Title: Designing linkers and MOFs for gas-based applications

Abstract:

Metal-organic frameworks (MOFs) are a diverse class of porous materials, formed by bridging metal ions/clusters (nodes) with organic multi-topic ligands (linkers). The tuneability in the combination of nodes/linkers has given rise to many varied topologies of MOFs, with different pore features that allow these materials to interact preferentially with desired gases. As such, MOFs have been applied in many areas, such as, but not limited to, catalysis, gas storage, gas separation, water treatment, and drug delivery.

Carbon dioxide, a leading greenhouse gas, requires an effective approach to separate it from other gases. Conventionally, the challenge lies in the physical similarity, differences in reactivity, and/or low concentrations of constituents of the mixture. In such cases, separation based on molecular size (molecular sieving) is a promising solution. Herein, we have characterized the gas adsorption properties of two metal-organic frameworks (Zn2M; M = Zn, Cd) with very small pores suitable for molecular sieving. The MOFs differ in the central metal of the trimetallic node. In the case where M = Zn, the pore aperture of the MOF is small such that it can accommodate CO2 while N2 and/or CH4 are excluded from entering the pore. Furthermore, due to the size exclusion behavior, the MOF has a calculated adsorption selectivity of 4800:1 CO2:N2 and 5×10^{28}:1 CO2:CH4. When M = Cd, the pore aperture of the MOF increases by approximately 0.15 Å, allowing both N2 and CH4 to enter the pore. This results in a 27.5:1 and a 10.5:1 adsorption selectivity, respectively. These two MOFs demonstrate that a small change in structure can be the difference between a promising sieve material, and a material that is less well suited to kinetically separate gases.

Porphyrins and porphyrinoids are a ubiquitous class of macrocycles, found naturally in hemoglobin and chlorophyll. They are synthesized for numerous applications (e.g., photo- and electro-catalysis, sensing, dyes, etc.). Their long synthetic history has unsurprisingly intersected with MOF chemistry, and a number of MOFs featuring porphyrin linkers have been made to date. Undoubtedly, the most common porphyrin linker is 5,10,15,20-tetrakis(carboxyphenyl)porphyrin, and its metalated derivatives. The latter half of the presentation will demonstrate synthetic progress towards a new, β-substituted porphyrin linker, which as of now have been absent from MOF materials. By placing coordinating moieties at the β-position, we envision new porphyrinic MOF structures, and access to increased functionality at the meso-positions, which could ultimately be applied in creating synthetic MOF enzymes.