FMRI RET 2015 - Computational Investigation of the Effect of Changing the Organic Linker on the Gas Adsorption Properties of Isoreticular Metal–Organic Frameworks

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Abstract

Hydrogen (H_2) and Carbon Dioxide (CO_2) adsorption simulations were performed on three similar Metal-Organic Frameworks to determine if the organic linker has an affect on the amount of gas sorbed by the MOF.

Background

Metal Organic Frameworks (MOF) are composed of metal clusters joined by organic linkers that form a crystalline structure with a high porosity. Current uses for MOFs focus on gas separation and gas storage.[1] MOFs are highly tunable as a number of different structures can be synthesized or envisioned by changing the metal cluster and/or linker. The isoreticular MOF (IRMOF) series is one of the earliest known examples of a MOF platform.[2] These MOFs are constructed from Zn_4O clusters and linear dicarboxylate linkers, resulting in a material that has primitive cubic topology. An example of an IRMOF is shown in Figure 1.

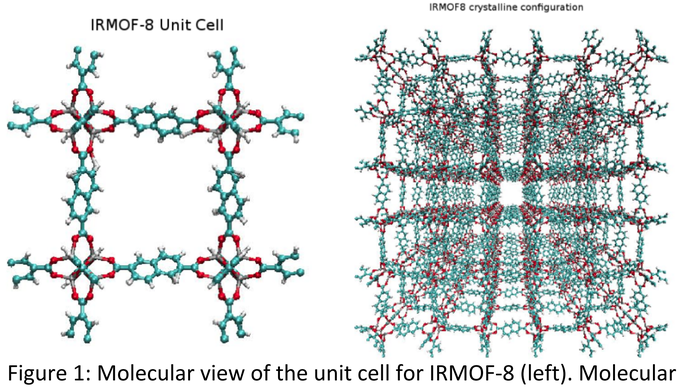

Figure 1: Molecular view of the unit cell for IRMOF-8 (left). Molecular view of a super cell of IRMOF-8 (right). Atom colors: C = cyan, H = white, O = red, Zn = silver.

Objective

To determine whether the organic linker present in IRMOFs plays an appreciable role in the amount of gas uptake within the MOF from computer simulations.

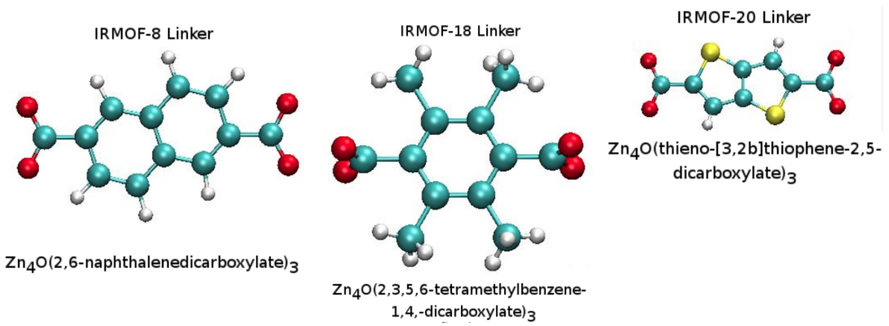

Figure 2: The organic linkers used to synthesize IRMOF-8 (left), IRMOF-18 (middle), and IRMOF-20 (right). Atom colors: C = cyan, H = white, O = red, S = yellow, Zn = silver.

Approach

Three MOFs (IRMOF-8, IRMOF-18, IRMOF-20) that contain the same Zn_4O metal cluster, but distinct linearly shaped dicarboxylate linkers were considered (Figure 2). The potential energy function, consisting of repulsion/dispersion and electrostatic parameters, for each MOF was developed using computational methods inherent in the Space research group.[3] The point partial charges for the different unique atoms in each MOF were determined through electronic structure calculations on various fragments that were extracted from the crystal structure of the respective MOFs. These calculations were performed using the NWChem software.[4]

Simulations of H_2 and CO_2 adsorption were performed in each MOF using the Belof Stern Space[5] (BSS) and CO_2-PHAST[6] models, respectively, to determine the H_2 and CO_2 gas uptake for each. All simulations were performed using the Massively Parallel Monte Carlo (MPMC) code.[7]

References

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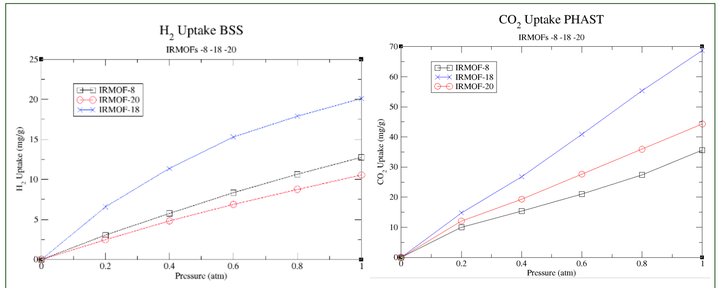

Figure 3: Simulated H_2 adsorption isotherms at 77 K (left) and simulated CO_2 adsorption isotherms at 298 K (right) in IRMOF-8 (black), IRMOF-18 (blue), and IRMOF-20 (red) for pressures up to 1 atm.

Conclusions

It was determined that the organic linker present in the IRMOF does affect the amount of gas uptake. As shown in figure 3, IRMOF-18 had a significantly higher H_2 and CO_2 uptake than the other IRMOFs tested for all pressures considered. This could be attributed to the shorter linker size for IRMOF-18 compared to the other two MOFs, which results in a MOF with smaller pore sizes. This demonstrates the effect that small pore sizes have on the H_2 and CO_2 uptake in MOFs, as narrower pores would allow more MOF components to interact with the molecules simultaneously. This could also be due to the higher calculated partial positive charges of the Zn^{2+} ions in IRMOF-18 compared to IRMOF-8 and IRMOF-20. In the future, further simulations using other H_2 and CO_2 models will be performed and compared to these results. Additionally, these results will be compared to experimental results.

Acknowledgments

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