Computational Design of Stable Metal-Organic Frameworks for Gas Adsorption

by

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Abstract

Metal-organic frameworks (MOFs) offer a highly tunable platform for addressing energy and environmental challenges, but their practical discovery requires computational approaches that can connect molecular-scale structure to valid application-level performance. In this thesis, various computational tools, including molecular simulations, density functional theory, machine learning (ML), and multi-objective optimization were used to develop computational workflows for discovering novel MOFs with practical relevance to gas storage, separation, and related materials applications. This thesis demonstrates that computational MOF design must account for the combined effects of structural diversity, chemistry, stability, and application-specific process conditions. The importance of the framework flexibility is validated through systematic rotation of linkers in UiO-66, revealing how framework motion affects pore geometry and therefore determines methane uptake. Next, this thesis examines how different MOF databases span distinct geometric and chemical regimes. Although ML models can predict the adsorptions for the studied databases, they are not transferable across databases. This suggests that gas adsorption design rules depend strongly on the chemical space being explored. Building on these insights, this thesis introduces a stability-aware MOF discovery framework for direct air capture that integrates ML model predictions of thermal, activation, water, acid, and mechanical stability along with adsorption using a multi-objective evolutionary algorithm. This workflow demonstrated that some of the existing chemical motifs in MOFs that exhibit high adsorption performance, such as open metal sites, may become less favorable when considering stability metrics and competitive adsorption. Similarly, to assess the effect of the process conditions in computational design, the same workflow was applied to the point-source carbon capture application conditions. Process conditions also played important role in determining the design rules of the MOFs, in which best performing MOFs identified for direct air capture application did not necessarily show high performance in point-source capture condition. In addition to adsorption applications, first-principles calculations are used to investigate how defect and side-chain engineering can play an important role in improving catalytic and electronic properties while maintaining stability in MOFs. These works further illustrate the importance of the local coordination environments and non-covalent interactions in balancing the tradeoffs. Overall, this thesis shows that reliable computational materials discovery requires not only optimizing the individual performance metrics, but also accounting for the database-dependent distribution, material stability, and process-specific operating conditions.

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