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Quantifying Structural Rigidity in Metal–Organic Frameworks with Increased Linker Dimensionality

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Given that chemical separations account for 15% of the world's total energy consumption, it is critical to design energy-efficient pathways for the purification of chemical mixtures.1 Membrane separations and adsorption processes are promising nonthermal alternatives to energy-intensive separation technologies, as they separate molecules by size or chemical affinity. Metal–organic frameworks or MOFs are some of the best materials for these applications due to their nanoporosity and high tunability. When tuning MOFs toward separating molecules with sub-Ångstrom differences in size, a common challenge in industrial separations, defining a MOF's local pore environment is the most important factor. However, researchers typically focus on the dimensionality of the overall structure when designing MOFs, rather than considering the dimensionality effects of the linker component itself. We sought to leverage increased linker dimensionality to achieve precise, nano-scale control over a MOF's pore size by mitigating effects of structural flexibility. Specifically, 3-dimensional linkers (3DLs) are sterically bulky, preventing global breathing transitions in MOFs. Additionally, they occupy the same amount of space, regardless of their orientation, alleviating the impact of linker rotation on pore size.2 Our groups have demonstrated that installation of 3DLs in structures analogous to MIL-53 – a structure known for its flexibility –results in global rigidity, allowing them to separate molecules with sub-Ångstrom differences in size, like hexane isomers and xylene isomers.3,4,5 Herein, we aimed to investigate the relationship between linker bulkiness and rigidity by using variable pressure X-ray diffraction studies to quantify each material's bulk modulus. Additionally, we used density functional theory (DFT) calculations to generate electronic energy profiles for MIL-53 and its 3DL isostructural analogues. These electronic energy profiles show energies obtained from fixed volume geometry optimizations as a function of unit cell volume. Finally, we used DFT to derive the elastic constants of these materials, which were used to calculate values of Young's moduli and to better understand the structural dynamics of these frameworks.

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