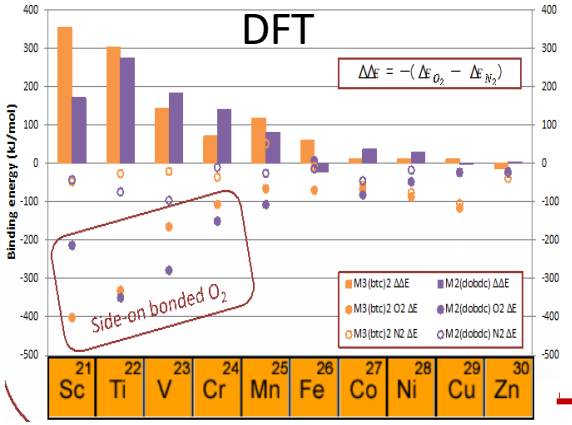


By December 2015, 160+ million gallons of Cs^+ contaminated seawater were cleaned with the *SARRY™ Process.*
Decon work completed.

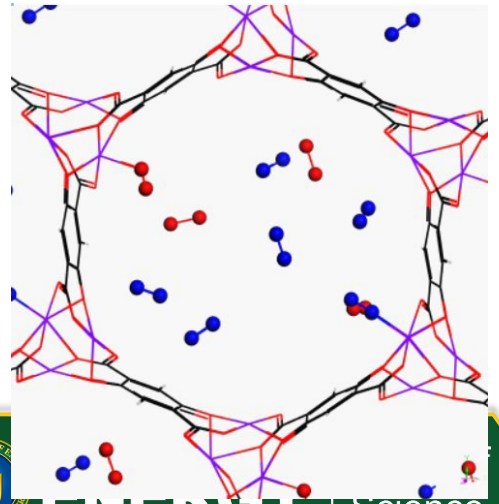
2010s, Computationally Designed: MOF for Ambient Oxygen Separations from Air. TRL 1 (LDRD) - 8 (DOE/SBIR I & II)

High Performance Computing (*4000 processor hrs, 6000 processor days (Redsky, Skybridge)*) to *design* materials, *guide synthesis,* and *validated* design via *testing.*

Computationally Designed Materials

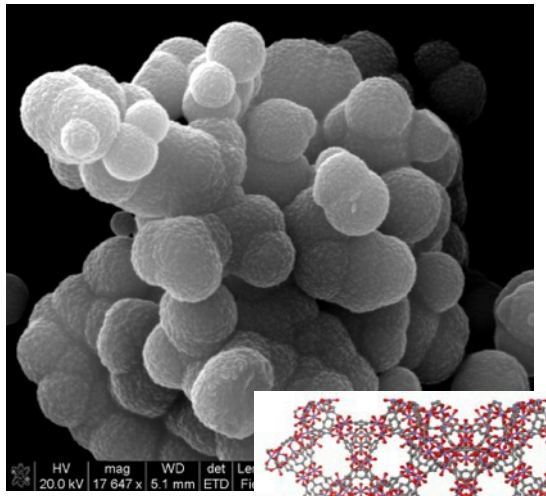


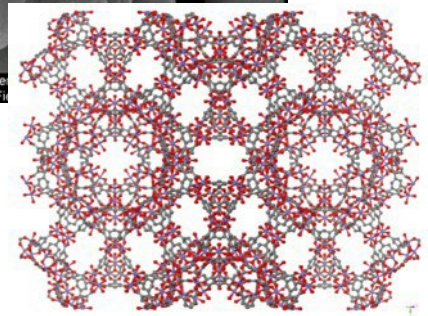
Ab initio MD



PCCP **2016**, *18*, 11528
J. Phys Chem C, **2015**, *119*, 6556

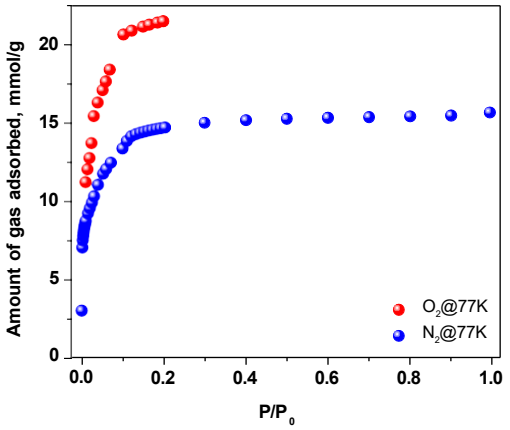
Novel Materials Synthesis

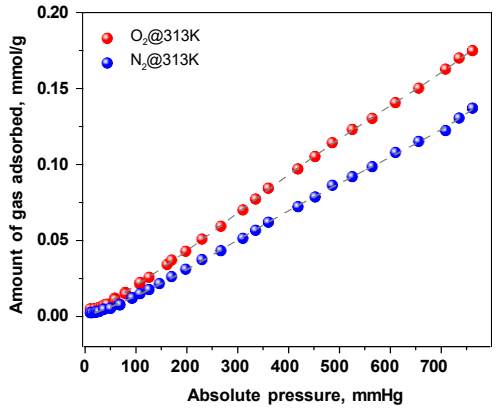




Chem. Mater. **2016**, 28(10), 3327
Chem. Mater. **2015**, 27(6), 2018

Exp Gas Testing





Industrial Scale Up To Commercialization

IP: US Patent # 10,549,261 Awarded Feb 4, 2020

DOE/SBIR Phase I FY19 (IP licensed), two industrial partners

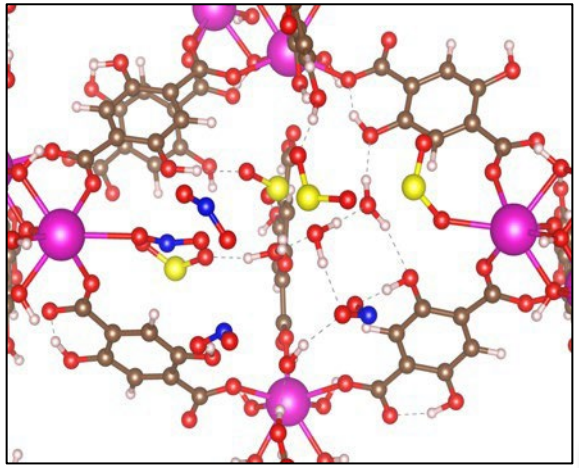
DOE/SBIR Phase II FY21 (IP re-licensed), 1+ industrial partners

DOE/SBIR Phase IIB FY22- 24 (scale up) 1 industrial partner

2020s Computationally Driven, Experimentally Validated, Rapid Materials Discovery

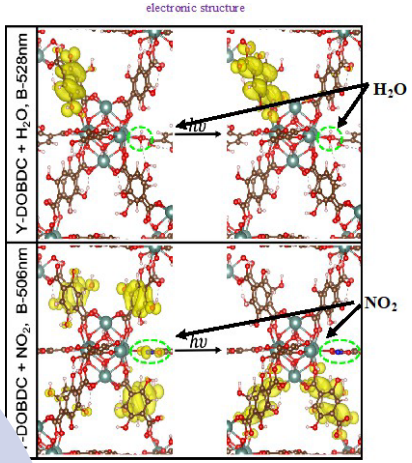
TRL 1: Materials design & realization of adsorbents to selectively adsorb industrial caustic acid gases

Optimized Eu-DOBDC + $4H_2O$ + $4NO_2$ + $4SO_2$



DFT & AIMD for mixed Gas competitive binding

PCCP, **2019**, 21, 23085
ACS AMI, **2020**, 12, 4, 4531
Angew Chem., **2021**, *60*(20), 11514
Chem-Eur. J., **2022**, *28*(58) e202201926



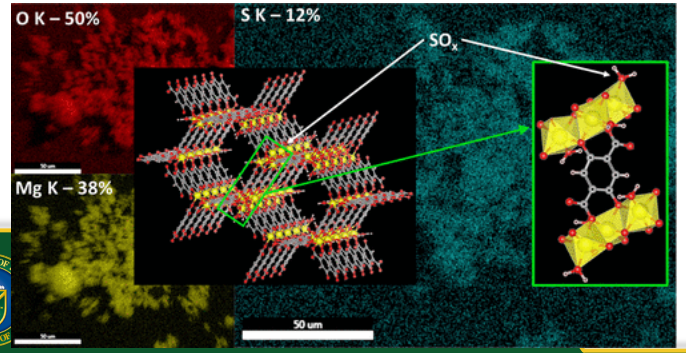
Industrial Acid Gas Adsorbents: RE-DOBDC MOFs

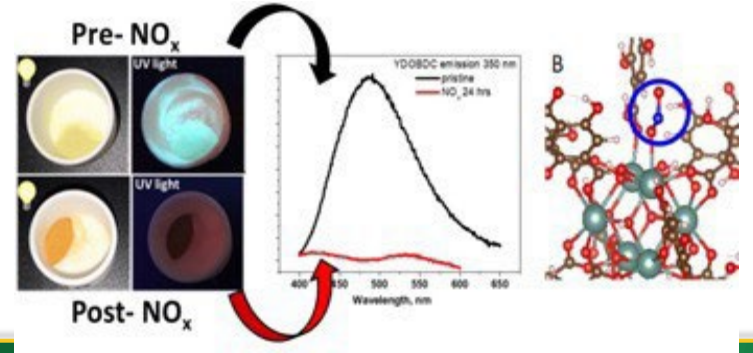
ACS AMI **2019**, *11, 46, 43270*
ACS AMI, **2020**, *12, 17, 19504*
ACS AMI, **2020** *12, 20, 22845*
ACS AMI, **2021**, *13, 47, 56337*
JACS Au, **2022**, *2*, 8, 1889

Computation → Materials Synthesis → Characterization → Mixed gas adsorption Testing → Computation

Mixed H_2O + SO_x adsorption testing

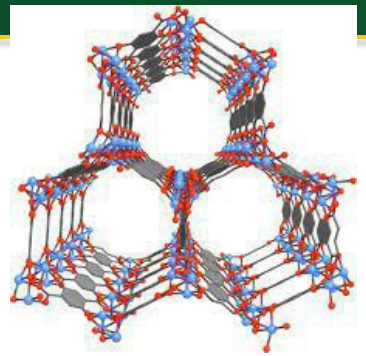
ACS AMI, **2021**, *13*, 6, 7278



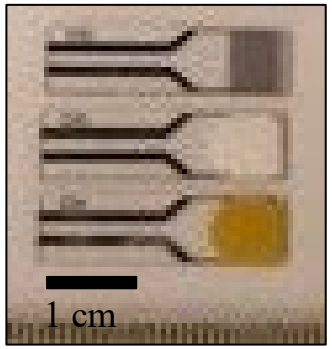


2020s con't: BES foundational Science to TRL 5-6+

NA-115 (A&L) Sensor Development

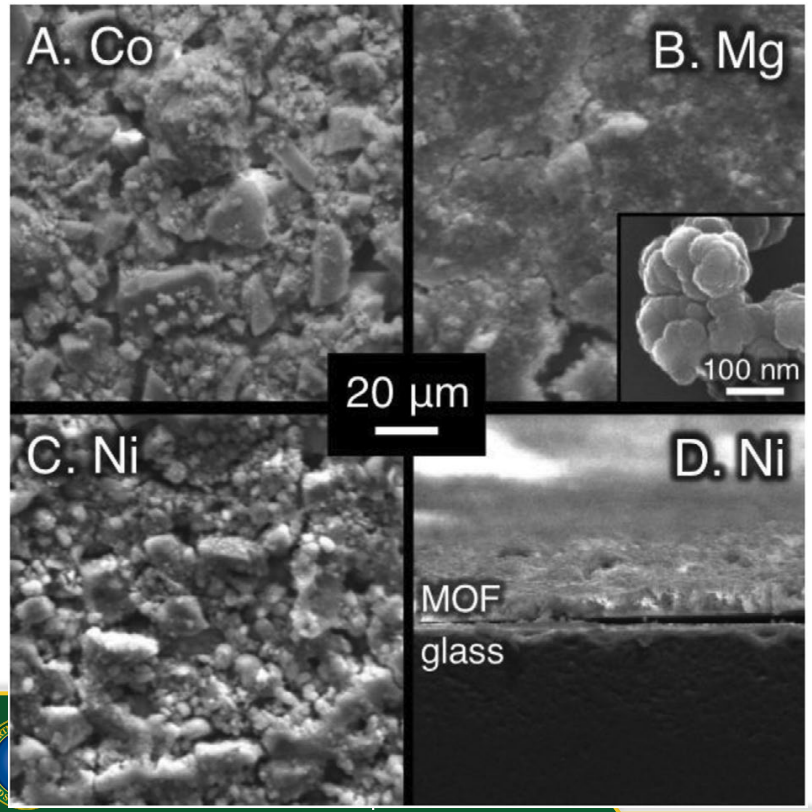


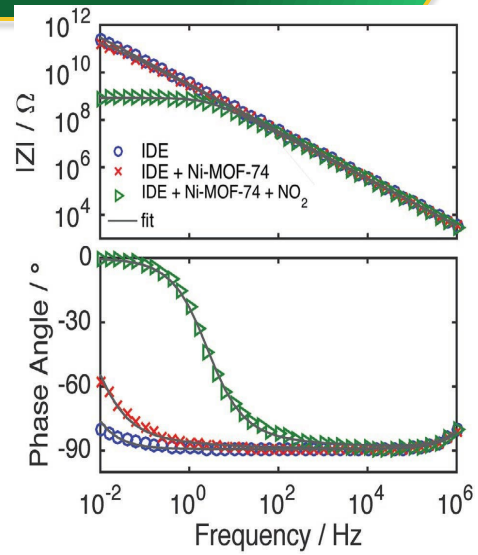
M-DOBDC MOF;
MOF-74; M= Co, Mg, Ni

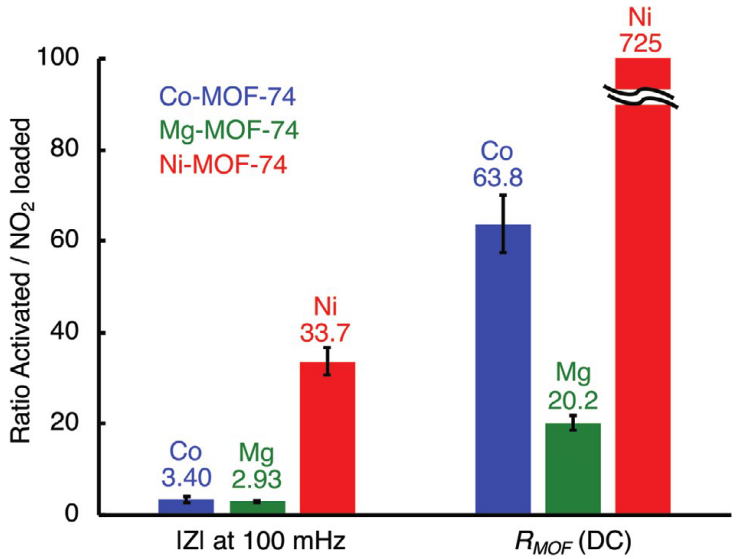


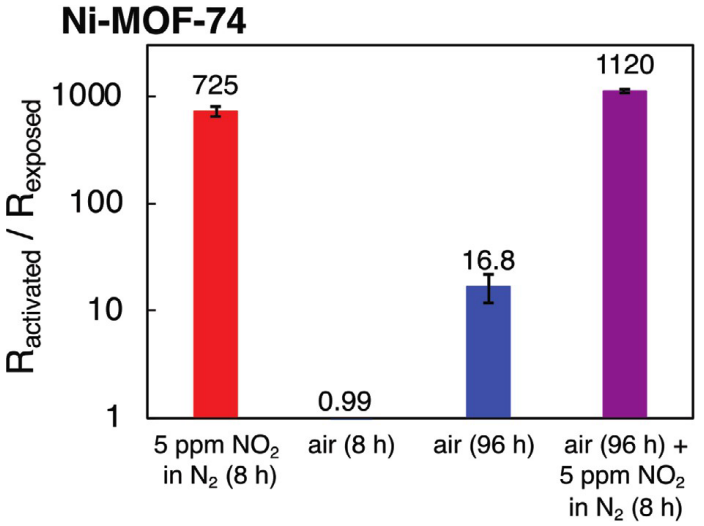
Supported by ***BES/EFRC fundamental studies*** including DFT, MOF synthesis, gas adsorption testing, & materials characterization, we produced a ***near-zero power, highly selective direct electrical readout gas sensors**** (***NA-115, A&L***)

- Leveraged to new FY21-25 DOE/DoD *JMP* project
- Leveraged to new FY22-24 *KCNSC project*, widget build
- Leveraged to Energy I-Corps National Winner 2022
  DOD contractors, licensing negotiations FY22-23









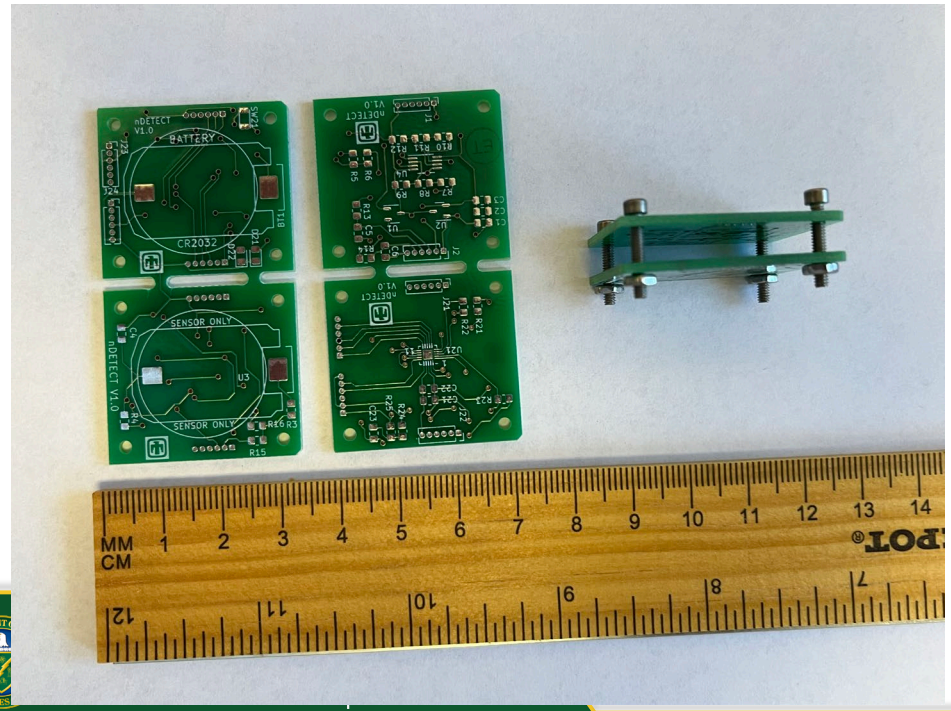
ACS AMI, **2017**, *9*, 44649
Micro. Meso. Mater. **2019**, *280*, 82
ACS AMI, **2019**, *11*, 27982
Adv. Func. Mater.* **2020, *1407*, 2006598

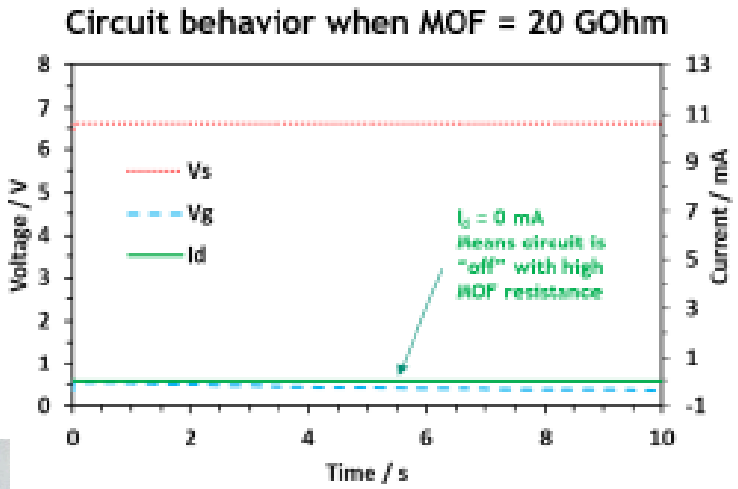
Membranes **2021**, *11*, 176
I&ECR **2021**, *60*, 21, 7998
I&ECR, **2021**, *60*, 40, 14371

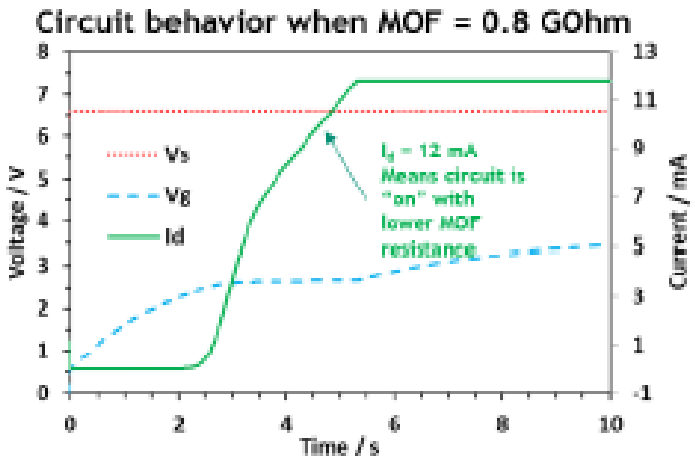
Chem. Soc. Rev. **2022**, *51*, 324
I&ECR, **2023**, *62* (5), 2336
ACS AMI, **2023**, *15*, 31, 37675

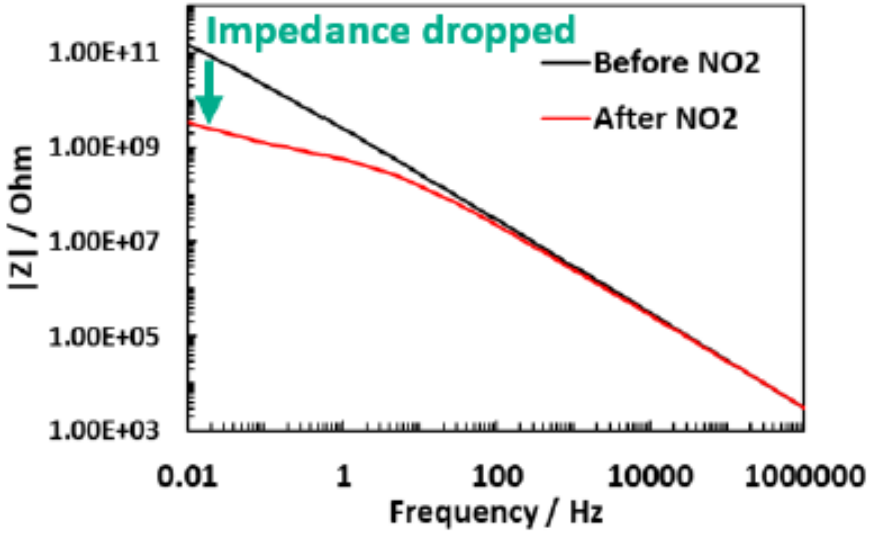
Low power MOF-based sensor with Simple, Passive Detection Gas System

It is comprised on a
-MOF resistance changes upon exposure to a target gas;
- an electrical circuit,
- a user interface indicator configured to signal exposure to the target gas
- a field-effect transistor (FET).
Current from the power source to flow in the electrical circuit and causing the user interface indicator to signal exposure to the target gas.









Wall Street Journal Profile: Nanoporous Sensors Research

These Tiny Ultra-Porous Crystals Could Transform Cancer Treatments and More

By Dominique Mosbergen

Oct. 15, 2022 9:47 am ET

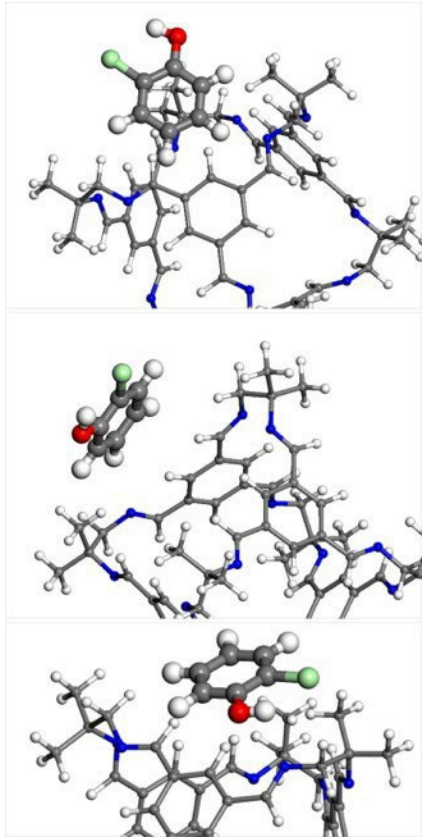
https://www.wsj.com/articles/these-tiny-ultra-porous-crystals-could-transform-cancer-treatments-and-more-11665841634?mod=life_work_featured_strip_pos1

Tina Nenoff, a senior scientist at Sandia National Laboratories: MOFs could be used as sensors to detect toxic gases or to separate gases.
PHOTO: STEPHANIE BLACKWELL/SANDIA NATIONAL LABORATORIES

- "Tina Nenoff, a senior scientist at Sandia National Laboratories, a federally funded research laboratory that specializes in national security, said MOFs can be expensive to make, particularly when they include costly metals like zinc or gold. As technology improves and more MOFs are created, she said she expected costs to drop. Dr. Nenoff is exploring how MOFs could be used as sensors to detect toxic gases or to separate one gas from another. The Department of Energy and Department of Defense have funded research into these sensors, Dr. Nenoff said, which she noted could one day be used by the U.S. military to detect the chemicals that aging munitions emit into the environment, among other uses. "Depending on how you design them, how you decorate them, you can make MOFs very selective for almost any application," said Dr. Nenoff."

2020s Computationally Driven, Experimentally Validated, Rapid Materials Discovery

TRL 1: Materials design & realization of adsorbents to selectively adsorb industrial caustic acid gases



CO_2 DAC adsorption and stability testing

-*ACS Applied Materials & Interfaces* **2023**, 15 (27), 32792

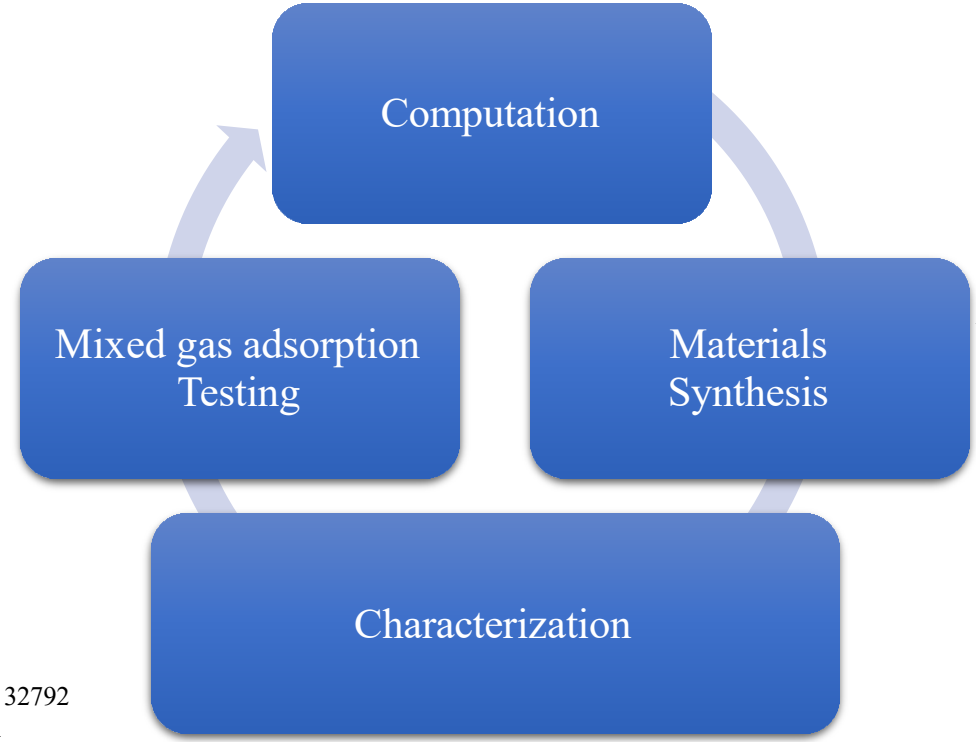
-"Deformation of ZIF-8 cages via CO_2 Adsorption in Type 3 Porous Liquid", *J. Phys. Chem. C*. **2023**, in preparation

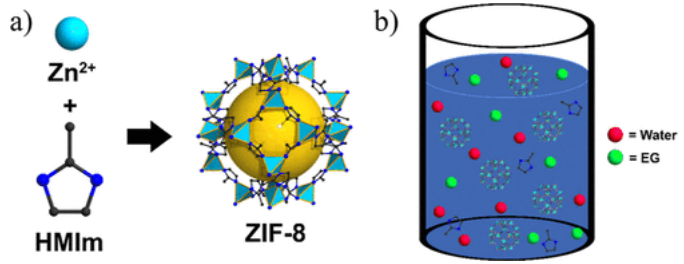
DFT & AIMD for mixed Gas competitive binding

-*ACS Appl. Mater. & Interfaces*, **2022**, 14(16), 18005

-*J. Mol. Liq.,* **2023**, 377, 1, 121536

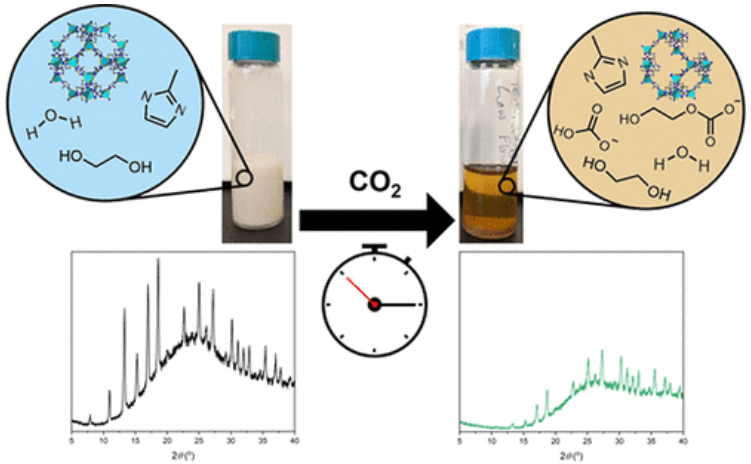
-*J. Phys. Chem. A,* **2023**, 127, 13, 2881





Green House Gases Adsorption: Porous Liquids

-*"Pore Space: Solvent Exclusion Limits of ZIF-based Type 23 Porous Liquids" ACS Mater. Au,* ***2023****, in prep.*



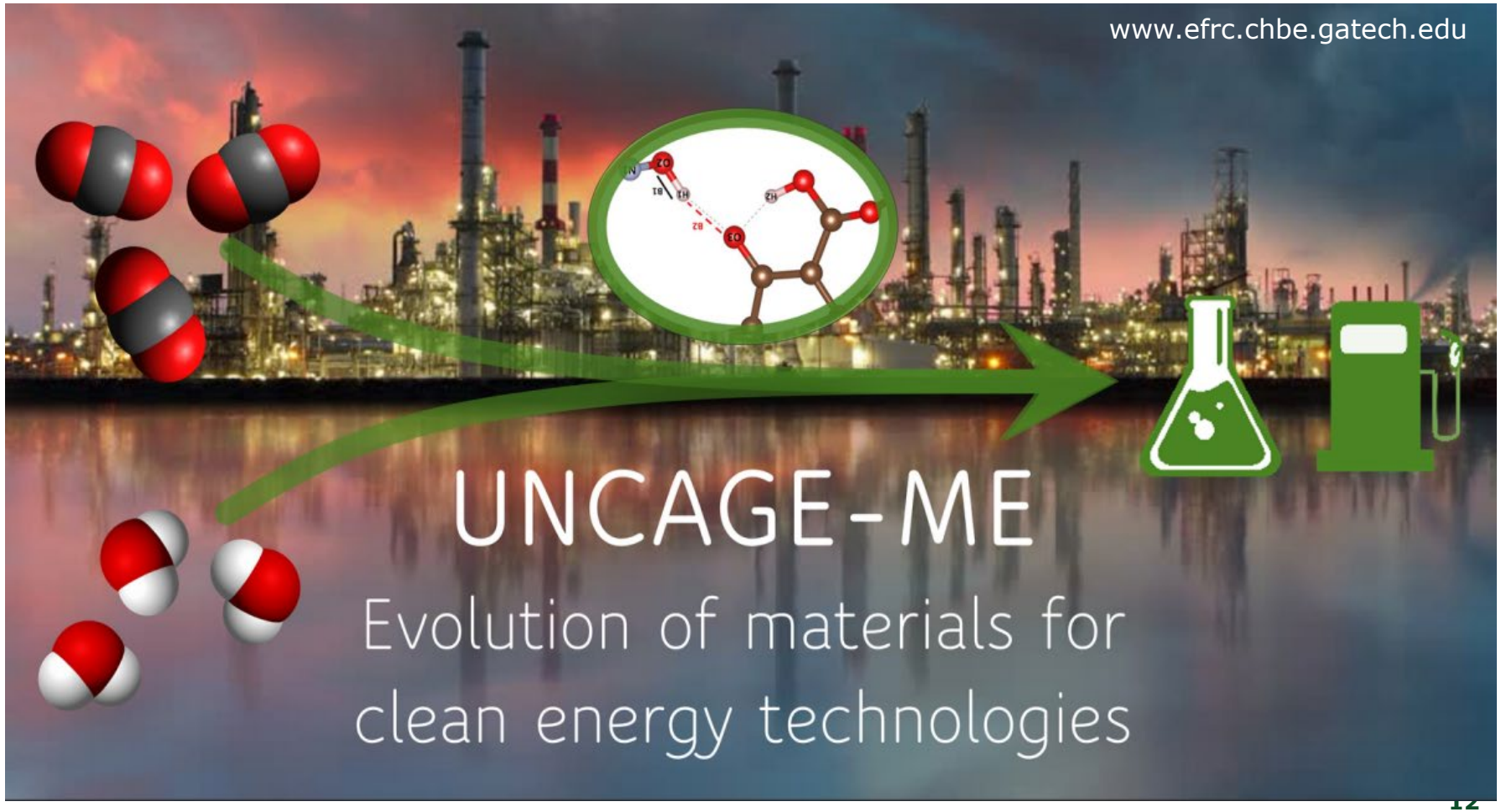
DOE/BES/EFRC: "UNCAGE-ME" Complex, Multidisciplinary Teamin

UNCAGE-ME Mission Statement: Develop a deep knowledge base in the characterization, prediction, control of materials evolution in the presence of realistic contaminants, processes & mixtures ***to accelerate materials discovery for sustainable production and utilization of H_2 and CO_2***

Phase 1 2014-2018
Phase 2 2018-2022

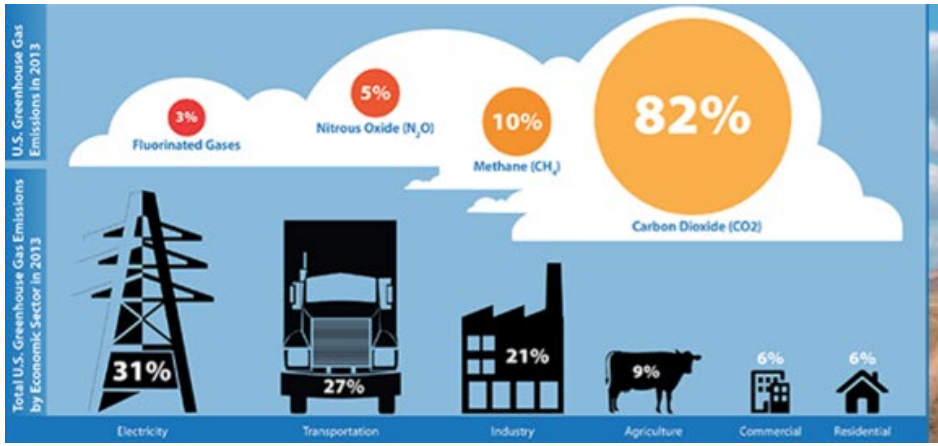
Phase 3 2022-2026:
4 years
$13.2M total

8 partner institutions:
GA Tech Univ
Oak Ridge National Lab
Sandia National Labs
University of AL
USC
Lehigh University
University of MI
University of FL



- International action is required to limit greenhouse gas emissions, primarily CO_2, to limit global warming to 2°C
- Direct air capture (DAC) is an emerging technology that allows for flexibility technology placement, but is technologically demanding with unique requirements compared with capture from post-combustion streams
- DAC is identified as a critical technology for global carbon management in the *US DOE Report on Basic Research Needs for Carbon Capture: Beyond 2020* and the *US National Academies Report on Negative Emission Technologies and Reliable Sequestration: A Research Agenda*

The ability to selectively capture CO_2 from dilute gases will enable *low cost, energy efficient* carbon capture that can be performed anywhere, without requiring technologies to be co-located with carbon sources.



CO_2 concentration in ambient air is ~400 ppm, requiring a CO_2/N_2 selectivity of ~2000 and a CO_2/O_2 selectivity of ~50 for DAC, far beyond current technological capabilities

Property	Ambient Air	Post-Combustion Streams
Amount of CO_2	3 Tt	20 Gt/year
Concentration	~400 ppm, infinite, uniform	5-15%, high flow
Temperature	10-30°C,	45-75°C
Contaminants	Low	SO_x, NO_x, Hg, particulates
Humidity	~49% RH	~80% RH

Oschatz and Antonietti. *Energy & Environ. Sci.* 11.1 (2018): 57-70.

Pacala et al. Negative emissions technologies and reliable sequestration: a research agenda. Washington, DC: The National Academies Press: **2018**. Jones *Annual review of chemical and biomolecular engineering* **2011,** *2*, 31-52.

Greenhouse Gas capture – Amine technologies

- Efficient and sustainable technologies to separate carbon dioxide (CO_2) from other gases is important for a number of processes, including post-combustion carbon capture, natural gas sweetening and biogas upgrading
- Current technologies for separating CO_2 from methane (CH_4) are based on CO_2-selective solvents such as aqueous amines or polyethylene glycol ethers (PEGEs)
- The high regeneration energy requirement of aqueous amines, and the relatively low selectivity and CO_2 capture capacity of PEGEs compared to aqueous amines
- Solvents that perform better in reversibly dissolving large amounts of CO_2 selectively in the presence of other gases are of high interest
- Porous liquids (PLs), are an emerging type of solvents that combine the advantages of the well-defined porosity of microporous solids with the fluidity of liquid

Porous Liquids (PLs)

- **Porous liquids (PLs)** = stable combination of solvent and porous cages that create a liquid with *permanent porosity*.
- Intrinsic porosity exists inside the porous hosts, which is stable due to steric exclusion of the solvent.
- Neat liquids have extrinsic and *transient porosity* due to cavity formation and does not provide stable adsorption sites.

- PLs are not simply mixtures of a solvent and a solid. The structural and chemical ordering governed by the interactions between the different components and molecules to form a stable, complex liquid with tunable adsorption properties.

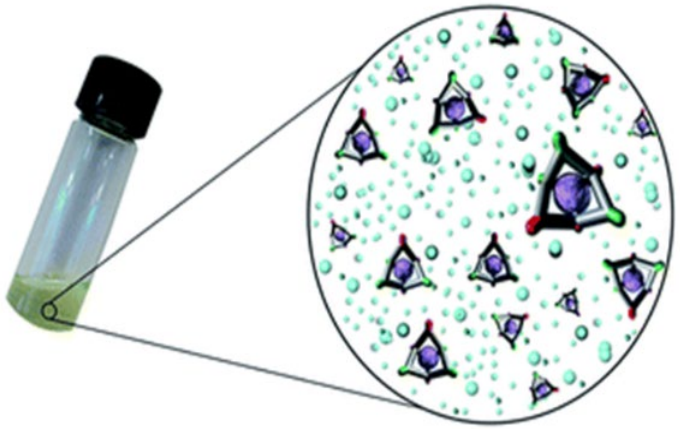
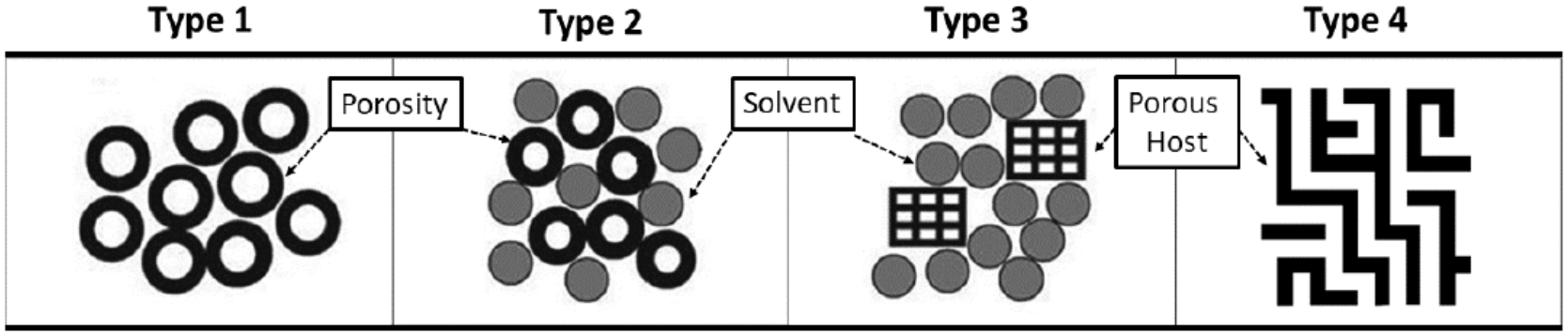


Figure 2: Schematic of Type 2 porous liquid with dissolved gases (purple)

Giri, Nicola, et al. *Nature* 527.7577 (2015): 216-220.

Four types of PLs have been reported since their discovery in 2015



PL Types

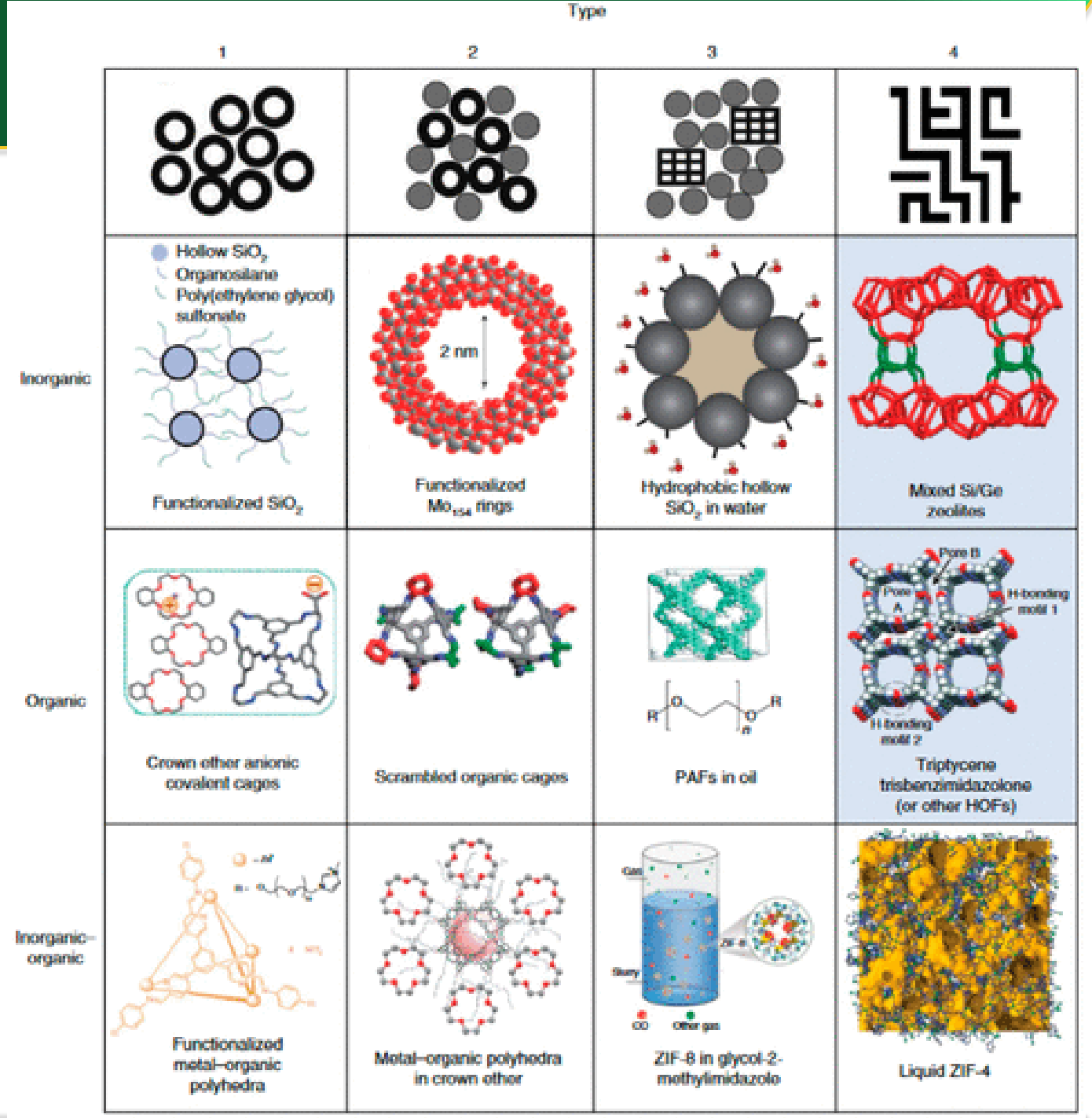
Schematics of PL types.

-Type 1 PLs consist of intrinsically porous hosts (open circles); RARE

-Type 2 PLs contain dissolved porous hosts in sterically hindered solvents (filled circles); true thermodynamic solutions; TUNABLE COMPOSITIONS.

-Type 3 PLs consist of microporous hosts (square grids) within a sterically hindered solvent; form suspensions and slurries and require control over particle size and solid-liquid interactions; *MOST TUNABILITY IN COMPOSITIONS*.

-Type 4 PLs are neat microporous hosts that form transient, strongly associated liquids; RARE



Invited Perspective:

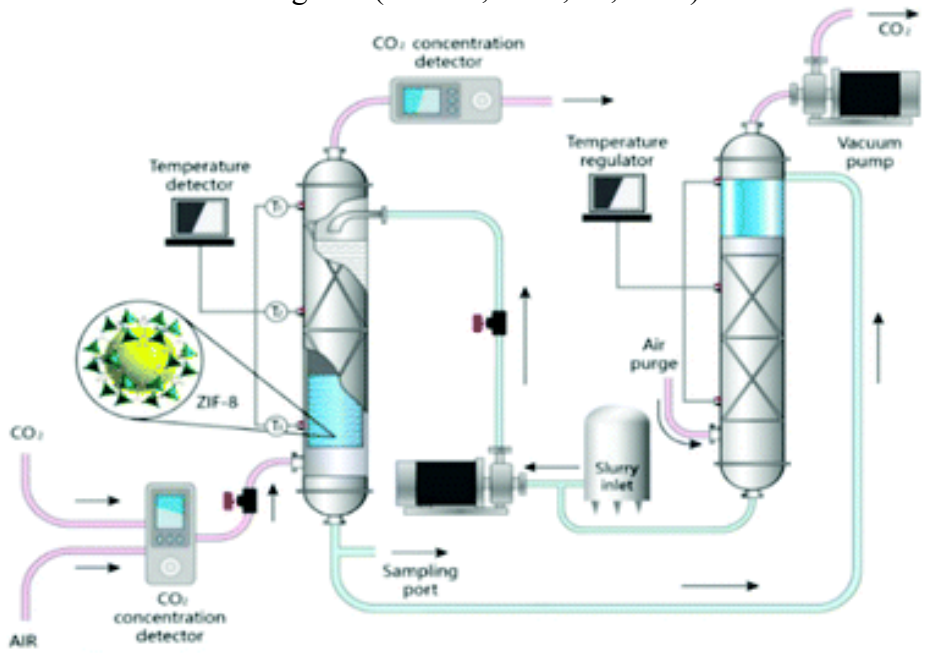
Rimsza & Nenoff, "Porous Liquids: Computational Design for Targeted Gas Adsorption" *ACS AMI* **2022**, *14*, 18005-18015

Porous Liquids (PLs)

- Utilization of industrial infrastructure with enhanced selectivity tuned to greenhouse gases of interest
- For Example: S. James team (Tsang, et.al, *Materials Today*, **2022**, *60*, 9-16)
  - Dispersing ca. 12.5 wt% CO_2-selective zeolite rho solid into the commercial CO_2 capture solvent Genosorb converts it into a porous liquid with at least 2.5 times greater CO_2 capacity and CO_2/CH_4 selectivity compared to Genosorb itself.
  - This is predicted to result in more economical separation processes, particularly for biogas upgrading.

- PLs performs as adsorption for selective separation
- PLs possess high adsorption capacity and efficiency compared to the solvent
- Can be engineered into continuous cyclic separations processes
- Translation from absorption to adsorption means the high required rege aspect compared to solvents decreases
- CO_2 captured by amine solutions is a traditional industrial process for CO_2 removal, possible to upgrade system to PLs instead of amines

Schematic diagram of sorption-desorption unit using PLs (I&ECR, 2020, 59, 6154)



Func. Org. Liq. 2019, 39; Angew. Chem. 2018, 57, 11909; ACS AMI 2021, 13, 932; Nat. Comm. 214, 5, 5147

1) Materials & Performance Design by Modeling: Computational design for targeted gas adsorption

Invited Perspective: Rimsza & Nenoff, *ACS Appl. Mater. Interfaces* **2022**, *14*, 18005

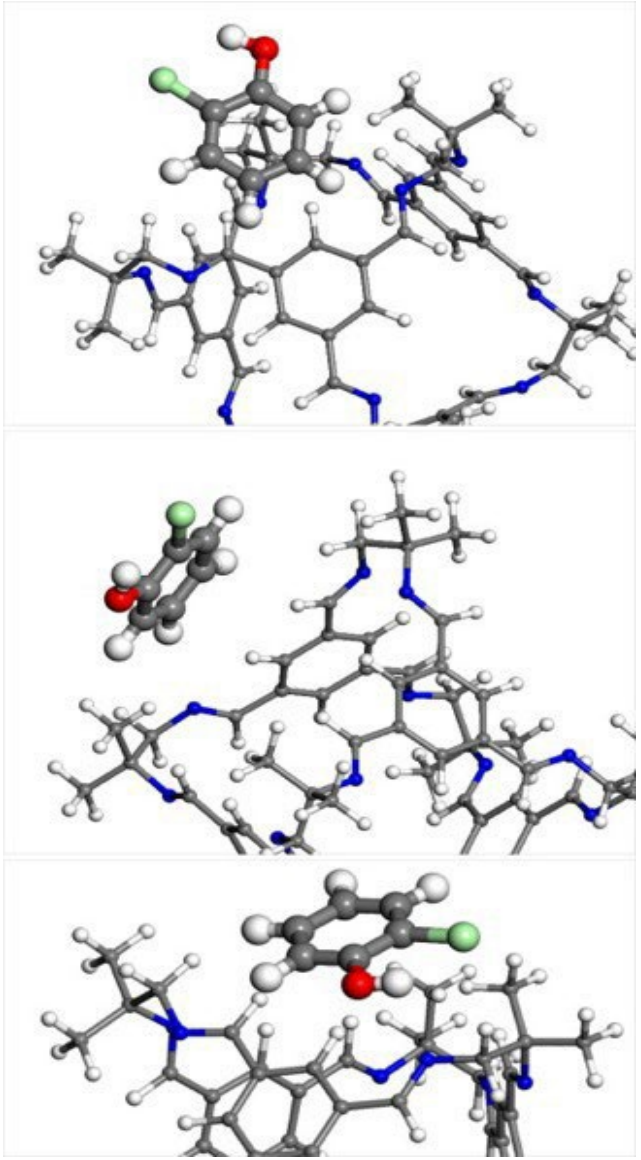
The unique gas adsorption capabilities of porous liquids (PLs) and the

Binding comes from
- the structure (multiple gas binding sites in the pore and on the cage surface)
- varying binding mechanisms (hydrogen-bonding and π–π interactions)
- selective diffusion in the solvent

Tunable PL compositions will require fundamental investigations of
- competitive gas binding mechanisms,
- thermal effects on binding site stability, and the
- role of nanoconfinement on gas and solvent diffusion

that can be accelerated through molecular modeling

Modeling of structure-property relationships can also help predict possible mechanical based regeneration

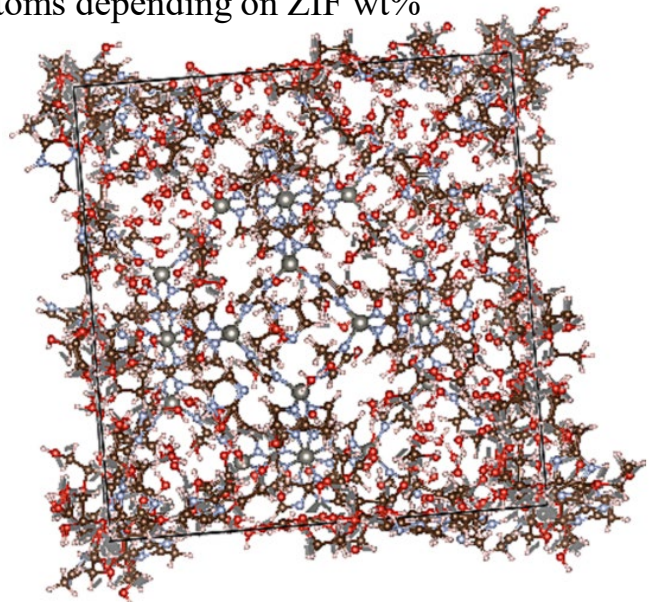


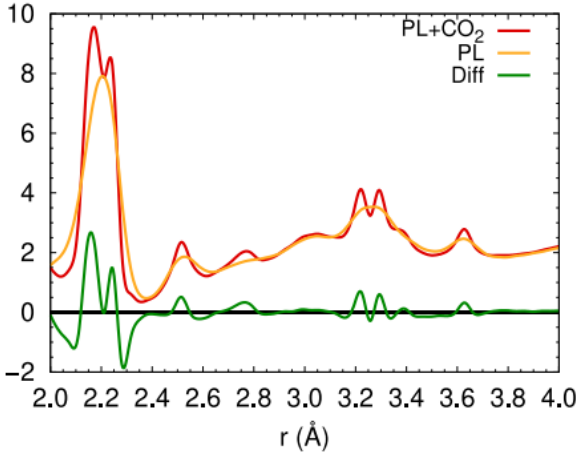
Predicting CO_2 adsorption mechanisms at the ZIF-9 interface in Type 3 PLs

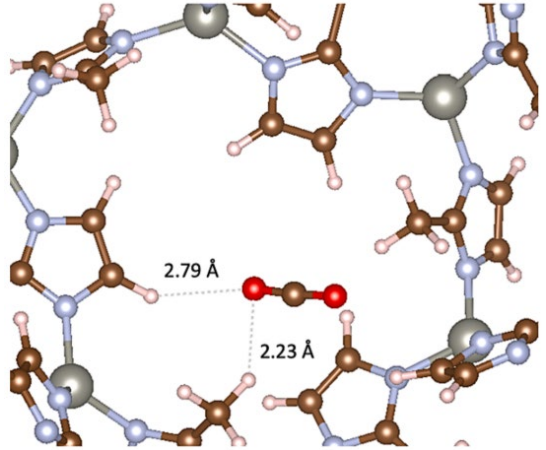
- PLs great interest due to their permanent porosity and high adsorption capacity
- Use of ZIF MOFs require exclusion of solvents from pores for gas diffusion
- Gas adsoption sites in/ ZIF PLs has been unknown, possibly in the ZIF pore or at the MOF-solvent interface
- DFT + ab initio molecular dynamics (AIMD) was used to predict CO_2 binding sites in a PL composed of a ZIF-8 particle solvated in a 17:33:128 ratio water, ethylene glycol, and 2-methylimidazole solvent system*

Christian, et.al., *J. Mole. Liq.* **2024**, *395*, 123913

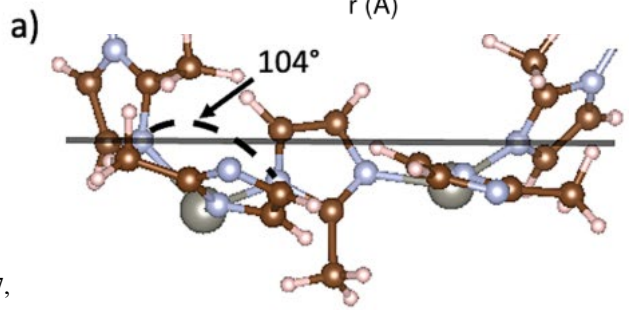
~2000 atoms depending on ZIF wt%

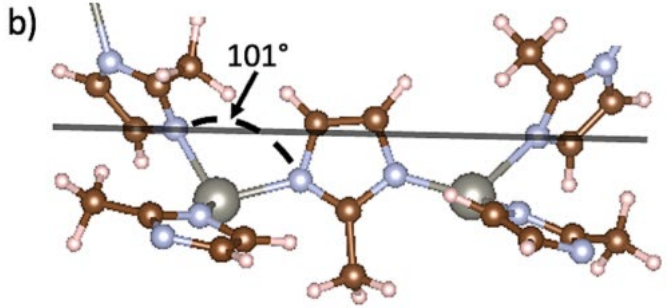






298K





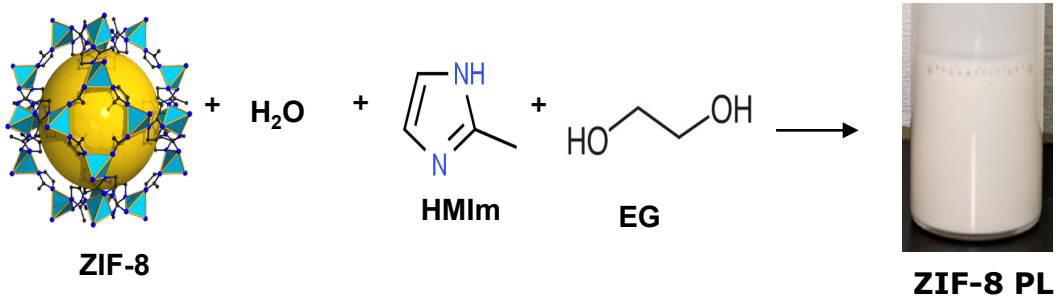
Ind. Eng. Chem. Res. 2018, 57, 37, 12494–12501

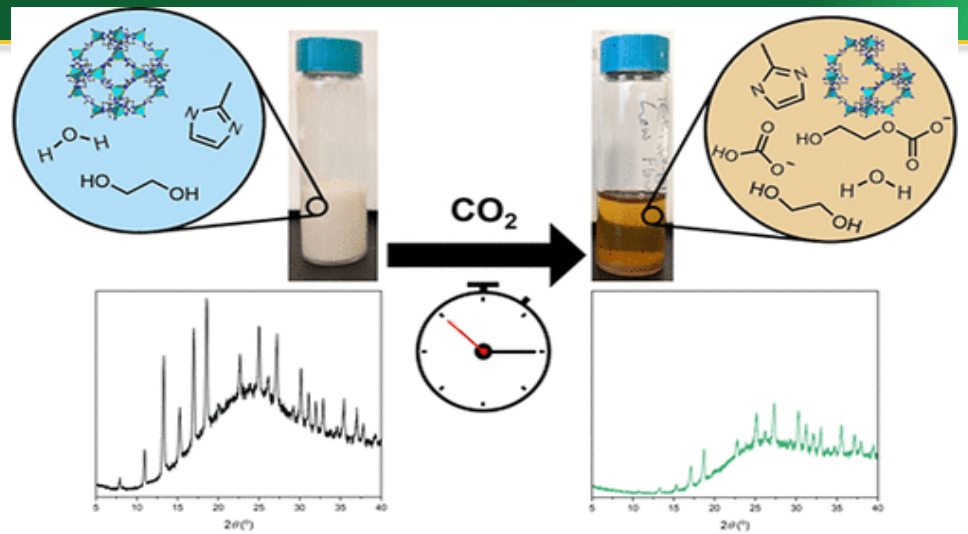
Nanoparticle of MOF dictating CO_2 adsorption

- The results show that CO_2 energetically prefers to reside inside the ZIF-8 pore aperture due to strong van der Waals interactions with the terminal imidazoles.
- However, the CO_2 binding site can be blocked by larger solvent molecules that have greater adsorption interactions.
- CO_2 molecules were unable to diffuse into the ZIF-8 pore, with CO_2 adsorption occurring due to binding with the ZIF-8 surface.
- the presence of solvent-nanoporous host interface in the PL is a driving force for the improved CO_2 capture in these Type 3 PLs.
- *Modeling predicts that future design of ZIF-based PLs for enhanced CO_2 adsorption should be based on the strength of gas binding at the solvated particle surface.*
- ***Guide for synthesis experimentation***

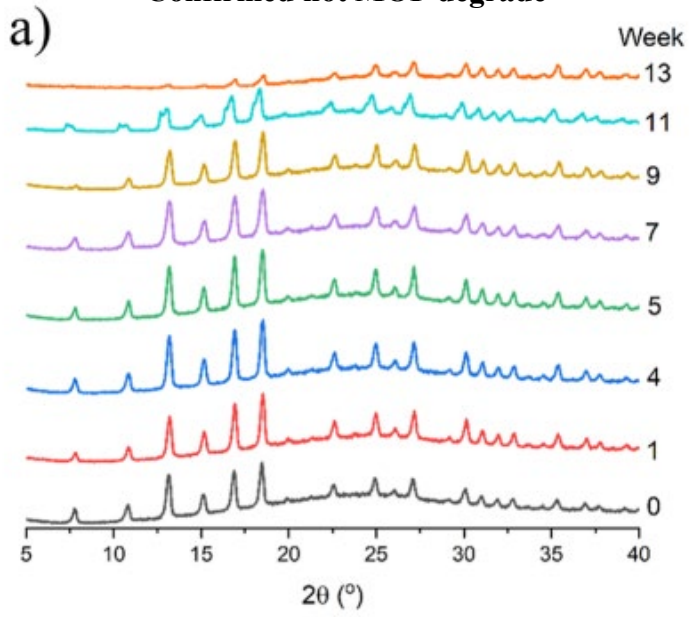
2) Type 3 PL aging mechanism under CO_2 adsorption: Modeling, Synthesis, NMR

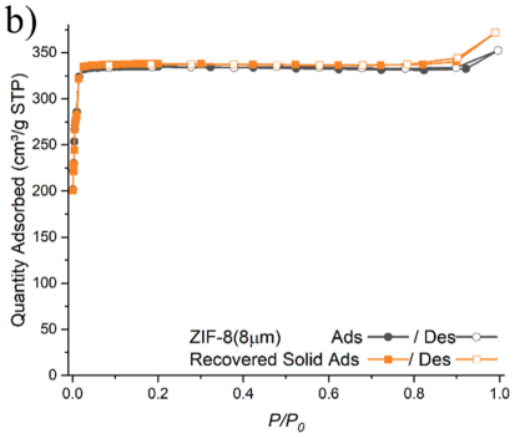
Synthesis: Exemplar ZIF-8 PL was formed with a solvent mixture of water, ethylene glycol (EG), and 2-methylimidazole (HMIm) at 40, 35, and 25 wt% respectively

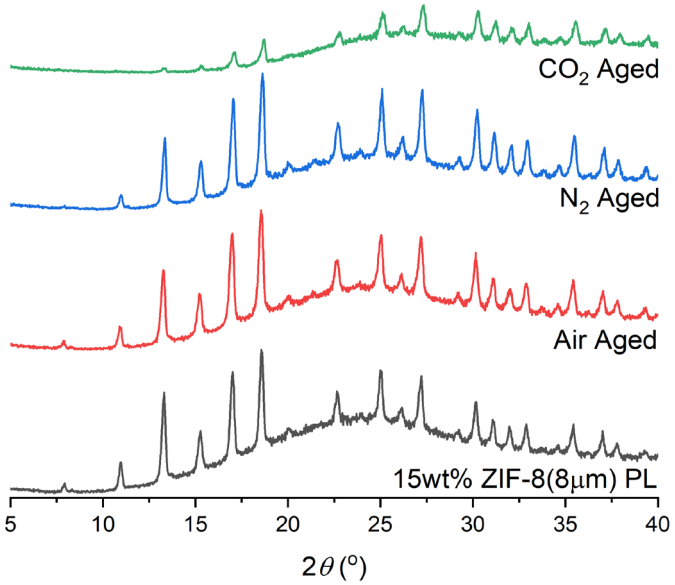




PL XRD post 7-day aging
Confirmed not MOF degrade







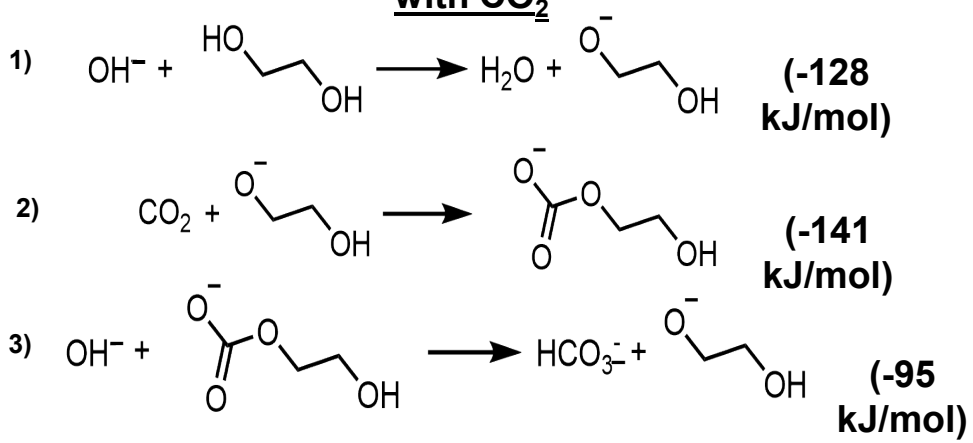
Hurlock, M. J.; *et. al. ACS Appl. Mater. Interfaces* **2023**, 15 (27), 32792

Christian, M.S., Hurlock M.J., Nenoff, T.M., Rimsza, J.M. *J. Mole. Liquids*, **2023**, *395*, 123913.

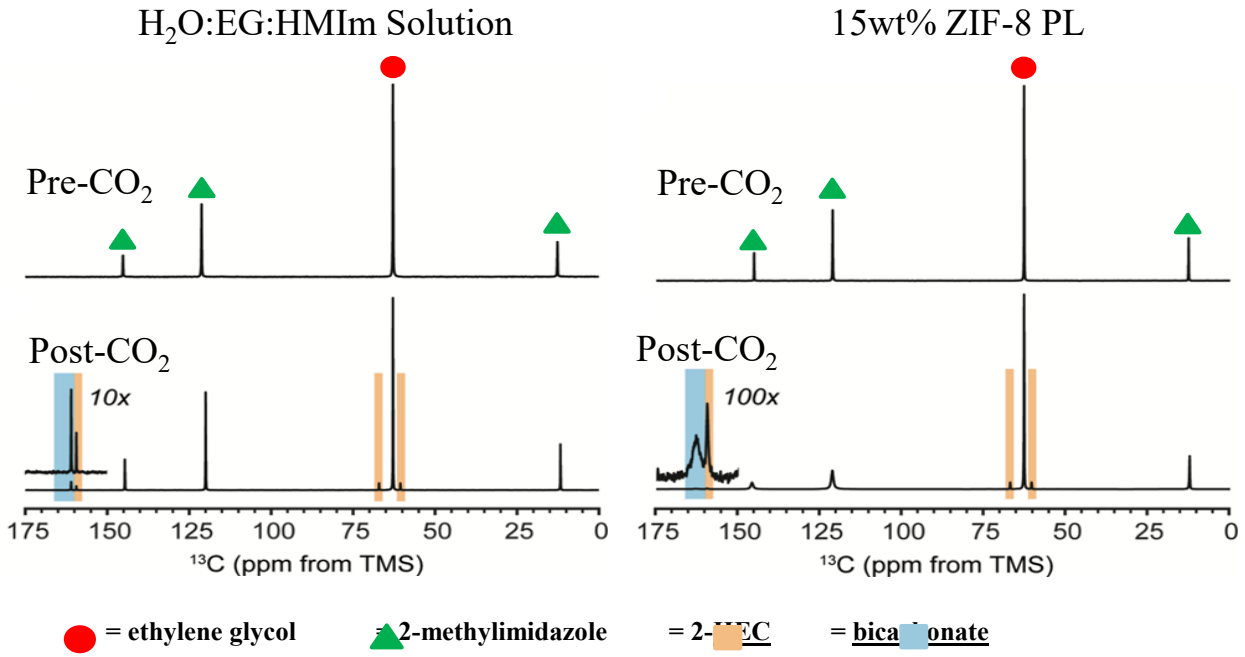
Type 3 PL aging mechanism under CO_2 adsorption: Modeling, Synthesis, NMR

Computational Data:
Density functional theory (DFT) FHI-AIMS was used to calculate formation enthalpies of possible CO_2 speciation in PLs
- Deprotonated EG reacts with CO_2 most energetically favorable reaction
- EG deprotonation via OH- species
- Modeling verified by NMR: new presence of carbonate species

Calculated Reaction Mechanism of EG with CO_2



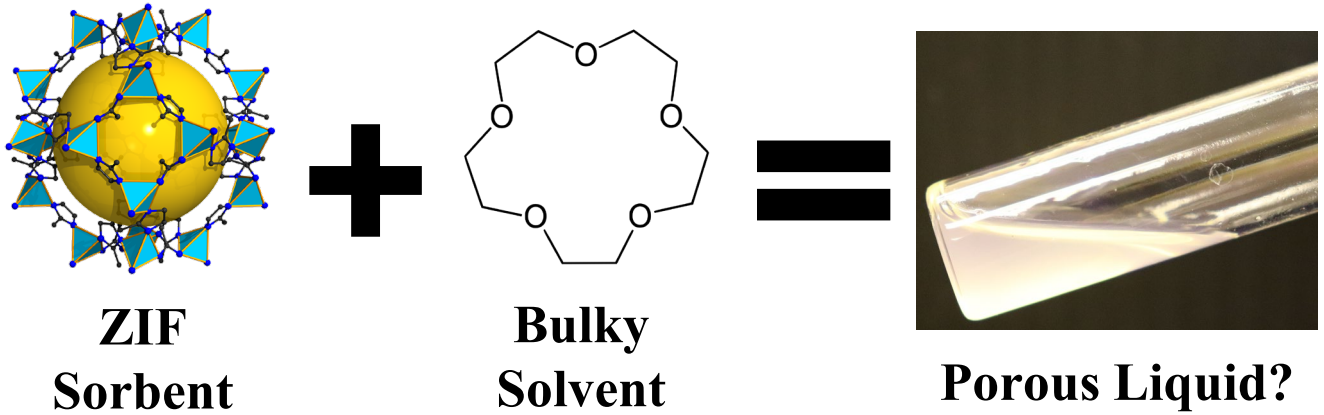
NMR Verification:



Solvent-CO_2 reactions cause degradation of PL.
Modeling: identify/predict solvent reactivity and speciation, particularly with complex mixed solvent systems

Hurlock, M. J.; *et. al. ACS Appl. Mater. Interfaces* **2023**, 15 (27), 32792

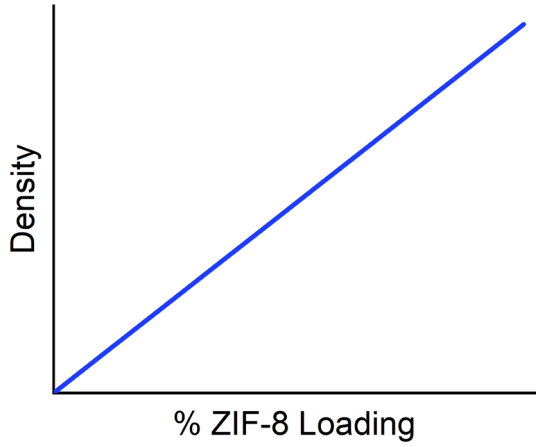
3) Ensuring Nanoporosity in PLs via Solvent Size-Exclusion within ZIF-Based PLs: Synthesis/Characterization, Modeling

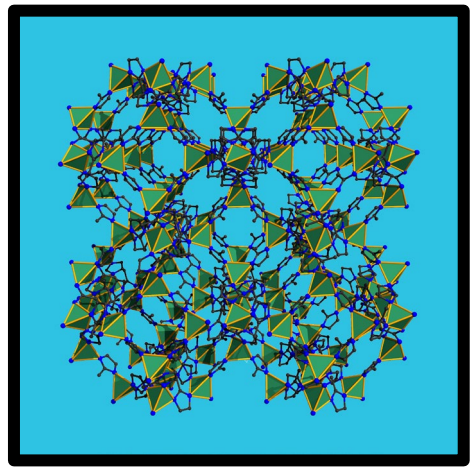


- PL formation requires a size-excluded solvent
- Solvent adsorption in Type 3 PLs is not well characterized in reported systems
- Density measurements are a simple method to evaluate sorbent porosity in Type 2 and 3 PLs

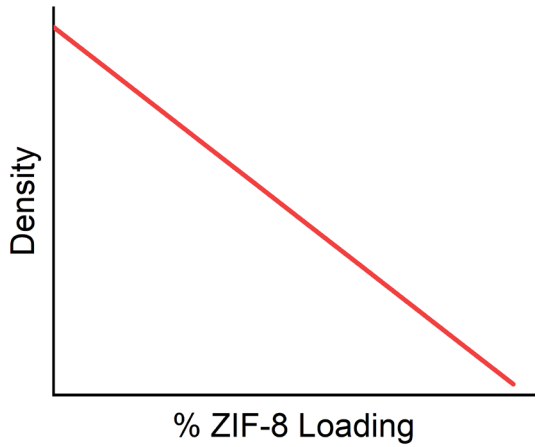
Nature, **2022**, *608*, 712; *Ind. Eng. Chem. Res.* **2023**, *63* (29), 11689-11696

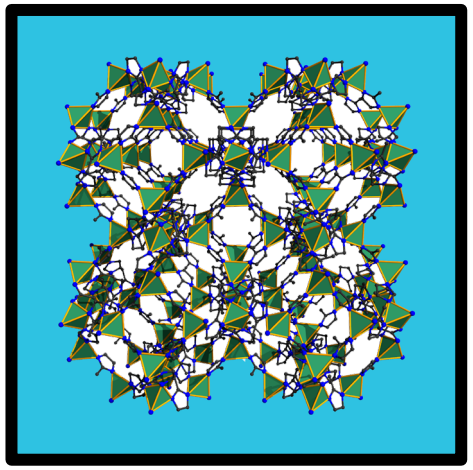
Increasing Density = Solvent **Adsorbed**





Decreasing Density = Solvent **Excluded**



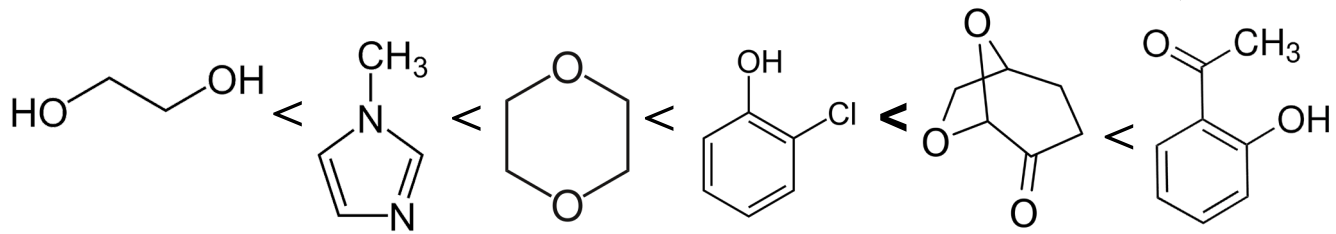


Hurlock, M. J.; *et. al. ACS Mater. Au,* **2024**, *4* (2), 224-237

Pore Aperture Expansion of ZIF-8 Influences Solvent Adsorption

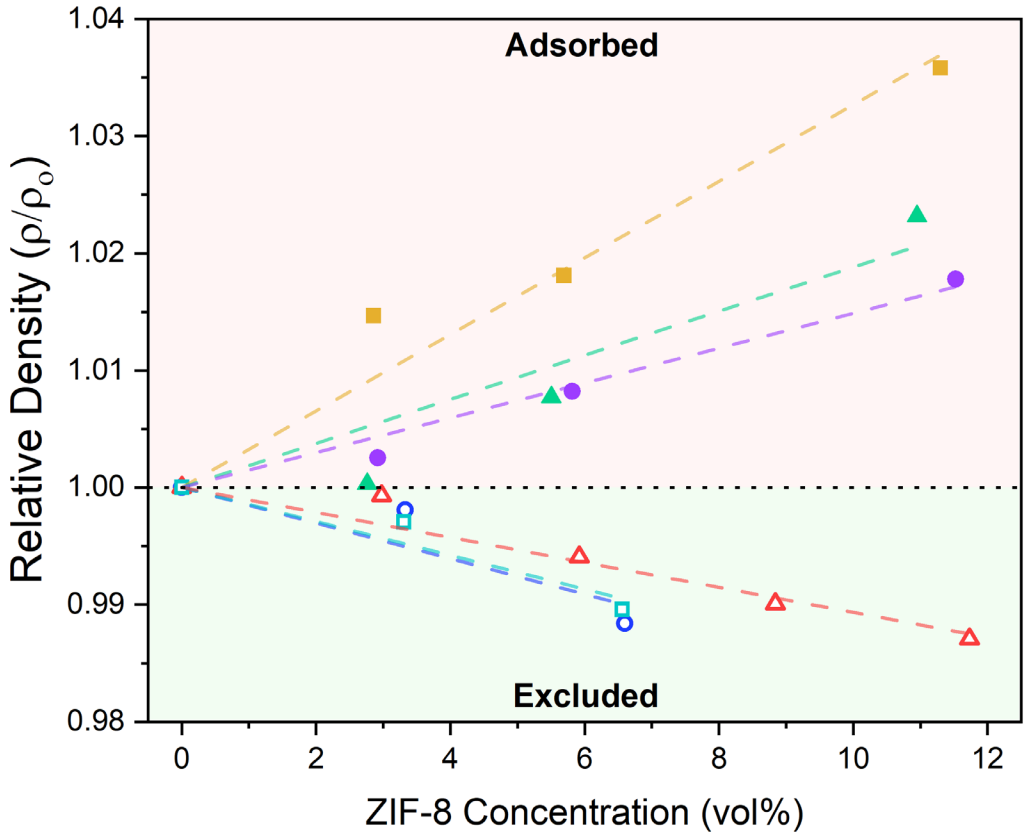
- Solvents selected over a range of molecular sizes
- Molecular diameters (d_v) were calculated from van der Waal volumes *J. Org. Chem.* **2003**, *68*, 19, 7368

Increasing Solvent Molecular Size



	EG	1MIm	p-diox	2CP	DHLG	2HAP
d_v =	4.9	5.1	5.4	5.9	6.0	6.3

- Density analysis was performed on ZIF+solvent combinations at varying ZIF loadings



Adsorbed Solvents
- EG
- 1MIm
- p-diox

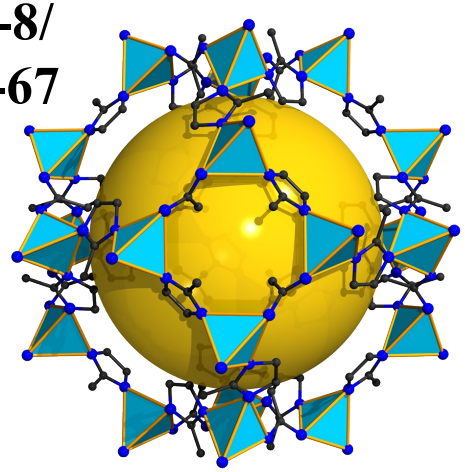
Excluded Solvents
- 2CP
- 2HAP
- DHLC

Adsorbed solvent diameters 60% larger than ZIF-8 pore aperture

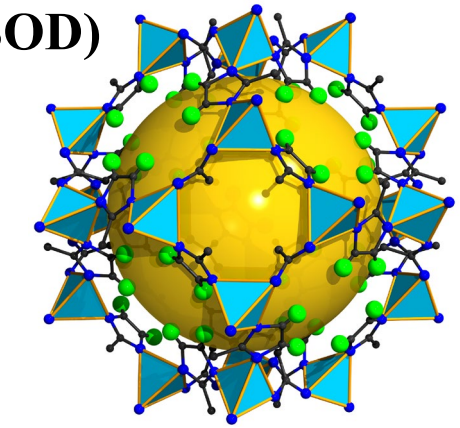
ZIFs Used to Examine Structure-Property Relationships

ZIF properties can be controlled through variation of the metal center, topology, pore aperture size, and linker functionalization

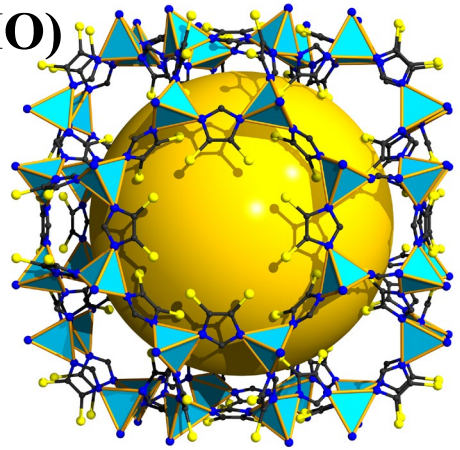
(Zn)ZIF-8/ (Co)ZIF-67



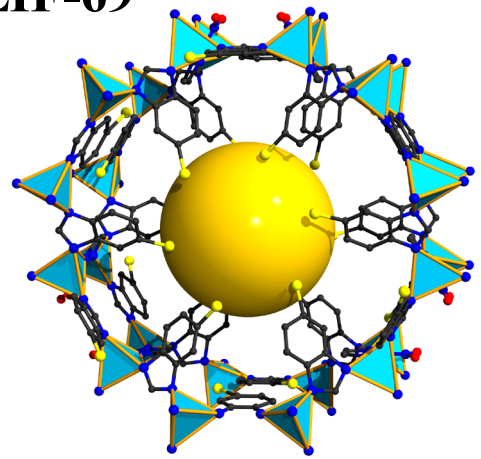
ZIF-71 (SOD)



ZIF-71 (RHO)



ZIF-69



Pore aperture

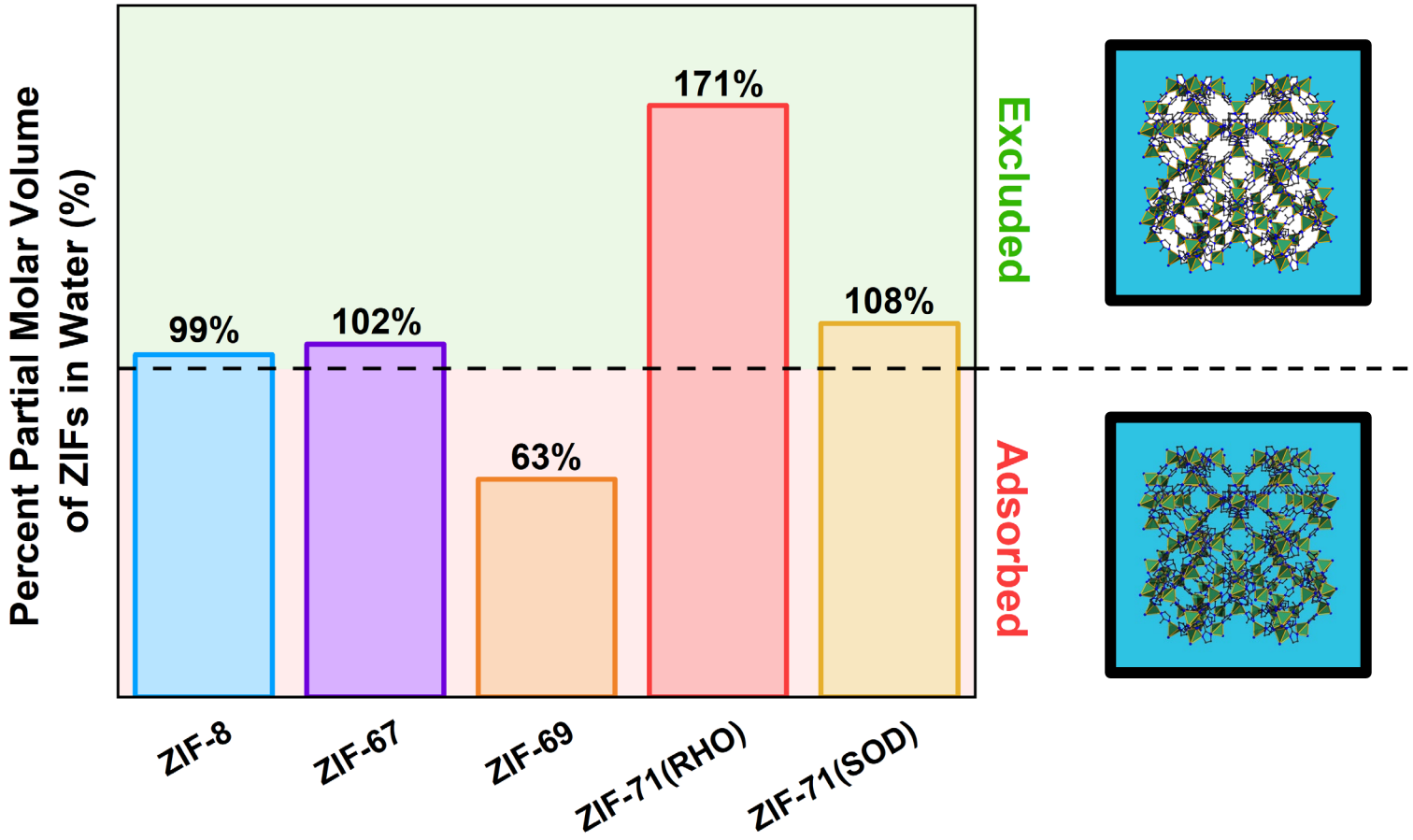
ZIF	Metal	Topology	Pore Aperture (Å)	Density (g/mL)
ZIF-8	Zn	SOD	3.4	0.94
ZIF-67	Co	SOD	3.4	0.90
ZIF-71	Zn	SOD	3.8	1.41
ZIF-71	Zn	RHO	4.2	1.16
ZIF-69	Zn	GME	4.4	0.99

J. Am. Chem. Soc. **2015**, *137* (38), 12304-12311
Science **2008**, *319* (5865), 939-943
CrystEngComm, **2016**, *18*, 2477-2489

Exclusion of Water from ZIF Pores is Influenced by Framework Hydrophobicity

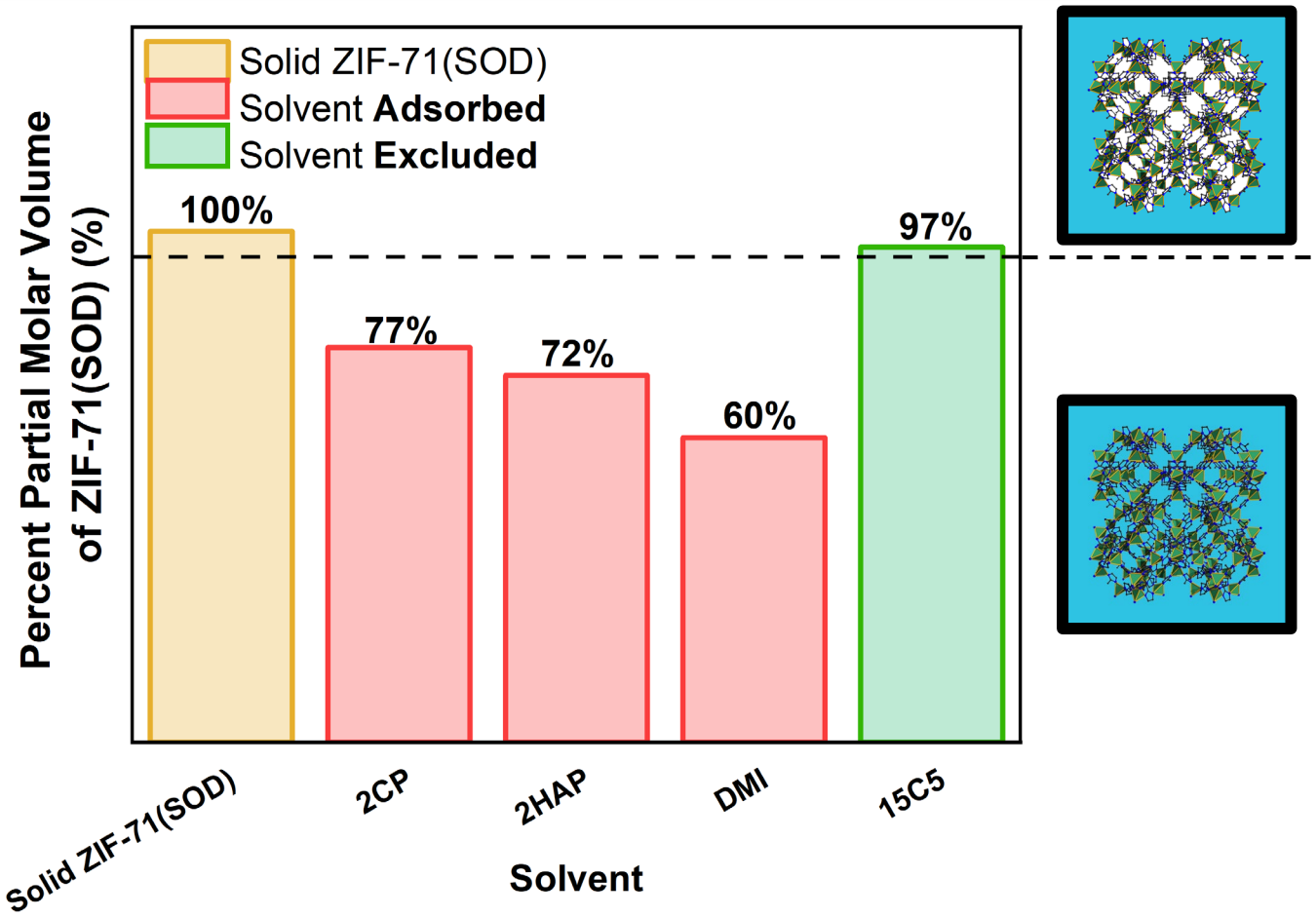
- Different systems compared through the change in partial molar volumes
- Partial molar volume changes were calculated from density measurements
  - **Decreased** partial molar volumes indicate solvent adsorbed
  - **Unchanged/Increased** partial molar volumes indicate solvent excluded
- Highly *hydrophobic* ZIFs showed increased partial molar volumes
- *Hydrophilic* ZIFs showed decreased partial molar volumes

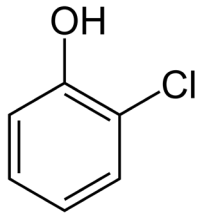
Polar linker functionalization led to water adsorption by ZIF-69



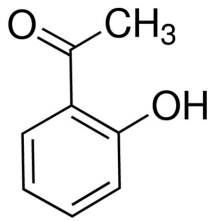
Pore Aperture Expansion Controls Solvent Size-Exclusion in ZIF-based PLs

- Density analysis applied to different ZIFs in solvents of varying molecular size
- Partial molar volume changes **<5%** indicated solvent exclusion
- Large pore aperture ZIFs showed larger aperture expansion >70%
- Identified eight new ZIF+solvent PL combinations

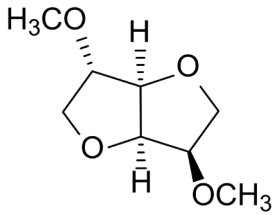




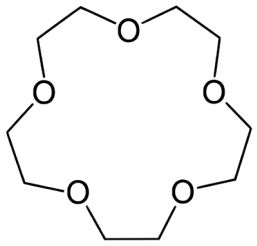
2CP



2HAP



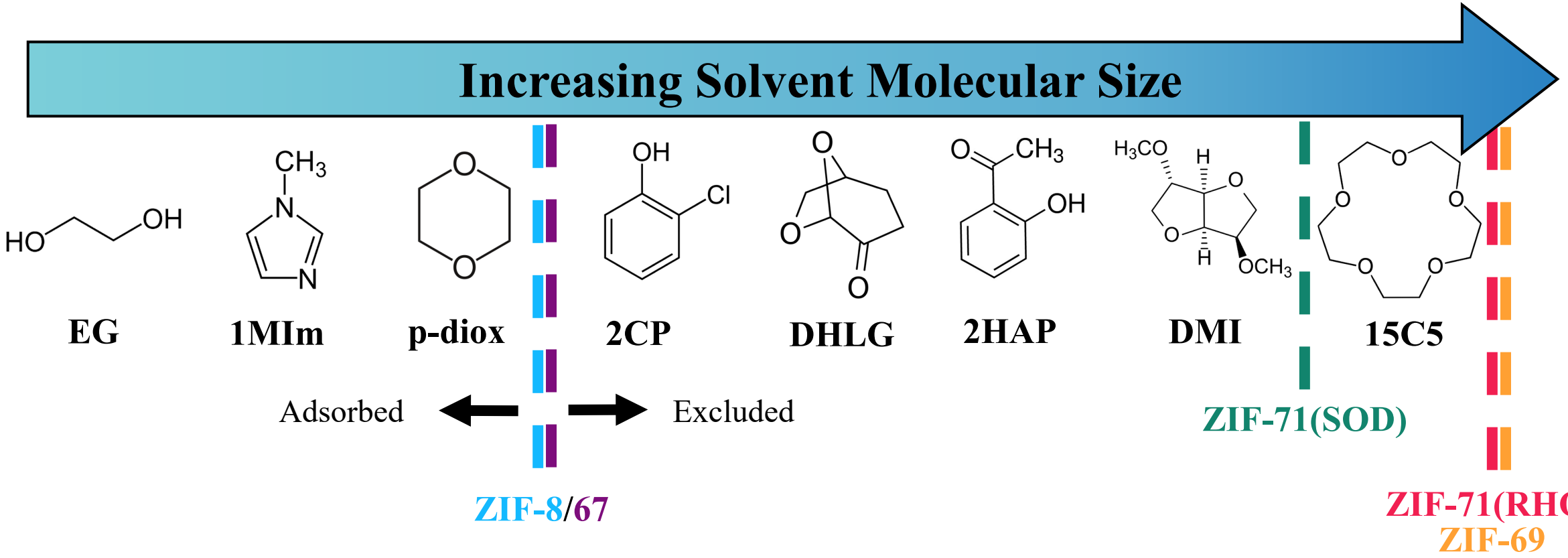
DMI



15C5

Size-excluded solvents were always larger than the ZIF pore apertures

Pore Aperture Expansion Controls Solvent Size-Exclusion in ZIF-based PLs



Solvents <u>1.8x</u> the size of the crystallographic pore aperture are size-excluded from pores in ZIF-based PLs

4) Solvent Size and Pore Aperture Effectson CO_2 Adsorption

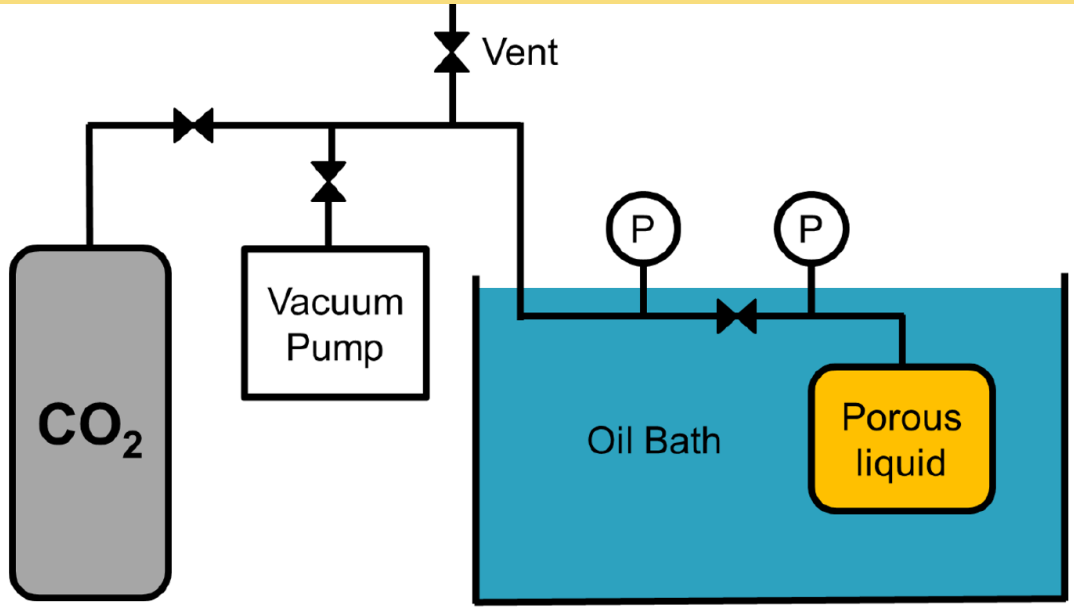
Synthesis: Three variations of MOF studied, porous ZIF-8, 2D ZIF-L, no pore a_mZIF-8

Modeling: Computational simulations identified 2HAP as selective for CO_2, and was chosen as size-excluded solvent

Testing: Gas adsorption isotherms of ZIF+solvent combinations performed using GA Tech's unique pressure decay system

Verification: Experiment validated computational predictions on selectivity of CO_2 vs N_2 under pressure and validated force fields used

CO_2 Gas adsorption isotherms collected using house-built apparatus at GA Tech.

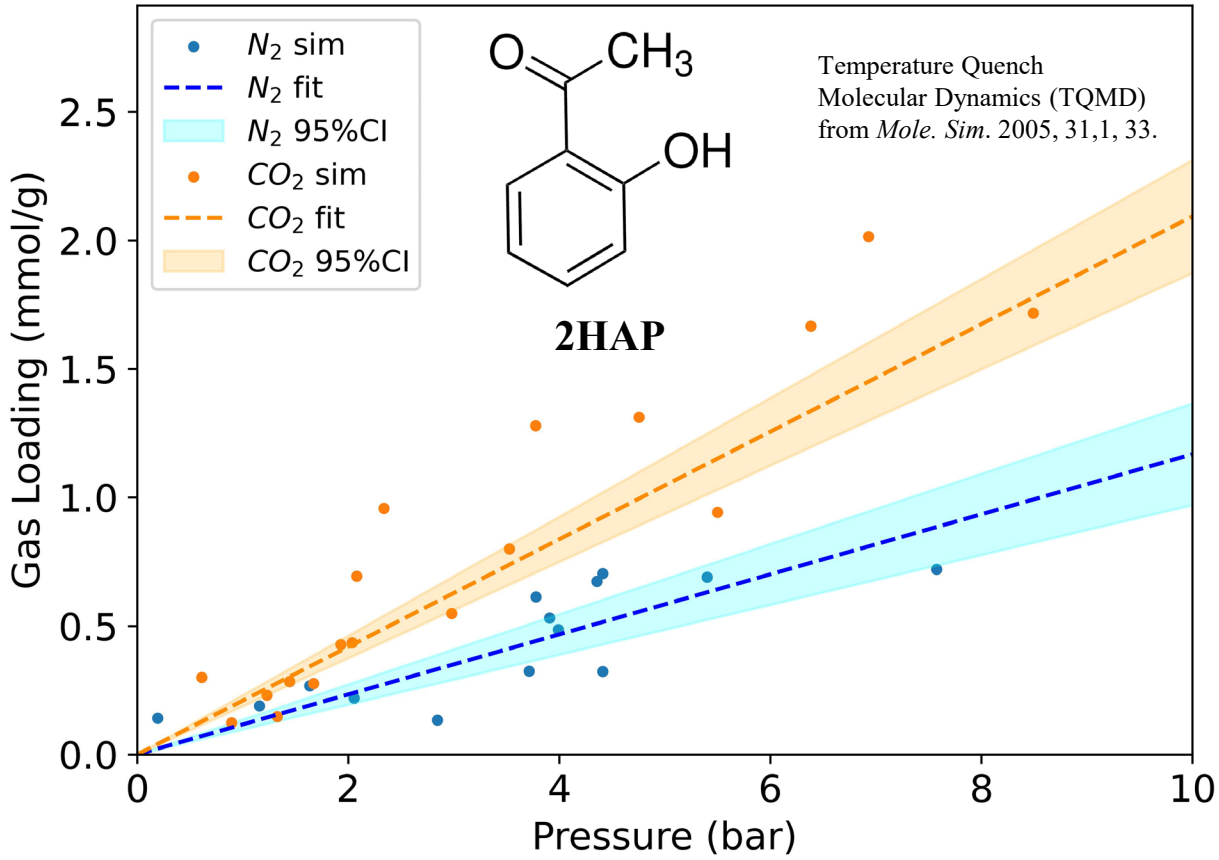


Pressure Decay Gas Adsorption Unit (GA Tech)

Hurlock, M. J.; Lu, L.; Sarswat, A.; Chang, C-W.; Rimsza, J.M.; Sholl, D.; Lively, R. Nenoff, T.M. "Exploitation of Pore Aperture Environment for Increased CO_2 Uptake in Type 3 Porous Liquids" *ACS AMI,* **2024**, *submitted.*

Prediction of CO_2 Selective Size-Excluded Solvents for ZIF-8-based PLs

- 2HAP solvent verified to be size-excluded from ZIF-8 using density measurements
- Temperature Quench Molecular Dynamics (TQMD) used to simulate CO_2 and N_2 gas solubilities in 2HAP
  - Simulations performed by Sholl Lab at GA Tech.
- Simulations predict higher CO_2 solubilities compared to N_2 in 2HAP
- Experimental results align with trends predicted by simulations



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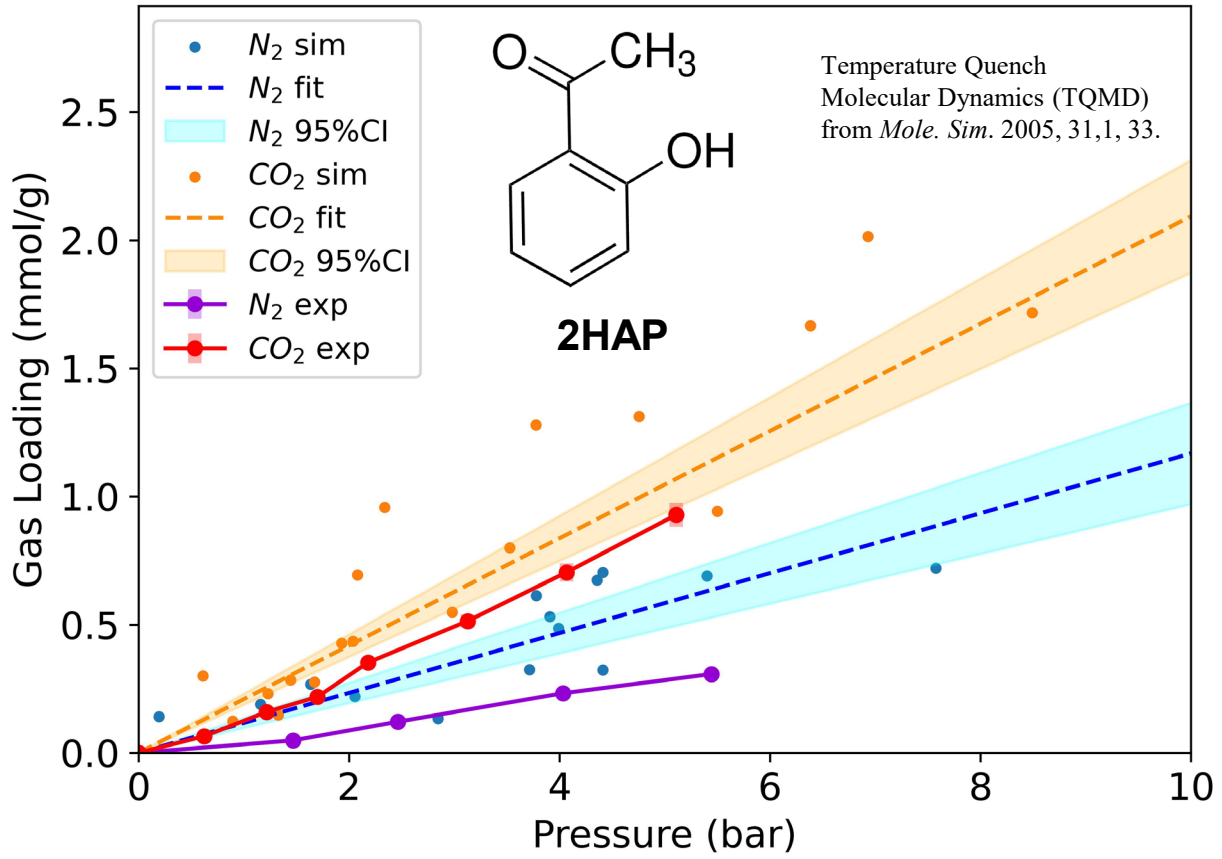
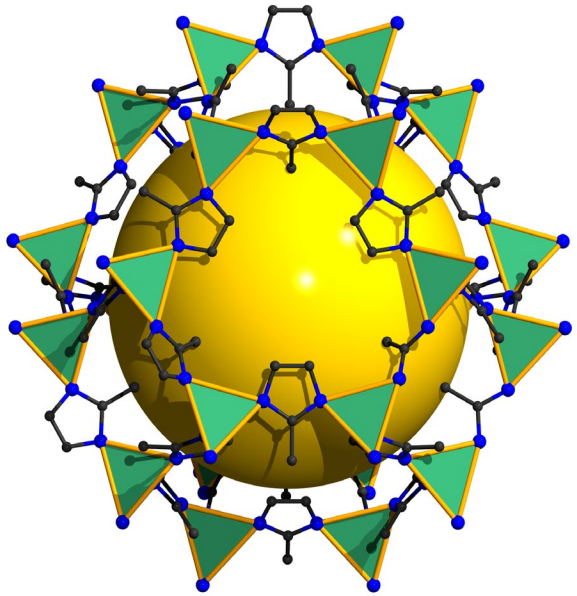
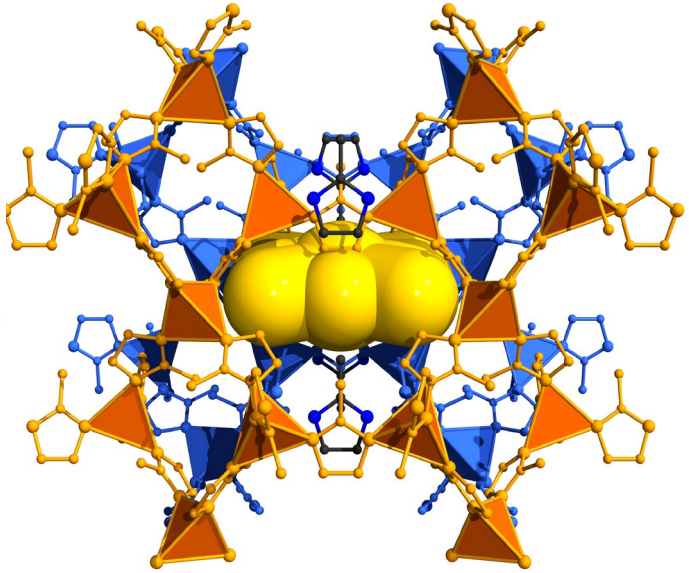


2HAP computationally predicted and experimentally confirmed to be selective for CO_2

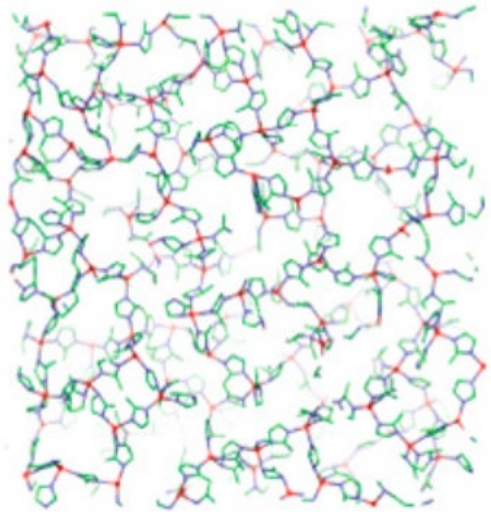
Solvent Size and Pore Aperture Effects on CO_2 Adsorption



3D ZIF-8 pore



2D ZIF-L surface "pore"

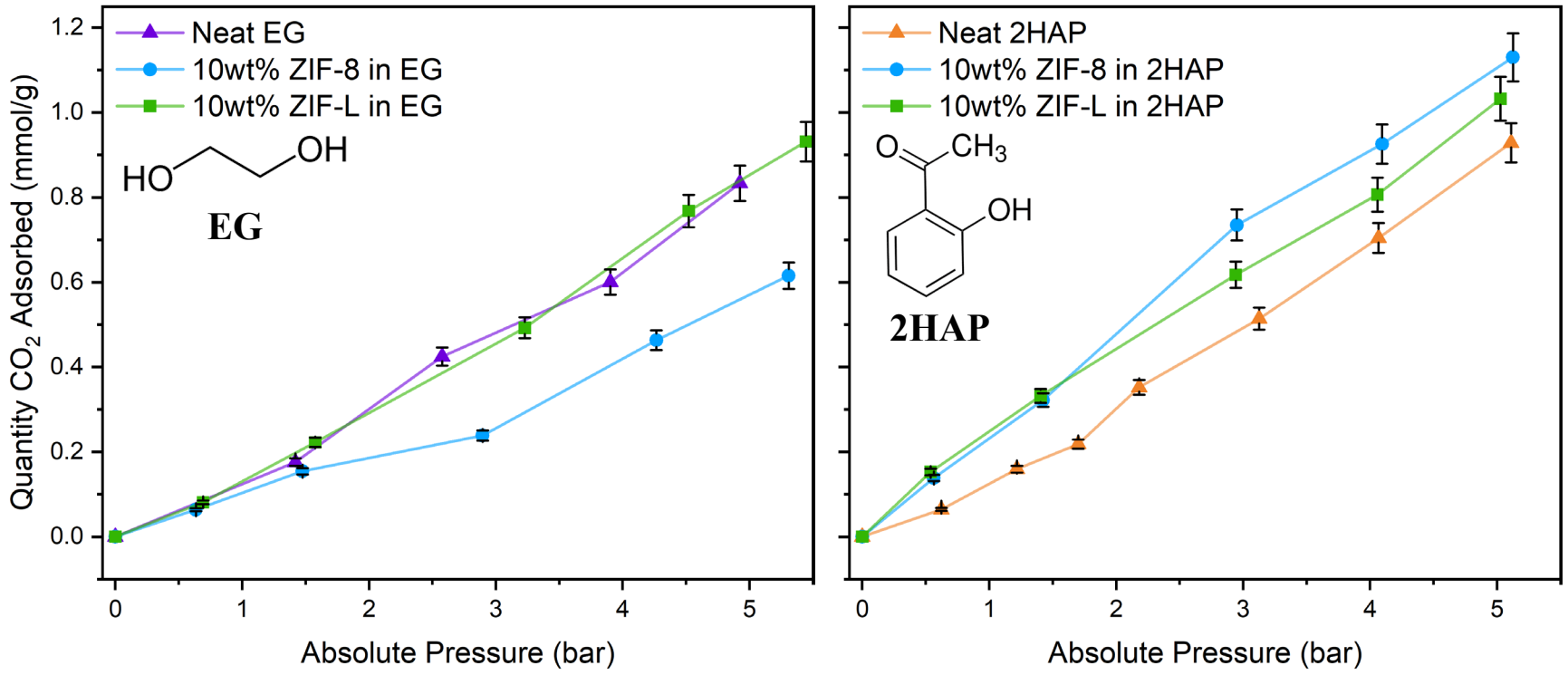


a_mZIF-8 (amorphous)

Is the internal pore or the MOF-solvent interface controlling the CO_2 adsorption in the PLs?

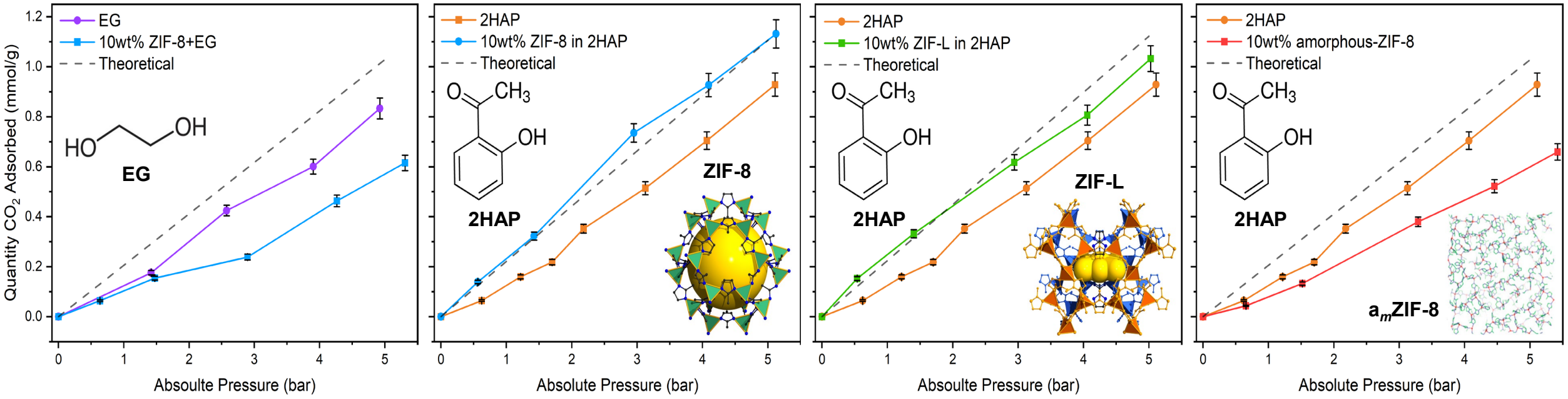
CO_2 Gas Adsorption Measurements Confirmed 2HAP Exclusion from ZIF-8 and ZIF-L

- ZIFs+EG showed **no** increase in CO_2 uptake compared to EG
  - Confirmed EG adsorbed
- ZIFs+2HAP **increased** in CO_2 compared to neat 2HAP
  - Confirmed 2HAP size-excluded
- ZIF-L+2HAP PL is the first example of a Type 3 PL formed using a 2D material



Gas sorption studies confirmed the formation of ZIF-8 and ZIF-L PLs with 2HAP

Solvent Size and Pore Aperture Effects on CO_2 Adsorption



Adsorbed solvents negatively impact CO_2 uptake

ZIF-8+2HAP formed PL w/ CO_2 uptake

Low-surface area ZIF-L formed PL due to pore aperture

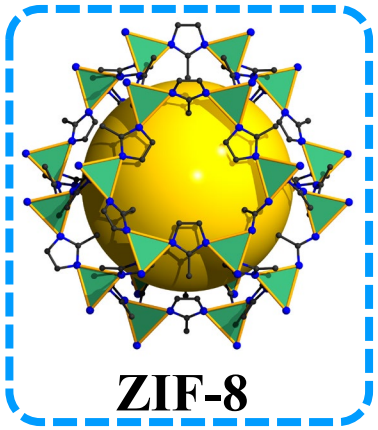
Lack of pore aperture decreased CO_2 uptake

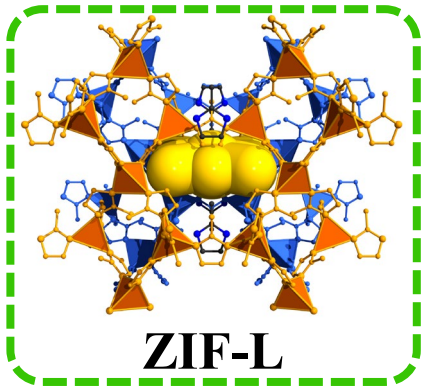
ZIF-L+2HAP system is the first example of PL formed using a 2D sorbent material

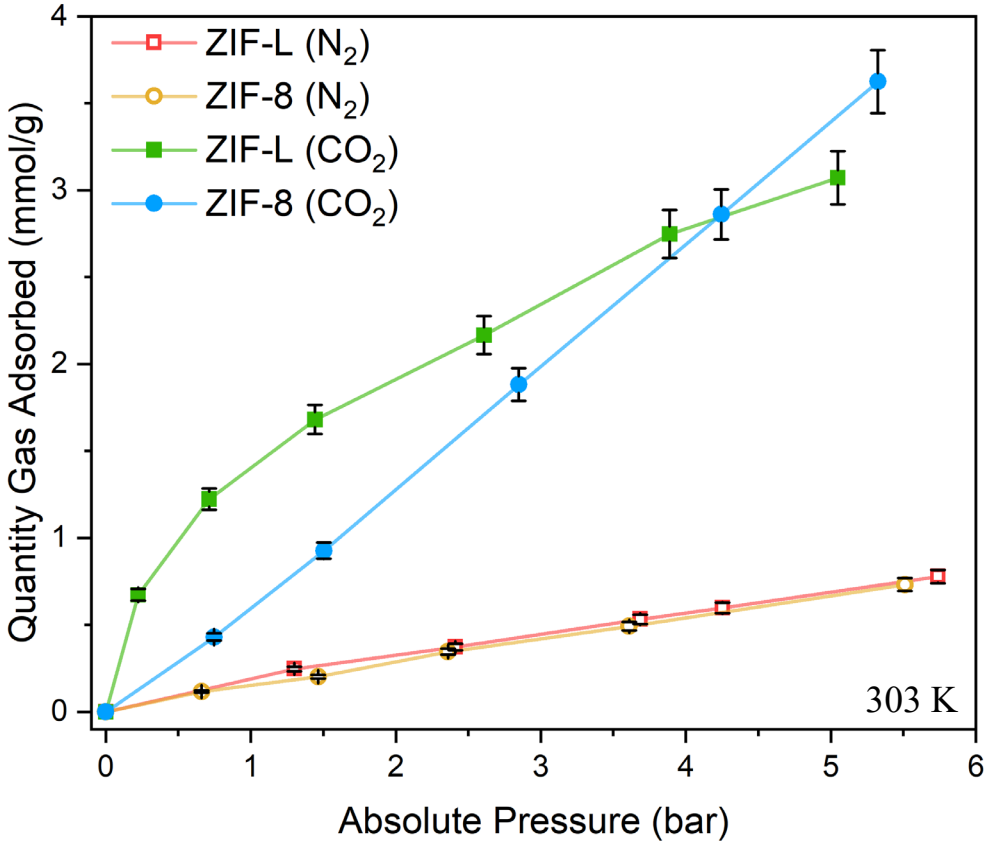
Hurlock, M. J.; Lu, L.; Sarswat, A.; Chang, C-W.; Rimsza, J.M.; Sholl, D.; Lively, R. Nenoff, T.M. "Exploitation of Pore Aperture Environment for Increased CO_2 Uptake in Type 3 Porous Liquids" *ACS AMI,* **2024**, *in preparation*

Controlling ZIF Pore Aperture Structure Will Allow the Formation of CO_2 Selective PLs

- Computational simulations have shown the pore aperture as a key CO_2-ZIF interaction site in ZIF-based PLs
  Christian, M. S.; *et. al. J. Mol. Liq.* **2024**, *395*, 123913
- All ZIFs expected to show similar guest interactions and solvent size-exclusion behavior
- ZIF-L is an isolatable 2D intermediate of ZIF-8 with similar pore aperture
- ZIF-L showed higher CO_2 uptake compared to ZIF-8





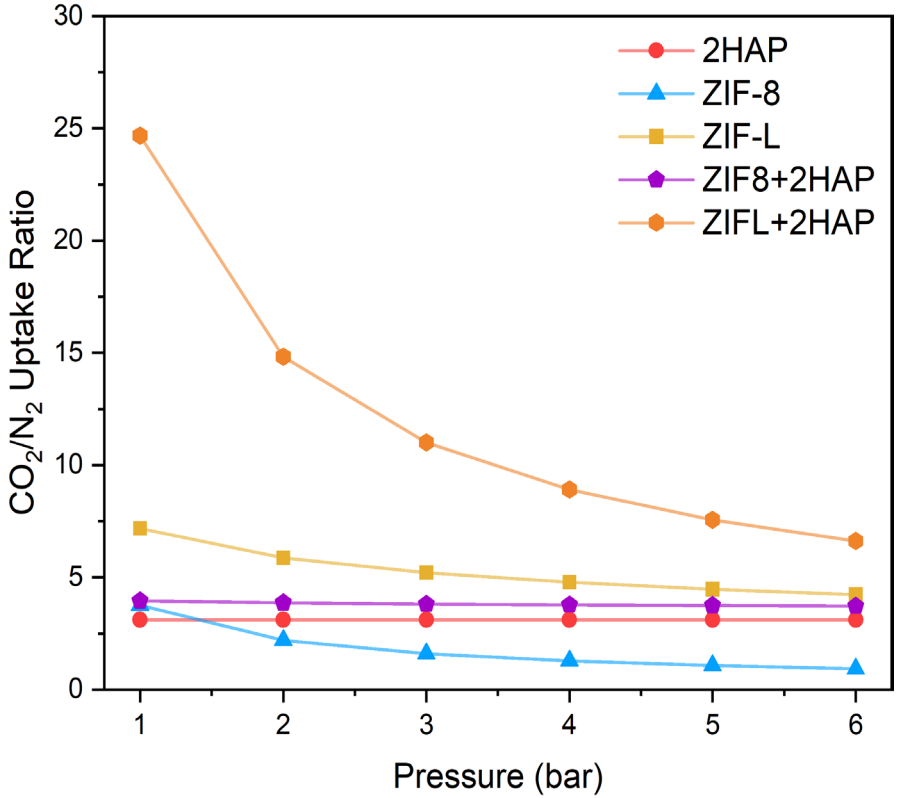


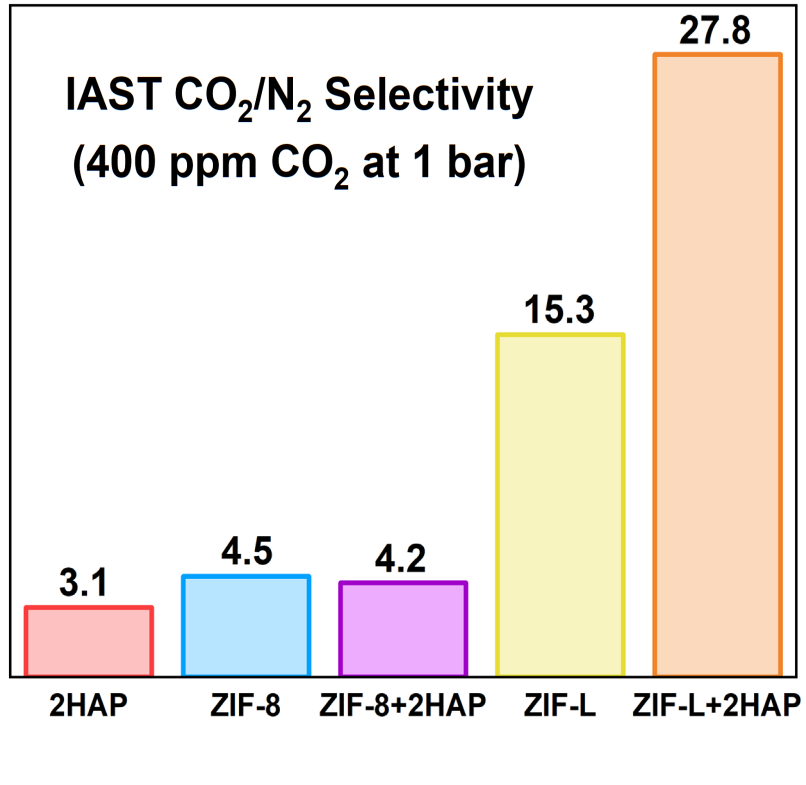
ZIF-L pore aperture structure will form CO_2 selective PLs

ZIF-L + 2HAP PL Revealed *Emergent Behavior* in CO_2 Adsorption, Not Predicted from Individual Components

- Single component N_2 adsorptions collected on ZIF+2HAP PLs
- CO_2/N_2 uptake ratio of ZIF+2HAP PLs increased compared to 2HAP
- IAST CO_2 selectivity calculated for PLs and individual components
  - Both ZIF+2HAP PLs showed increased selectivity compared to neat 2HAP
  - ZIF-8+2HAP PL revealed lower CO_2 selectivity than ZIF-8

ZIF-L+2HAP PL showed decrease in N_2 uptake, compared to neat 2HAP



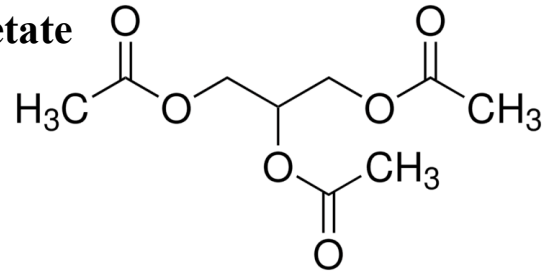


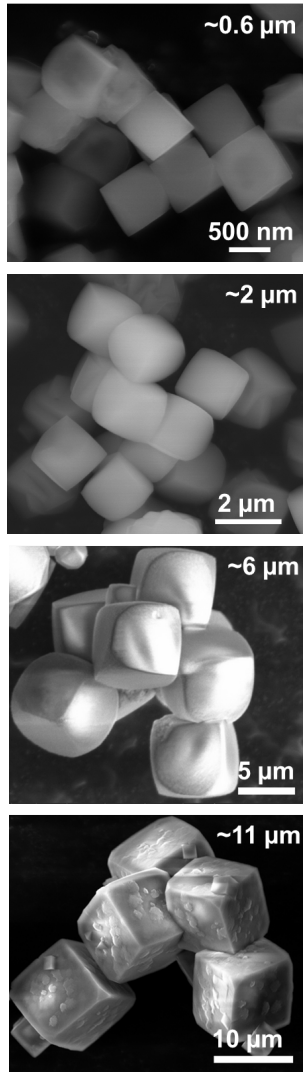
ZIF-L+2HAP PL showed > 2x CO_2/N_2 selectivity in air compared to individual components

5) Type 3 Porous Liquids with Nanozeolites

- Zeolite-based Type 3 PLs are potential economical CO_2 sorbents (*Mater. Today*, **2022**, *60*, 9-16)
- Nanozeolites in Porous Liquids to study effects of zeolite particle size and porosity on PL CO_2 adsorption
- In collaboration with Rimer Lab at the University of Houston
  - SSZ-13 of various nanoparticle sizes (0.6, 2, 6, and 11 µm)
- N_2 gas adsorption showed mesoporosity due to interparticle cavities caused by particle aggregation (*Chem. Soc. Rev.*, **2013**, *42*, 3689-3707)
  - Mesoporosity increased with decreasing zeolite particle size
- Glyceryl triacetate (GT) is predicted to be size excluded and possesses desirable properties

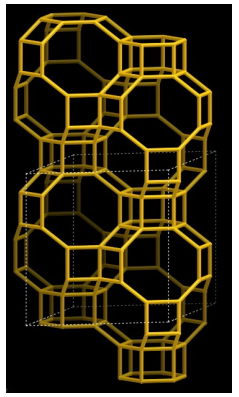
Glyceryl Triacetate

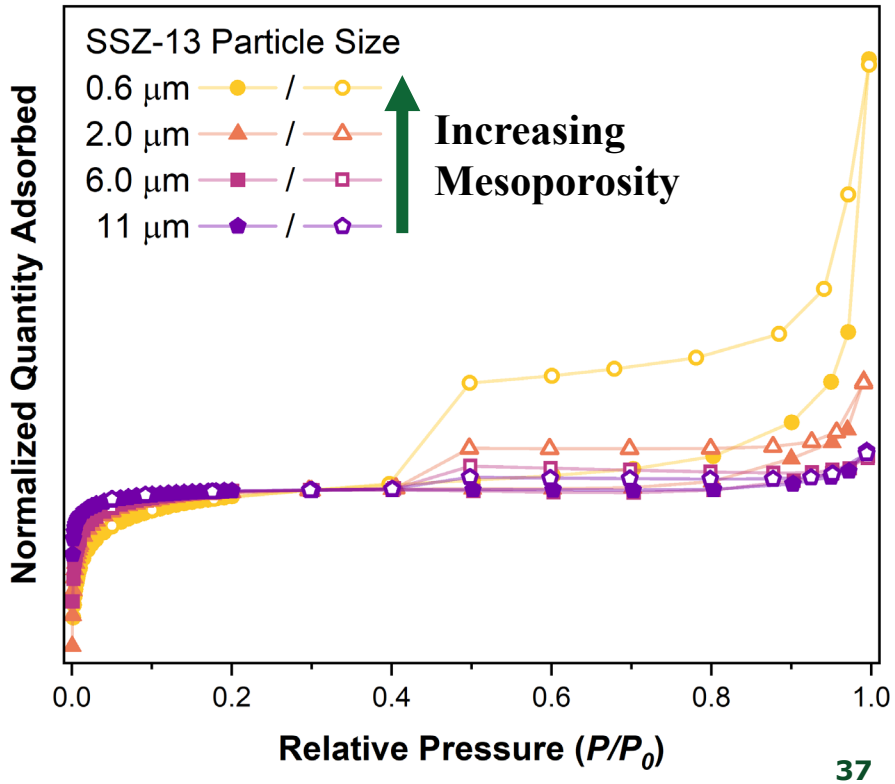




Increasing Particle Size

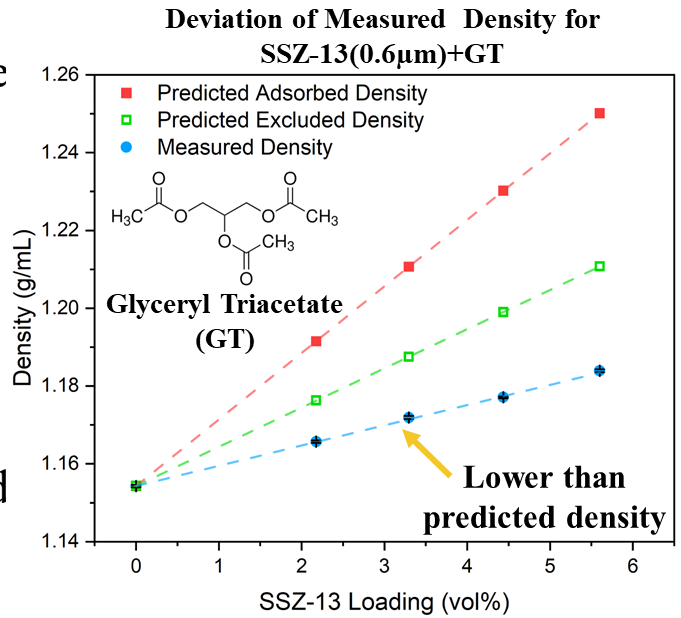
SSZ-13 Structure

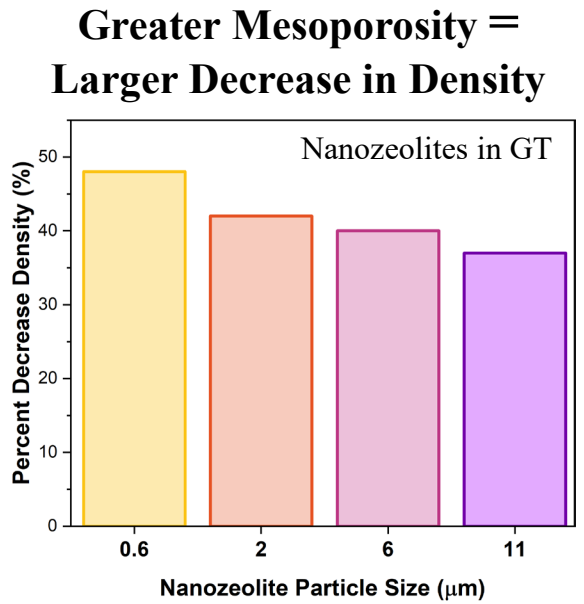


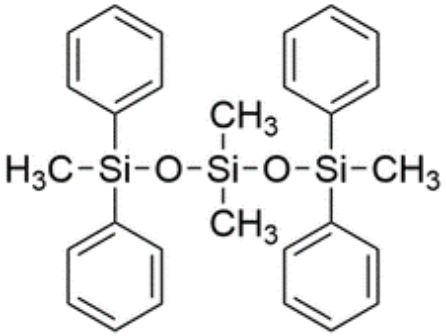


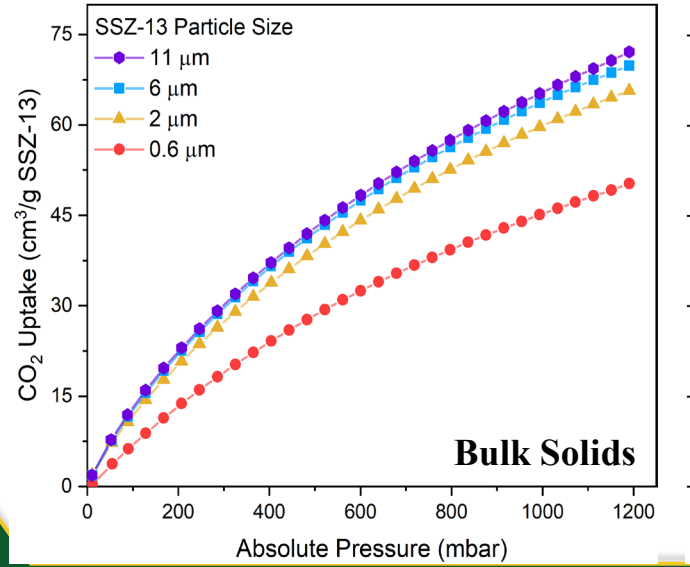
Initial Porous Liquids studies

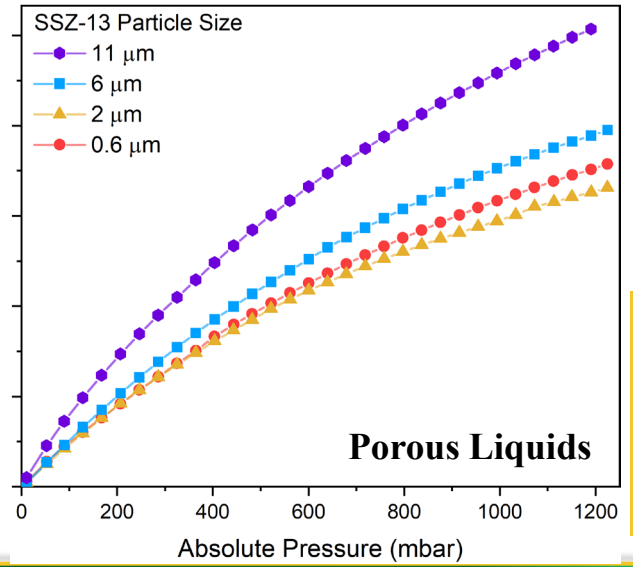
- Density measurement simple method for verifying Type 3 PL formation (*ACS Mater. Au* **2024**, *4*, 2, 224-237)
- Density analysis of SSZ-13+GT dispersions showed lower than predicted values
  - Low measured densities caused by trapped air pockets in interparticle cavities
- Due to vapor pressure of GT, Invoil 704 was substituted as size-excluded solvent for CO_2 adsorption of PLs









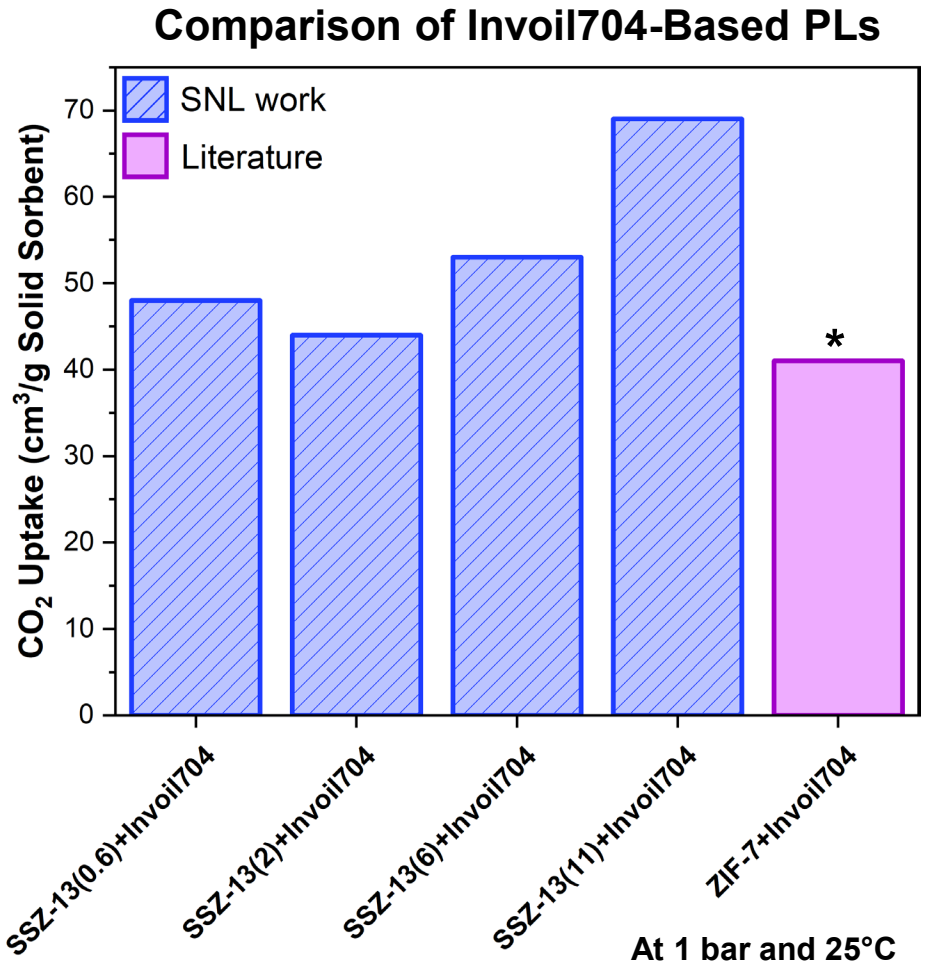


- **Physical property changes will effect PL handling in applications**
- **CO_2 uptake of solids increased with particle size**
- **0.6 and 11 µm zeolites CO_2 uptake slightly increase in PL**

Results suggest: Interparticle cavities do not have direct impact on CO_2 uptake of PLs in Invoil

Next Steps with Nanozeolites PLs, on-going experiments…

- Analyze CO_2 adsorption trends and structure-property relationships of nanozeolite PLs in application relevant solvents (e.g. GT)
  - In collaboration with the Ryan Lively lab at Georgia Tech. using house-built PL gas adsorption apparatus
- Analyze both single and mixed CO_2 gas adsorption of formed PLs to elucidate CO_2 selectivity
- Development of methodology for the comparison of PL sorbents using instrumentation available to average research lab
  - Standardization of solvent to Invoil 704, allows use of commercially available gas adsorption analyzer (e.g. ASAP2020Plus)
  - Standardization of data reporting for direct comparisions, gas uptake *per gram of solid sorbent in PL* at 1 bar and 25°C
  - Result validation with house-built apparatuses
- Utilized this methodology to identify design principles for zeolite-based Type 3 PLs



* Nat. Commun. **2023**, *14*, 4200

Conclusions and Ongoing/Future Work

- **Porous liquids (PLs), solvent-based systems containing permanent porosity through the incorporation of a porous host, increase the CO_2 adsorption capacity.**
- Rapid materials design enabled by combined multidisciplinary modeling, synthesis, characterization and testing.
- Aging studies of known type 3 PLs identify that the nanoporous ZIF MOF maintains its integrity, but solvent breakdown hinders the overall system
- Solvent exclusion necessary for gas diffusion and selective CO_2 capture, solvents must be ***1.8x*** the ZIF pore aperture size
- TQMD simulations allow high throughput identification of CO_2 selective solvents
- Pore aperture structure controls CO_2/N_2 selectivity of ZIF-based Type 3 PLs
- **Porous Liquids are a combination of CO_2 capture materials. Data herein identify that there are enhancing mechanisms that result in an optimized PL composition results in an *Emergent Behavior* of the PL** (higher CO_2 selectivity for the PL than any of the individual components)

Ongoing and Future Work:

- Examination of sorbent particle size effects on CO_2 adsorption of Type 3 PLs
- Identification of exemplar Type 3 sorbent-solvent combinations for DAC and electrochemical conversion of CO_2
- Variable temp. and pressure effects on solvent size-exclusion of ZIF-8 based PLs

SNL Postdocs, Interns/students, Technologist and Young Staff*

Strong Advocate for Mentoring and Supporting Young People throughout their Careers

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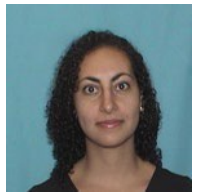
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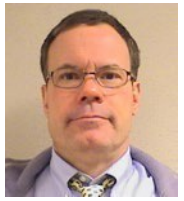
Technologist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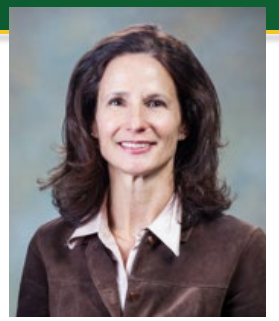
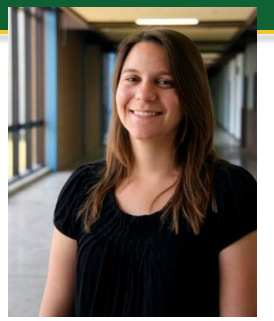
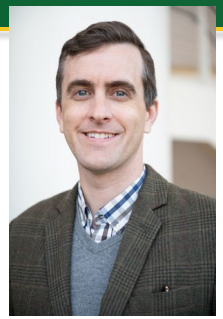

T. Nenoff


J. Rimsza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D. Sholl


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J. Rimer

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