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Light Gas Separations and Storage with MOFs *via* DFT Modeling, Synthesis and Pressurized Induced Structural Changes

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The ability to design, tune and successfully test porous crystalline materials allows for the development and commercialization of materials for many different environmental and energy applications. Metal-organic frameworks (MOFs) have shown great potential in challenging separations of molecules with very similar kinetic diameters. One area of strong focus in our lab is toward a fundamental understanding of the structure-property relationship of selective O_2 over N_2 adsorption in MOFs. Emphasis is placed on identifying key structural features for highly selective oxygen adsorption, leading to efficiency improvements through oxy-fuel combustion.

Here we implement a synergistic approach involving predictive molecular modeling, experimental synthesis, and synchrotron crystallographic analysis of known and novel MOF materials. Density functional theory (DFT) calculations were used to measure the binding energy for oxygen and nitrogen on coordinatively unsaturated metal sites in MOFs. A periodic trend in oxygen binding energies was found, with early transition metals exhibiting greater oxygen binding energies compared to late transition metals; this trend was independent of MOF structural type. Differential Pair Distribution Function (d-PDF) analyses were used to determine guest-host structure relationships on both gas sorbed MOFs and pressure induced gas retention in MOFs.

Several different transition metal analogs of prototypical MOFs with these built-in features were evaluated. The effect of the metal on preferential guest binding was examined in detail. MOFs synthesized with the metals selected by DFT exhibited increased sensitivities in O_2/N_2 adsorption upon these modifications conducted at or in the room temperature range.

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