Project title: Engineering Metal-Organic Frameworks for Stability in Gas Storage Applications
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Final report

Proposal scope and goals

The overarching goal of this MPP Seed proposal was to develop novel computational strategies to identify optimal MOF materials for greenhouse gas (i.e., CH_4 and CO_2) capture. This proposal aimed to address critical challenges for VHTS by 1) creating a set of MOFs with high thermal and mechanical stability and 2) screening these MOFs with molecular simulation to identify stable materials for gas capture. It leveraged experience from José Paulo Mota and Rui Ribeiro, collaborators at Universidad NOVA de Lisboa, in synthesis and characterization of materials (e.g., MOFs) for greenhouse gas mitigation.

Accomplishments during the proposal period

Creation of a set of MOFs with high thermal and mechanical stability. High-throughput screening of hypothetical metal–organic framework (MOF) databases can uncover new materials, but their stability in real-world applications is often unknown. We leveraged community knowledge and machine learning (ML) models to identify MOFs that are thermally stable and stable upon activation. We separated these MOFs into their building blocks and recombine them to make a new hypothetical MOF database of over 50,000 structures that samples orders of magnitude more connectivity nets and inorganic building blocks than prior databases. This database showed an order of magnitude enrichment of ultrastable MOF structures that are stable upon activation and more than one standard deviation more thermally stable than the average experimentally characterized MOF. For nearly 10,000 ultrastable MOFs, we computed elastic moduli to confirm these materials have good mechanical stability, and we reported methane deliverable capacities. We identified privileged metal nodes in ultrastable MOFs that optimize gas storage and mechanical stability simultaneously. This work was published[1] in Nandy et al. *Matter* 2023, was featured in MIT News, and the resulting materials were disseminated on our MOFSimplify website.

Identification of the effect of framework rigidity on gas uptake. The flexible degrees of freedom in MOFs can have significant effects on guest molecule behavior. However, in the majority of studies applying molecular simulations to MOFs, the framework is assumed to be rigid in order to minimize computational cost. We assessed the significance of this assumption on a representative example of methane uptake and diffusion in UiO-66. We introduced an open-source code to modify MOFs through functionalization and linker rotation and we performed Grand Canonical Monte Carlo and molecular dynamics simulations of methane in each of the functionalized and linker-rotated derivatives of UiO-66. We found that linker rotation moderately influences methane uptake and significantly influences methane diffusion. Our assessment provides

ranges of property values that serve as measures of uncertainty of these two properties associated with linker rotation. We further determined that void volume fraction and minimum pore size are the features that govern methane uptake and diffusion, respectively. These findings illustrated the impact of linker rotation on MOFs and provide design principles to guide future investigations. This work was published[2] in Yue et al. *Mol. Sys. Des. Eng.* 2023, and the code was disseminated on our Github.

Screening ultrastable materials for CO_2 and CH_4 uptake. We extended our prior screen of ultrastable materials to cover not just methane uptake but also to obtain comparative carbon dioxide uptake and working capacity. We discovered a novel behavior of our ultrastable MOFs, namely that some of them preferentially store more carbon dioxide than they do methane. This is distinct from experimentally characterized MOFs that always tend to store more methane. We trained machine learning models on these properties and analyzed feature importances from the models to further deduce which aspects of structure are predictive of high carbon dioxide uptake. This work is currently in preparation for publication (*C. Oh,* et al, in preparation).

Other efforts. We developed a web interface to a tool for predicting gas isotherms of MOFs called SESAMI App in collaboration with a sabbatical visitor (Greg Chung, Pusan National University). This work was published[3] in G. G. Terrones et al, *Journal of Open Source Software*, 2023.

Interactions with Portugal Collaborators

One graduate student visited Portugal to present his work (Aditya Nandy) at the MIT-Portugal Workshop in Fall 2022. The PI (Kulik) visited Universidad NOVA de Lisboa to meet with José Paulo Mota and Rui Ribeiro for a full day discussion and tour of their labs in Spring 2023. This sparked ongoing collaborations that are extending beyond the proposal period.

Summary of outputs and personnel trained

Three graduate students and one postdoc were trained as part of this award. In total three major publications resulted from the award period.[1-3] One more publication is forthcoming on the relative uptake of CO_2 and CH_4 in metal-organic frameworks.

Longevity for the Project beyond MPP Seed funding

The outcomes of this award have led to interest from industry, and the PI Kulik is currently pursuing funding for screening of MOFs for direct air capture through a collaborative grant with the Murata Manufacturing Co Ltd. based in Japan as well as other potential opportunities from both industry and federal agencies.

Publications resulting from the award

1. Nandy, A.; Yue, S.; Oh, C.; Duan, C.; Terrones, G. G.; Chung, Y. G.; Kulik, H. J., A Database of Ultrastable MOFs Reassembled from Stable Fragments with Machine Learning Models. *Matter*, **6**, 1585-1603 (2023).

2. Yue, S.; Oh, C.; Nandy, A.; Terrones, G. G.; Kulik, H. J., Effects of MOF linker rotation and functionalization on methane uptake and diffusion. *Molecular Systems Design & Engineering*, **8**, 527-537 (2023).
3. Terrones, G. G.; Chen, Y.; Datar, A.; Lin, L.-C.; Kulik, H. J.; Chung, Y. G., SESAMI APP: An Accessible Interface for Surface Area Calculation of Materials from Adsorption Isotherms. *Journal of Open Source Software*, **8**, 5429 (2023).