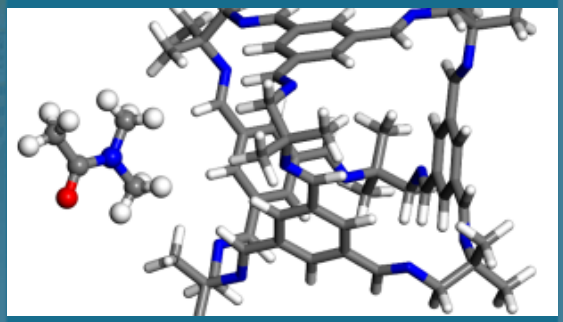
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2022-11351C

Sandia National Laboratories

Gas Interactions with CC13-based Type 2 Porous Liquids



Jessica M. Rimsza and Tina Nenoff

Sandia National Laboratories

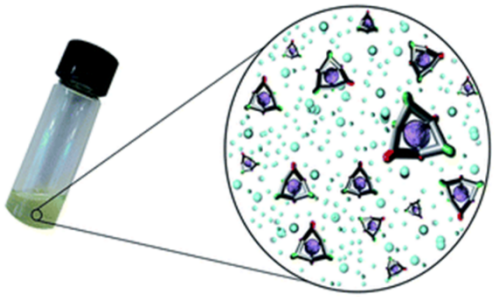
Albuquerque, NM 87123

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

What are porous liquids?

- **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.

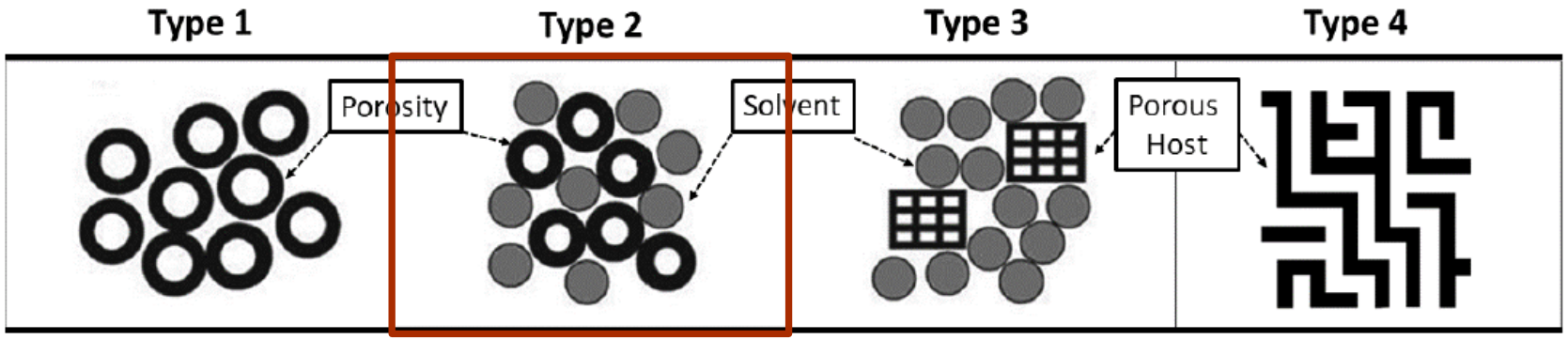


Schematic of Type 2 porous liquid with dissolved gases (purple)

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

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.

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



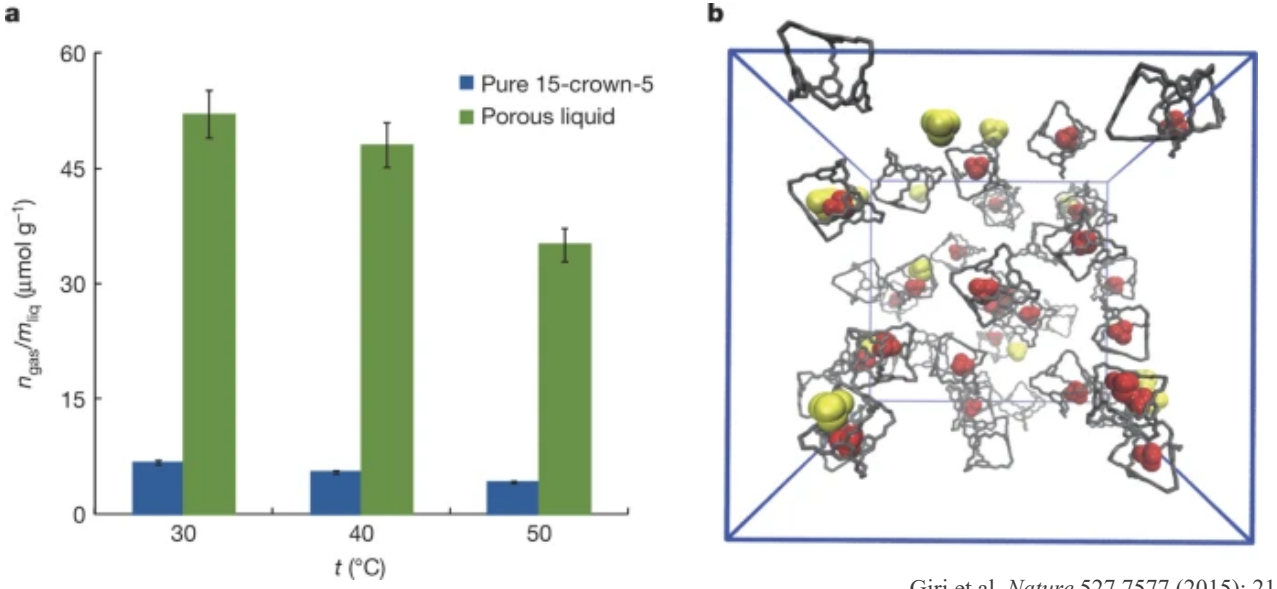
Gas Adsorption in Type 2 Porous Liquids

- Gas adsorption is consistently higher in Type 2 porous liquids then in a solvent or the porous host alone

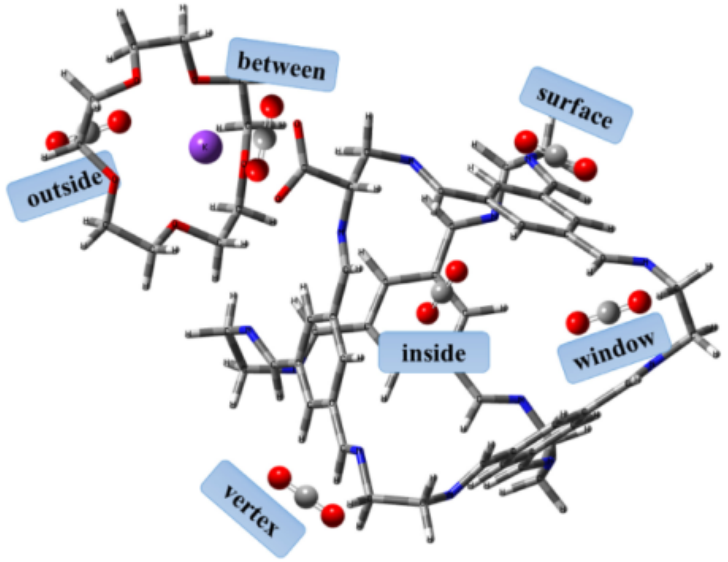
- Phenomena is consistent across gas molecule types and in multiple porous liquid compositions

- Numerous binding sites (6+) exist in porous liquids (inside the pore, in the window, at the vertex of the POC, between the POC and the solvent, etc).

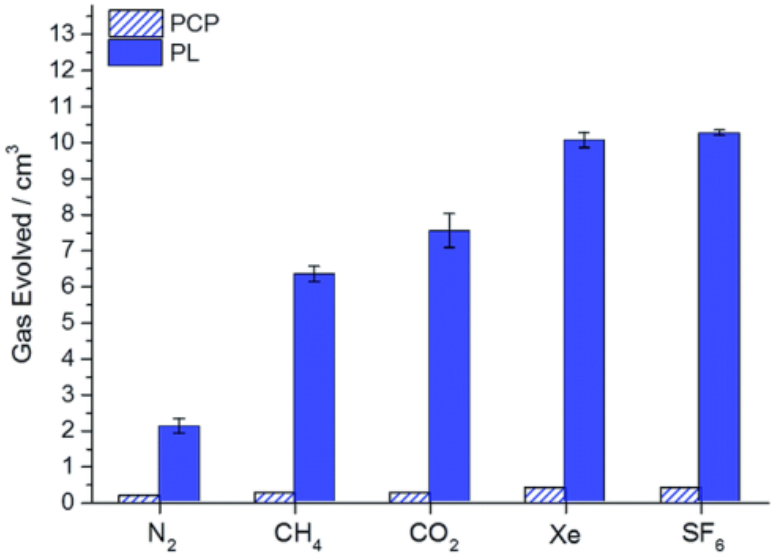
How do these binding sites and the structure of the POC change during the formation of PLs?



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



Yin et al. *J. Mole. Liquids* 344 (2021): 117676.

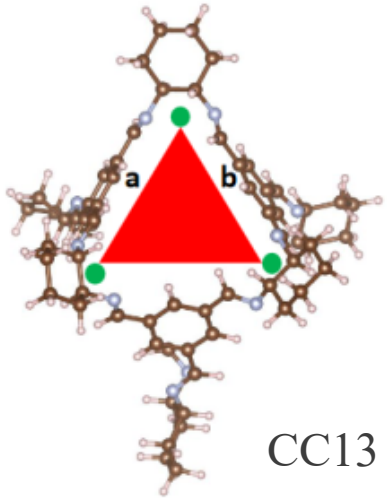


Greenaway et al. *Chem. Sci.* 8.4 (2017): 2640-2651.

Computational Methods

Porous liquid model systems:

- Composed of CC13 porous organic cages (POC) with coordinating solvent molecules
- Twelve different coordinating solvents were investigated (based on proposed solvents for high solubility of CC13)



CC13

#	Name	Abbreviation	Molecular Formula	Molecular Weight
1	Dimethylacetamide	DMA	C_4H_9NO	87.12
2	2-chlorophenol	2CH	C_6H_5ClO	128.50
3	2-fluorophenol	2FH	C_6H_5FO	112.10
4	2-bromophenol	2BH	C_6H_5BrO	173.01
5	2-isopropylphenol	2-IPH	$C_9H_{12}O$	136.19
6	2-Tert-butylphenol	2-TBH	$C_{10}H_{14}O$	150.22
7	Cyclohexanone	CHX	$C_6H_{10}O$	98.14
8	4-hydroxytoluene	4-HT	C_7H_8O	108.14
9	2,4-dimethylphenol	2,4-DMH	$C_8H_{10}O$	122.16
10	2-isopropyl-5-methylphenol	IMH	$C_{10}H_{14}O$	150.22
11	1-acetylindole	1-A	$C_{10}H_9NO$	159.18
12	2-chloro-6-methylphenol	2-CMH	C_7H_7ClO	142.58

Porous Liquids

- POC was placed in a 25 x 25 x 25 Å box and surrounded with 40 solvent molecules
- The porous liquid compositions were relaxed and the packing structure around the POCs were analyzed

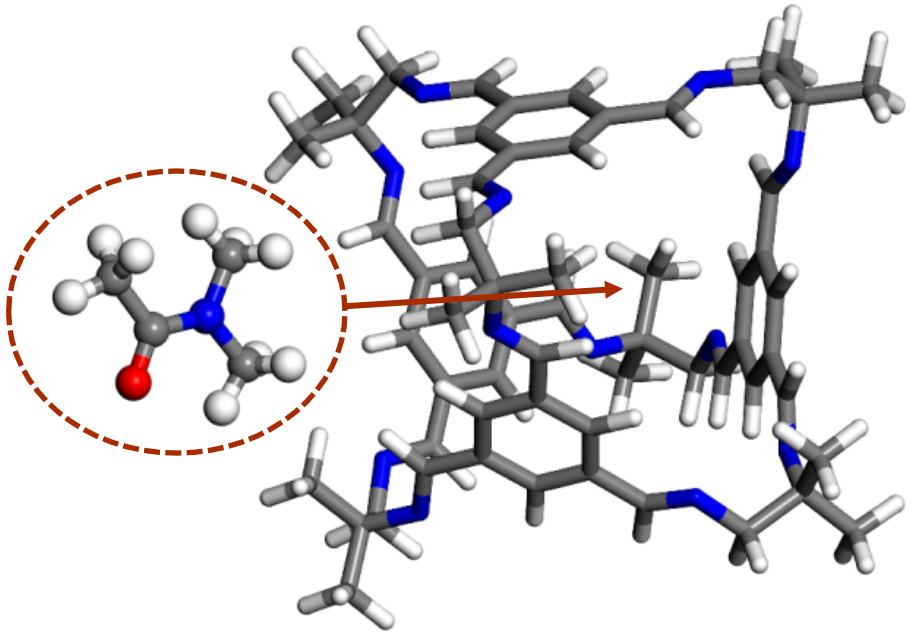
Density Functional Theory (DFT) calculations

- Vienna *ab initio* Simulation Package (VASP)
- Generalized Gradient approximation with PBEsol functional
- Plane wave basis set with Projector Augmented Wave pseudopotentials
- DFT-D3 dispersion corrections
- 1x1x1 K-points
- 400 eV cut-off energies

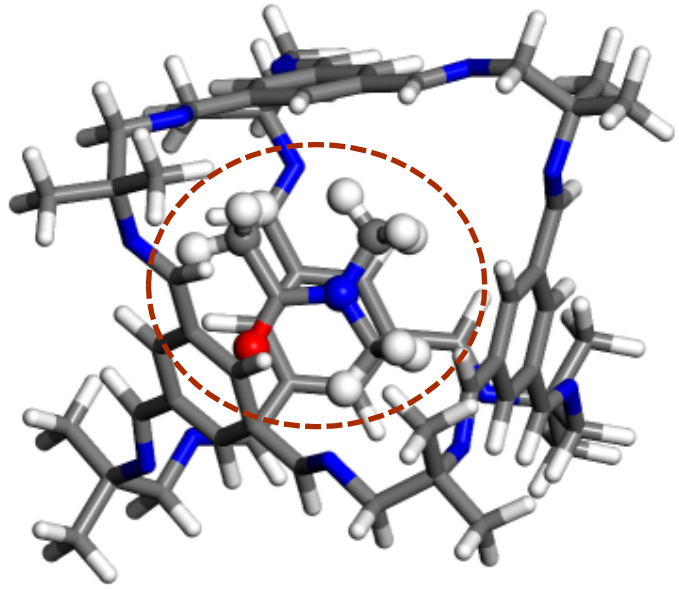
Solvent Molecules are More Stable Inside the POC

- A key feature of porous liquids is the existence of *stable* and *intrinsic* porosity based on solvent molecules staying *outside* the POC
- Evaluated stability of solvent molecules inside and outside the CC13 POC structure

$$B_E = E_{POC+Sol} - \sum E_{POC} + E_{Sol}$$



DMA solvent on the surface of the POC



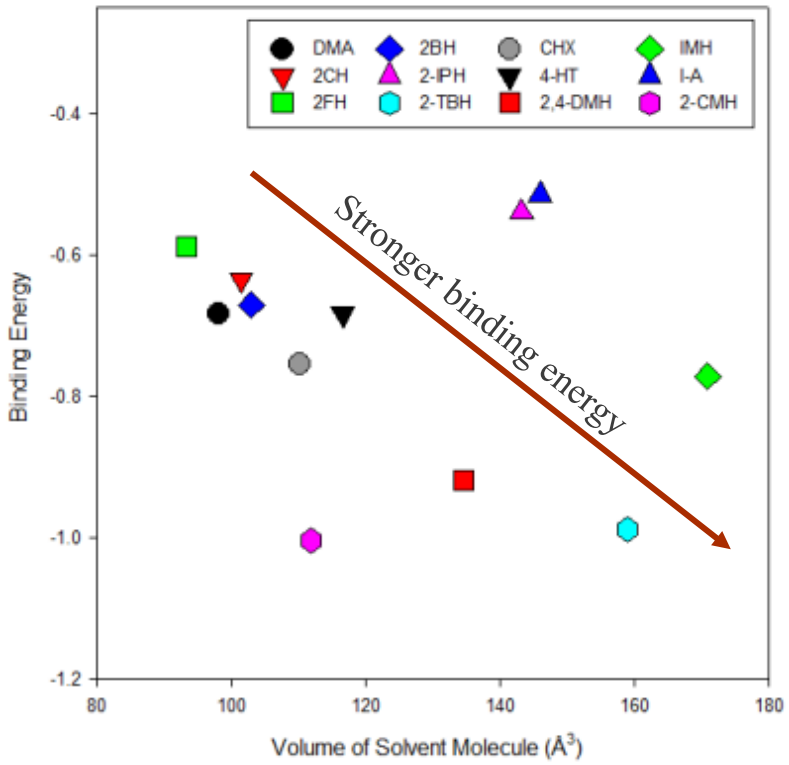
DMA solvent inside the POC

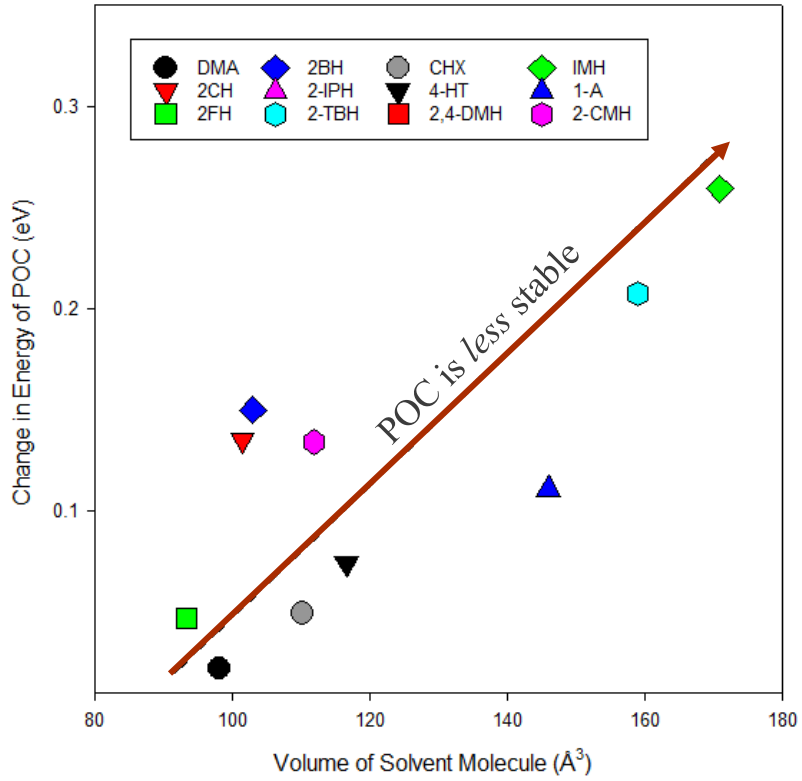
Solvent		Binding Energy (eV)	
		Inside POC	Outside POC
1	DMA	-0.68	-0.16
2	2CH	-0.63	-0.47
3	2FH	-0.59	-0.21
4	2BH	-0.67	-0.52
5	2-IPH	-	-
6	2-TBH	-0.99	-0.60
7	CHX	-0.76	-
8	4-HT	-0.93	-0.51
9	2,4-DMH	-0.68	-0.42
10	IMH	-0.22	-
11	1-A	-0.52	0.18
12	2-CMH	-1.00	-
AVG + SD		**-0.71±0.20**	**-0.34±0.24**

Infiltration by Solvent Molecules Stabilizes the CC13 POC

- Binding energies for solvent inside the POC varied from -1.00 eV (2-CMH) to -0.22 eV (IMH) with a slight negative relationship with increasing molecule volume?

$$B_E = E_{POC+Sol} - \sum E_{POC} + E_{Sol}$$



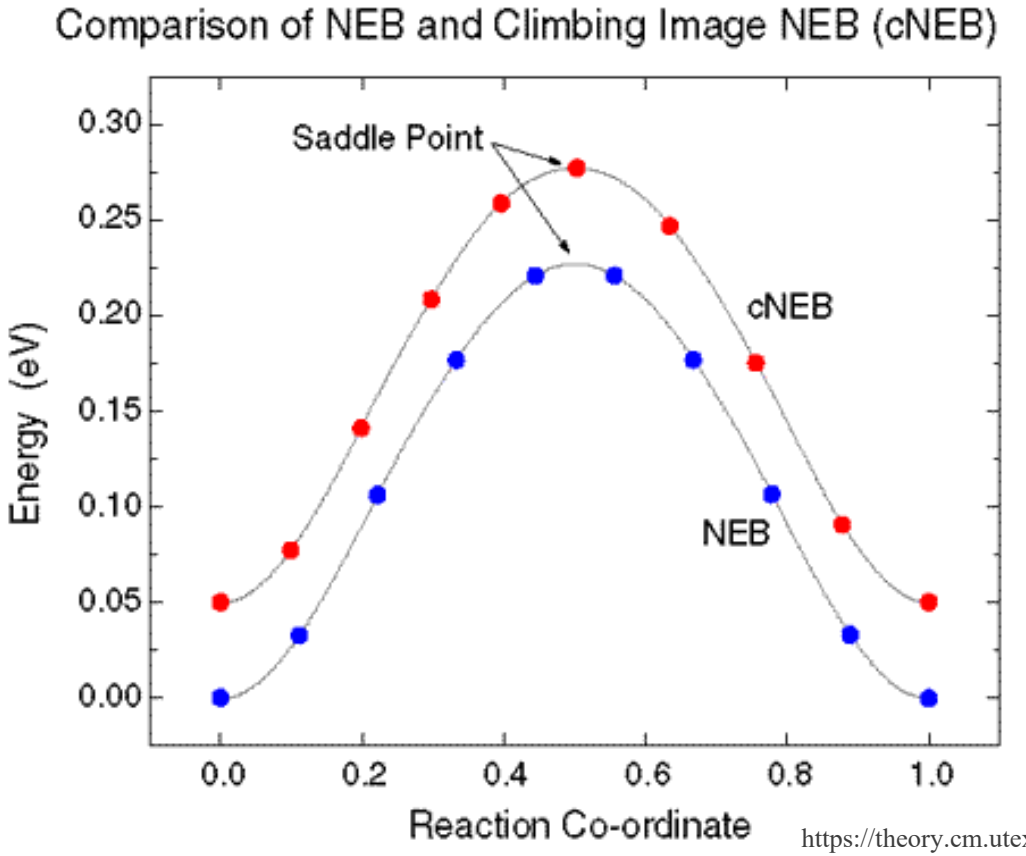


Solvent		Binding Energy (eV)	
		Inside POC	Outside POC
1	DMA	-0.68	-0.16
2	2CH	-0.63	-0.47
3	2FH	-0.59	-0.21
4	2BH	-0.67	-0.52
5	2-IPH	-	-
6	2-TBH	-0.99	-0.60
7	CHX	-0.76	-
8	4-HT	-0.93	-0.51
9	2,4-DMH	-0.68	-0.42
10	IMH	-0.22	-
11	1-A	-0.52	0.18
12	2-CMH	-1.00	-
AVG + SD		**-0.71±0.20**	**-0.34±0.24**

- The structure of the POC changes to to accommodate larger solvent molecules, which has a slight stabilization effect

Does the Solvent Infiltrate the POC?

- Solvents *inside* the POC are more stable than those on the exterior of the POC (by ~0.36 eV).
- Solvent exclusion from the interior of the POC is based on infiltration through the pore window (which can expand to allow for diffusion).
- Performed climbing image nudged elastic band (cNEB) simulation for evaluation of activation energy for solvent infiltration



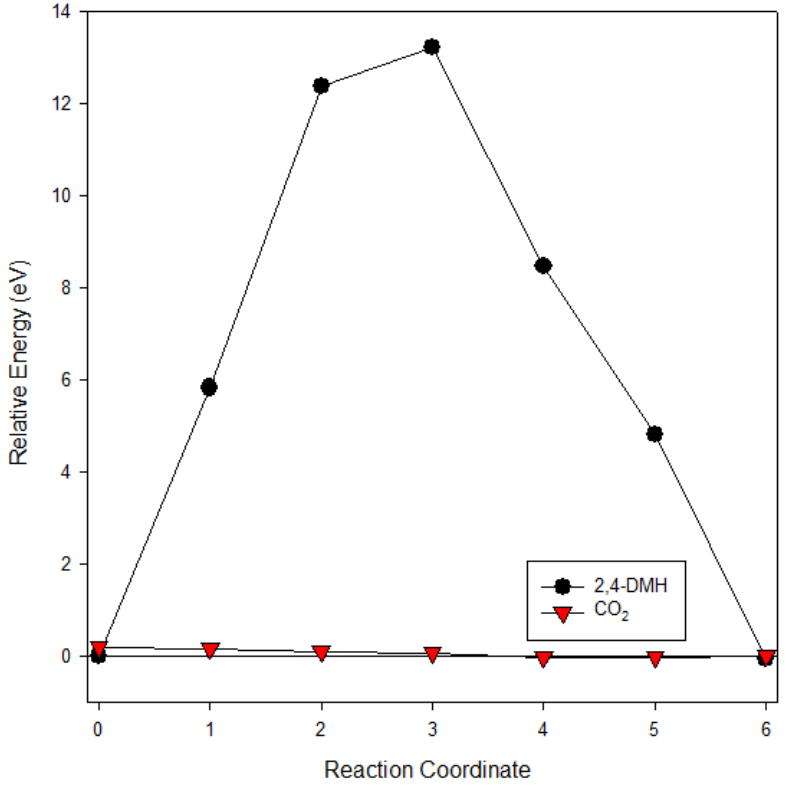
https://theory.cm.utexas.edu/vtsttools/neb.html

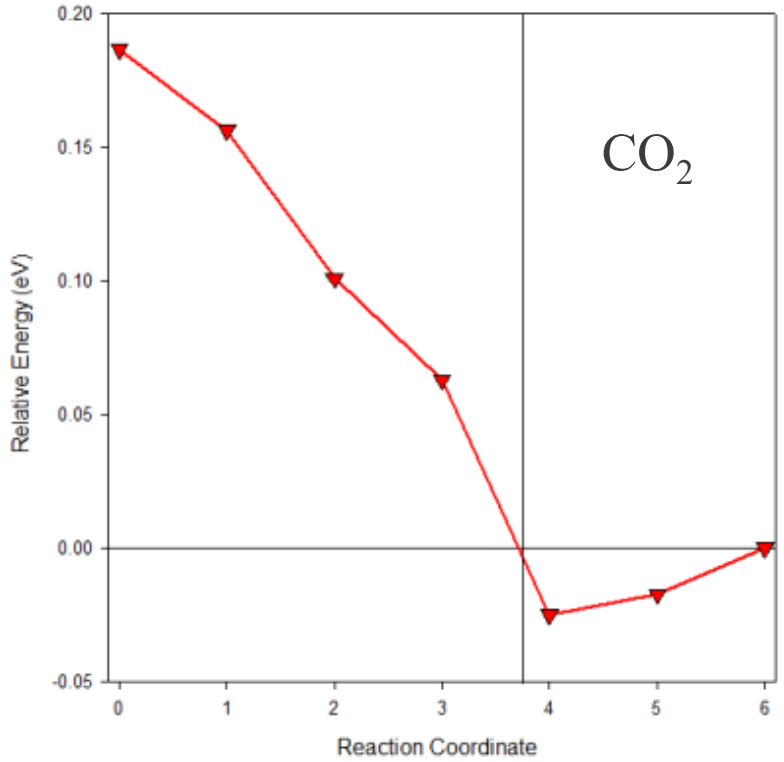
Solvent		Binding Energy (eV)		
		Inside POC	Outside POC	Difference
1	DMA	-0.68	-0.16	0.61
2	2CH	-0.63	-0.47	0.13
3	2FH	-0.59	-0.21	0.44
4	2BH	-0.67	-0.52	0.12
5	2-IPH	-	-	-
6	2-TBH	-0.99	-0.60	0.29
7	CHX	-0.76	-	-
8	4-HT	-0.92	-0.43	0.50
9	2,4-DMH	-0.68	-0.50	0.17
10	IMH	-0.22	-	-
11	1-A	-0.52	0.18	0.68
12	2-CMH	-1.00	-	-
	CO_2	-0.26	-0.16	0.18
AVG + SD		**-0.69±0.20**	**-0.38±0.16**	**0.36±0.20**

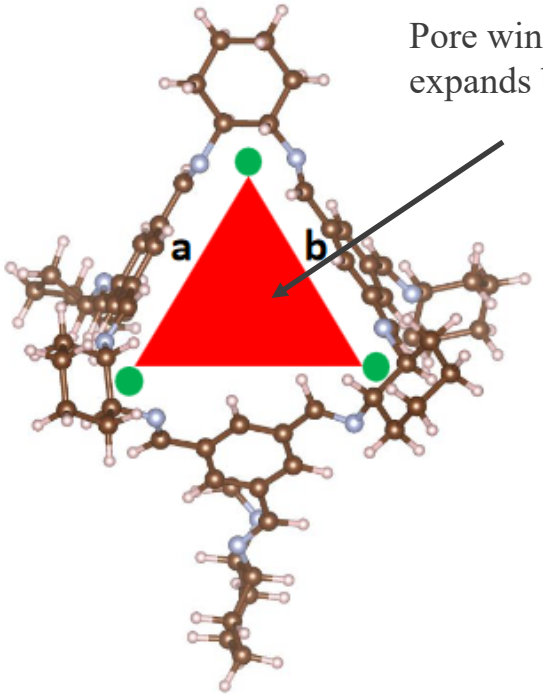
High Activation Energy for Solvent Infiltration Enables CO_2 Capture

- Despite low binding energy of CO_2 within the POC, the activation energy extremely low for capture
- Stable binding site of CO_2 in the POC is in the window, not in the center of the pore

Could the POC expand to accommodate multiple gas molecules?

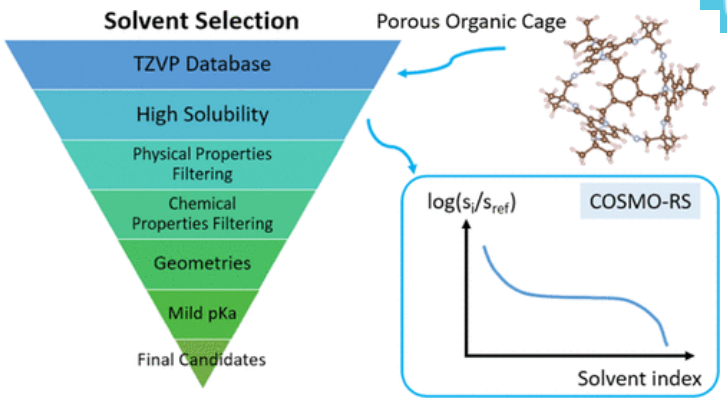




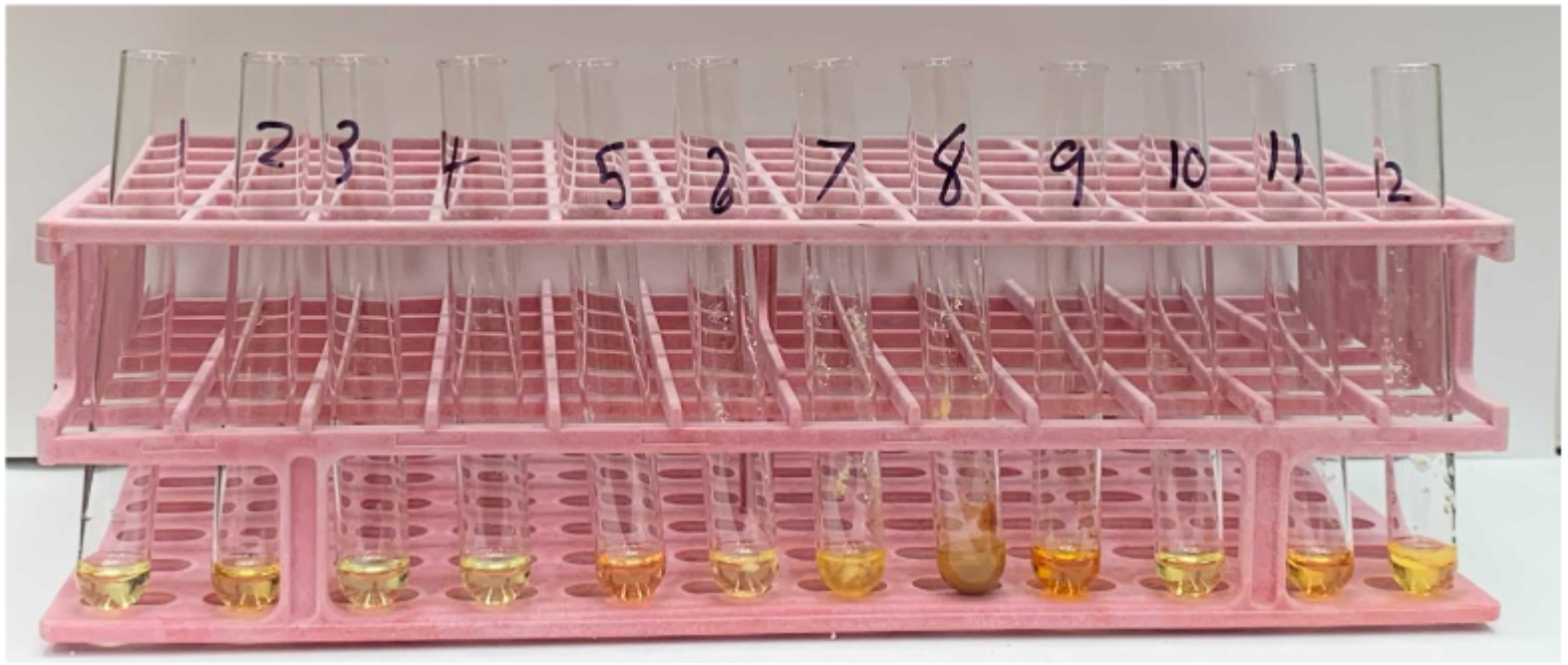


Does Binding Energies Control CC13 Solubility?

- Does the binding energy of the bulk or individual solvent molecules influence the solubility?
- Experimental solubility from previously published results based on machine learning prediction of solvents with high CC13 solubility (from COSMO-RS calculations)



Chang et al (2022). *J. Amer. Chem. Soc.*, *144*(9), 4071-4079.

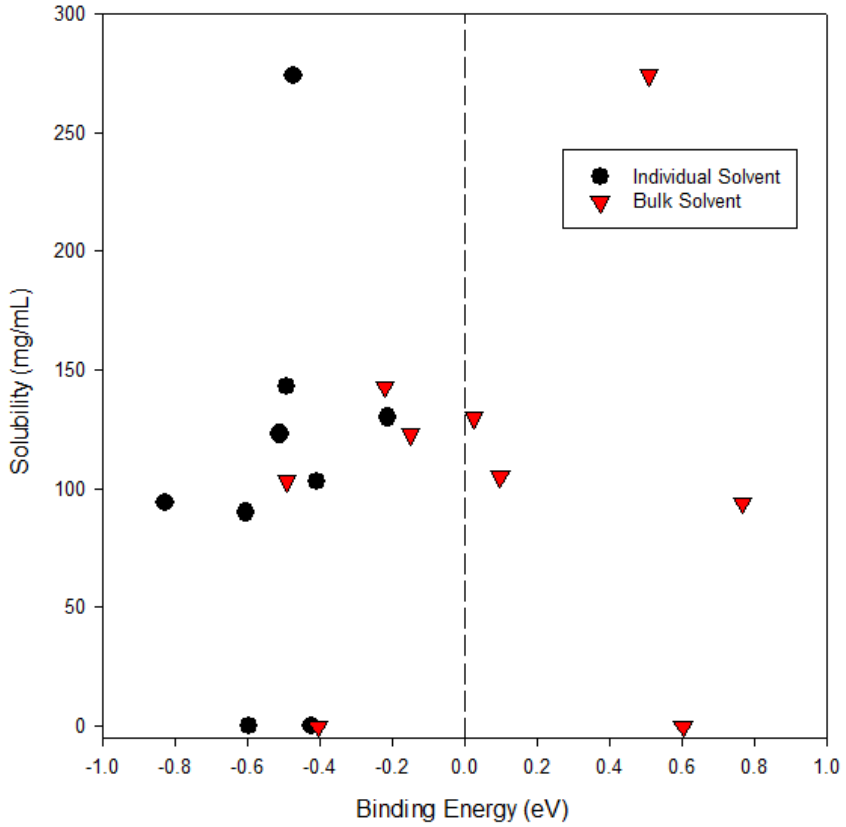


Experimental solubility test for solvent candidates predicted to dissolve CC13 well by COSMO-RS filtering scheme. Solvents from left to right labeled 1-2 in the figure: (1) 2CH, (2) 2FH, (3) 2BH, (4) 2-IPH, (5) 2-methyl-6- chlorophenol, (6) 2-TBH, (7) cyclopentanone, (8) CHX, (9) 4- HT, (10) 2,4-DMH, (11) 2-isopropyl-5-methylphenol, and (12) 1-A.

Solvent		Solubility (mg/mL)
1	DMA	-
2	2CH	274
3	2FH	130
4	2BH	123
5	2-IPH	105
6	2-TBH	0
7	CHX	0
8	4-HT	143
9	2,4-DMH	103
10	IMH	94
11	1-A	-
12	2-CMH	90

No Strong Correlation Between Solubility and Binding Energies

- Solubility of the POC in different solvents is uncorrelated ($R^2 < 0.1$) with the surface area or molecular volume of the solvent
- Binding energy of individual ($R^2 = 0.03$) and bulk ($R^2 = 0.02$) solvent also do not exhibit a correlation.
- What is causing the anomalous high solubility of the CC13 cage in 2CH?



Solvent		Surface Area (Å²)	Molecular Volume (Å³)	Solubility (mg/mL)	Binding Energies (eV / molecule)	
					Single	Bulk
1	DMA	116.46	-	-	-0.16	-0.52
2	2CH	122.44	274	274	**-0.47**	0.51
3	2FH	114.13	130	130	-0.21	0.02
4	2BH	126.22	123	123	-0.51	-0.15
5	2-IPH	157.31	105	105	**1.39**	0.10
6	2-TBH	169.37	0	0	**-0.59**	0.60
7	CHX	123.20	0	0	**-0.39**	-0.41
8	4-HT	133.05	143	143	**-0.47**	-0.22
9	2,4-DMH	150.69	103	103	**-0.40**	-0.49
10	IMH	182.43	94	94	**-0.48**	0.77
11	1-A	165.48	-	-	**0.19**	0.614
12	2-CMH	136.16	90	90	**-0.59**	-

Chang et al (2022). *J. Amer. Chem. Soc.*, *144*(9), 4071-4079.

Conclusions

- A suite of twelve Type 2 porous liquid compositions are under investigation through density functional theory (DFT) simulation methods
- Of the 12 candidate solvents, 11 of them were more stable inside the pore due to flexibility of the CC13 POC structure
- High activation energies for diffusion of the solvent molecule through the small pore window of the CC13 POC cage kept the interior of the pore from being filled
- Experimental solubilities of the CC13 cages in the candidate solvent did not vary with the binding energy of the solvent to the exterior of the cage (from single or bulk solvents)

Future work:

- Evaluation of changes in the POC following solubility
- Binding structure of solvents with high solubility (e.g., 2CH) to the POC
- Differences in binding of N_2 versus CO_2 inside and outside the POC when dissolved

Acknowledgement

Co-Authors

- Tina Nenoff (Sandia National Laboratories)

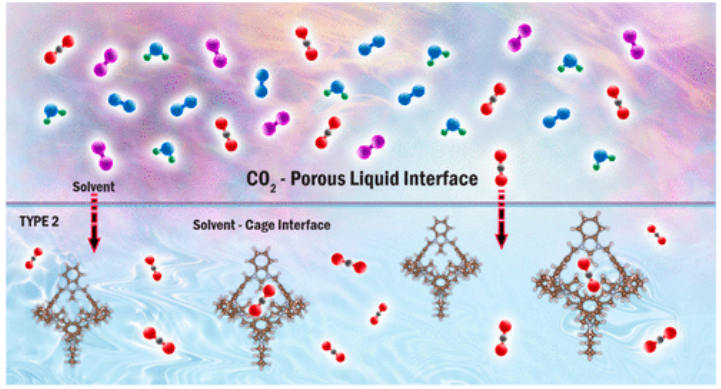
Collaborators

- Sandia National Laboratories: Matthew Christian, D. Jon Vogel
- Georgia Tech: Ryan Lively, Chao-Wen Chang, Isaiah Born
- Oak Ridge National Laboratory: David Sholl

Funding

The work was supported through the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories and by the UNCAGE-ME Energy Frontier Research Centers funded by the U.S. Department of Energy, Office of Science

More information:



Rimsza, J. M., & Nenoff, T. M. (2022). Porous Liquids: Computational Design for Targeted Gas Adsorption. *ACS Applied Materials & Interfaces*, *14*(16), 18005-18015.

Questions?

Via email: jrimsza@sandia.gov