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# Gas Interactions with CC3-based Type 2 Porous Liquids

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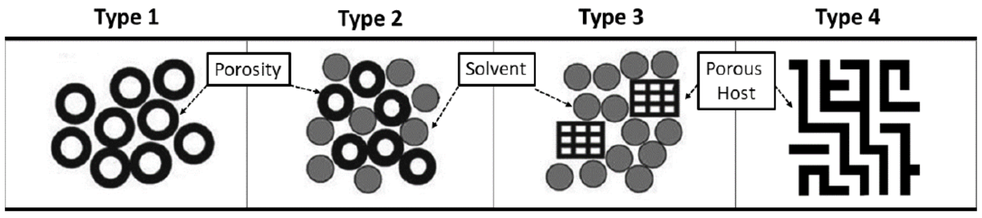
## Introduction

- Porous liquids = stable combination of solvent and porous host materials.
- Permanent porosity is from steric exclusion of solvent from the internal porosity
- First reported by Giri et al. "Liquids with permanent porosity." *Nature* 527.7577 (2015): 216-220.

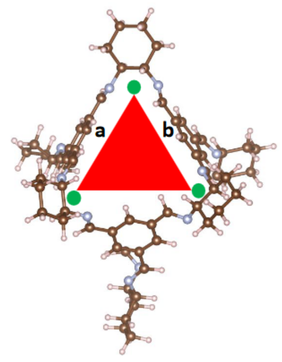



**The four types of PLs**

- Type 2 PLs are composed of a porous organic cage (POC) and a bulky solvent (e.g., crown ethers).
- PLs have potential for high capacity and highly selective gas separation and adsorption. [1]
- Several features of PLs may be controlling their properties:
  - Solvent packing around the POC and POC-solvent interface
  - Changing stability of $CO_2$ *inside* the PL structure
- Periodic density functional theory (DFT) calculations can identify fundamental structural and chemical features of PLs and mechanisms of $CO_2$ adsorption and separation.

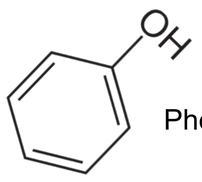
## Computational Methods

- Vienna *ab initio* Simulation Package (VASP)
- Generalized Gradient approximation with PBEsol functional. [2]
- Plane wave basis set with Projector Augmented Wave (PAW) pseudopotentials and dispersion corrections treated by DFT-D3 method with Becke-Johnson Damping. [3,4]
- 1x1x1 K-points, 400 eV cut-off energies

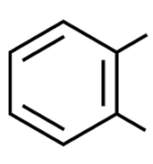



**CC3 POC Structure [5]**

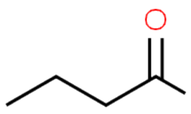
### Coordinating Solvents




Phenol (Ph)




2-Chlorophenol (2-Cl)




Butyramide (Bt)

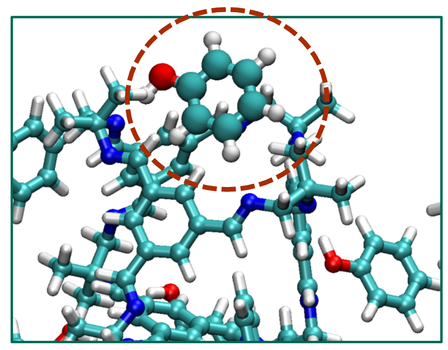
- 10 molecules are packed around the CC3 POC in a 30x30x30 Å box
- Following structural relaxation changes in the CC3 POC were identified through single point calculations of the final structure
- Binding energies for $CO_2$ and solvents inside the PL structures were calculated:

$$E_B = E_{POC+Gas/Solvent} - \sum E_{POC} + E_{Gas\ OR\ Solvent}$$

## Results

**Stability of $CO_2$ and the solvent molecules *inside* the POC**

- Ph and Bt are stable in the POC, while 2-Cl and $CO_2$ are not.
- Benzene rings keep the solvent from diffusing into the POC, even for small molecules (e.g. Ph stays outside the POC while Bt diffuses in).
- Ph and 2-Cl sit in the pore window of the POC.



**2-Cl molecule in the pore window of the POC**

| | $E_B$ (eV) | Diffuse into POC? | Molar Volume (Å$^3$) |
|---|---|---|---|
| $CO_2$ | -0.02 | Yes | 36 |
| Ph | -0.729 | No | 110 |
| 2-Cl | 1.007 | No | 130 |
| Bt | -0.667 | Yes | 119 |

**Changing Structure of the POC**

- POC undergoes structural changes through coordination by the solvents forming less energetically favorable structures.
- Pore windows, identified by position of nitrogen in the linkers, increased by 2-7%.
- Changing pore window could impact ability to form stable PLs.

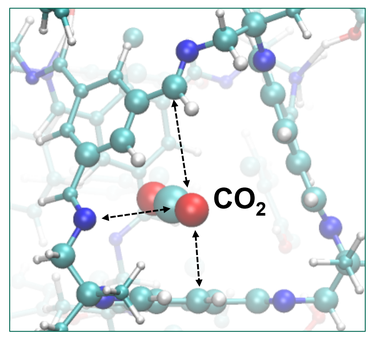
| | Change in Energy (eV) | Size of Pore Window (Å$^2$) |
|---|---|---|
| Vacuum | - | 29.1 |
| Ph | 0.201 | 31.2 (7.4%) |
| 2-Cl | 0.251 | 29.7 (2.2%) |
| Bt | 0.103 | 30.1 (3.6%) |

**$CO_2$ binding energies inside candidate PLs**

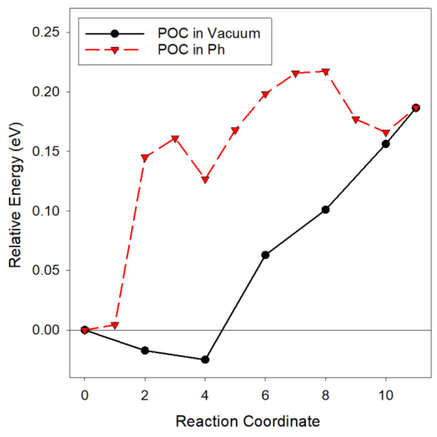
- Coordinating solvents increase the stability of $CO_2$ in the POC by -0.1 to -2.0 eV.
- $CO_2$ is most stable *in* the pore window rather than in the center of the pore.

| | $CO_2$ Binding Energy (eV) |
|---|---|
| Vacuum | 0.025 |
| Ph | -0.164 |
| 2-Cl | -2.023 |
| Bt | -0.525 |

**Low energy $CO_2$ binding structure in the 2-Cl PL**




- Nudged-elastic-band (NEB) calculations [6] identified *energy barriers* for $CO_2$ entrance into the pore
- Phenol increased the energetic barrier to 0.22 eV compared to the POC in a vacuum




## Conclusions and Future Work

- Three candidate PL compositions were simulated with DFT for potential applications as $CO_2$ capture materials.
- Solvents with benzene rings were large enough to be hindered from entering the POC despite being stable in the internal pore space.
- Coordination of the POC by the solvents increased the pore window size, increasing the solvent size necessary for PL formation.
- $CO_2$ is more stable in the POC in a PL than in the same POC in vacuum, which is promising for improved $CO_2$ selectivity in PLs over POCs.
- 12 additional coordinating solvents are being evaluated to identify trends in $CO_2$ adsorption properties and PL stability.

**Candidate Solvents**

1. Dichloromethane
2. Dimethylacetamide
3. 2-fluorophenol
4. 2-bromophenol
5. 2-isopropylphenol
6. 2-tert butylphenol
7. Cyclohexane
8. 4-hydroxytoluene
9. 2,4-dimethylphenol
10. 2-isopropyl-5-methylphenol
11. 1-acetylindole
12. 2-chloro-5-methylphenol

## References

[1] Rimsza, Jessica M., and Tina M. Nenoff. "Porous Liquids: Computational Design for Targeted Gas Adsorption." *ACS Appl. Mater. Interfaces* 14.16 (2022): 18005-18015., [2] Kresse, Georg, and Jürgen Hafner. *Phys. Rev. B* 47.1 (1993): 558, [3] Kresse, Georg, and Daniel Joubert. *Phys. Rev. B* 59.3 (1999): 1758. [4] Grimme, Stefan, et al. *J. Chem. Phys.* 132.15 (2010): 154104. [5] Vogel, Dayton J., Tina M. Nenoff, and Jessica M. Rimsza. *ACS Omega* 7.9 (2022): 7963-7972. [6] Henkelman, Graeme, Blas P. Uberuaga, and Hannes Jónsson. *J. Chem. Phys.* 113.22 (2000): 9901-9904.

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