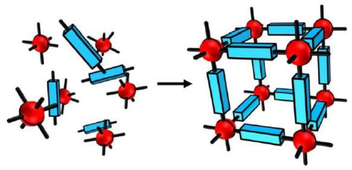
Self-Assembly of Metal-Organic Frameworks

Yamil J. Colón, Ashley Guo, Lucas Antony, Kyle Hoffmann, and Juan de Pablo
Institute for Molecular Engineering, University of Chicago, Chicago, IL
Argonne National Laboratory, Lemont, IL

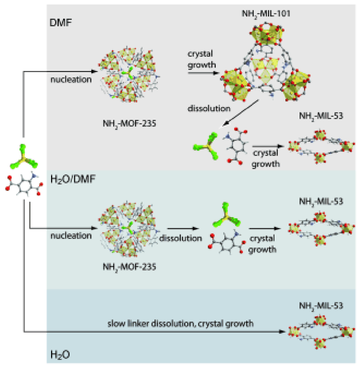
Metal-Organic Frameworks

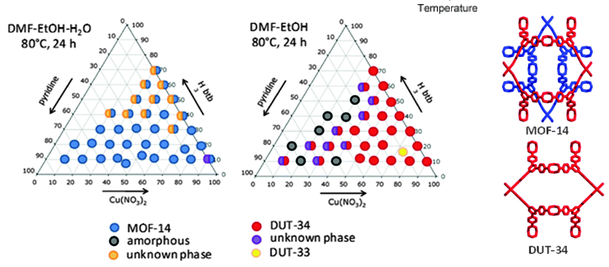
Nanoporous Materials

- Metal-organic frameworks (MOFs) are nanoporous crystalline materials self-assembled in solution from inorganic and organic building blocks.
- Judicious choice of building blocks allows for tailoring towards particular applications such as: storage, catalysis, sensing, delivery, etc.
- Large number of combinations of building blocks has led to MOF-generation algorithms and high-throughput screening studies.[1]
- However, MOF self-assembly remains poorly understood.



Experimental Studies



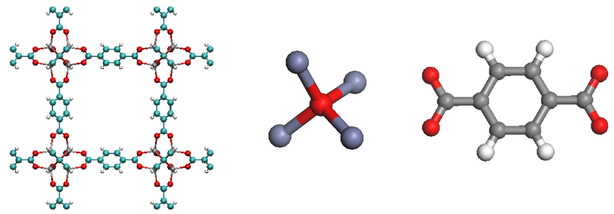


- Rich self-assembly behavior.
- Solvent, temperature, and concentration dependent.[2,3]
- Same conditions can lead to different MOF structures.
- Computational self-assembly studies can provide meaningful insight.[4]

Model

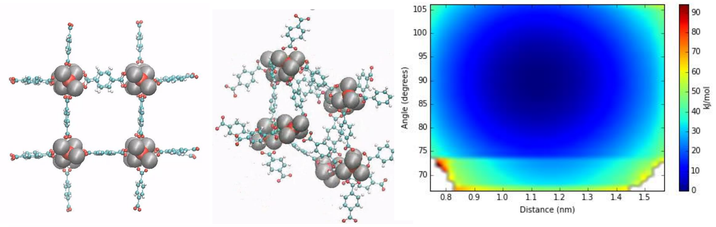
MOF-5

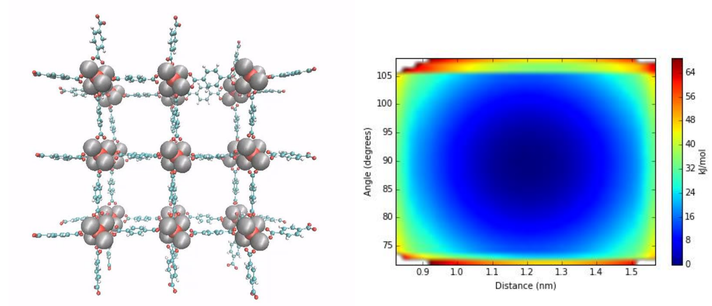
- MOF-5 model was taken from Dubbeldam *et al.*[5]
- MOF-5 is a **pcu** structure formed by ZnO_4 nodes and benzene dicarboxylate linkers.



Validation

- Replica Exchange with Solute Tempering (REST2).
- DMF as explicit solvent.



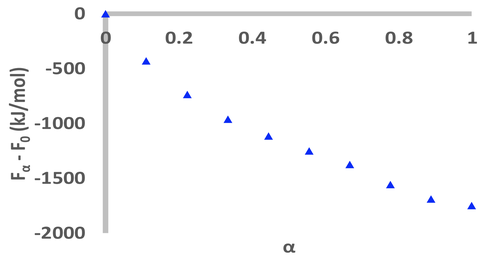


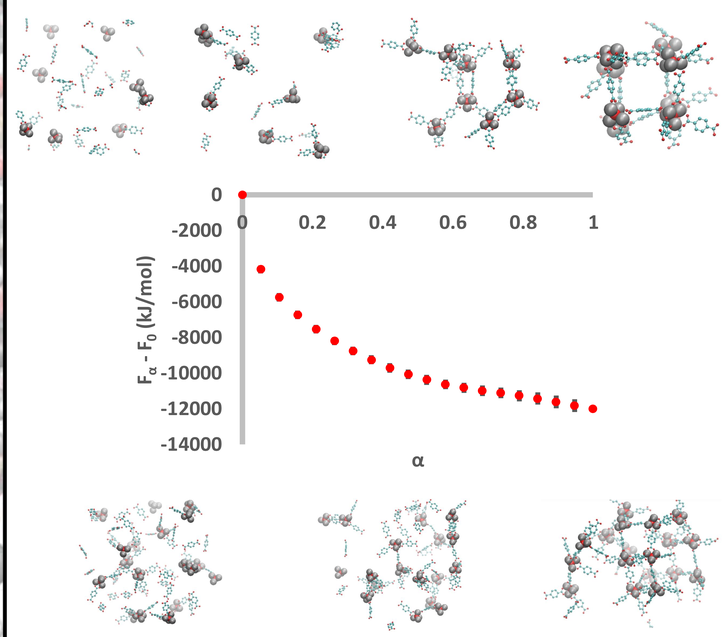
- 16 replicas between 300 and 500 K for 60 ns.
- Collective variables: average angle between adjacent nodes in unit cell, average distance between adjacent nodes.
- Location of minima agree well with experimental unit cell values: 90 degrees, 1.3 nm.

Self-Assembly

Finite Temperature String Method

- FTS method can give us a pathway between two states and the free energy associated with the pathway.
- Added coordination collective variable.
- Transition between disassembled to assembled state.





- Results show the process to be downhill.
- Simulations show the formation of dimers and trimers followed by multiple nodes linked together and finally, the full assembly of the MOF.
- These are the first time these simulations tools are used to study and characterize the self-assembly of MOFs.

References:

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2. Stavitski, E., Goesten, M., Juan-Alcaniz, J., Martinez-Joaristi, A., Serra-Crespo, P, Petukhov, A. V., Gascon, J., and Kapteijn, F. *Angewandte Chem. Int. Ed.* **2011,** 50(41): 9624-9628
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4. Yoneya, M.; Tsuzuki, S.; Aoyagi, M., *Phys. Chem. Chem. Phys.* **2015,** 17(14), 8649-8652.
5. Dubbeldam, D., Walton, K. S., Ellis, D. E., Snurr, R. Q., *Angew. Chem.* **2007,** 119 (24), 4580-4583.