Control of Interpenetration in Metal-Organic Frameworks via Spatial Protecting Groups

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Crystallographically ordered metal-organic frameworks (MOFs) witnessed explosive growth in the past two decades. These porous, robust, and modular structures offer new possibilities for studies of physisorption (relevant to gas storage and separation) and chemical compartmentalization (of importance to catalysis) of molecular species within their ordered pores. Objectives of our research are to: (a) engineer functionalized MOFs for sensing and separation applications by using highly sophisticated organic linker modules, and (b) investigate the influence of MOF encapsulation and other irreversible processes on the chemical ordering of complex libraries of equilibrating compounds.

Our most recent results in the first area include the synthesis and characterization of highly fluorescent MOF linkers based on benzobisoxazole ‘cruciforms’—cross-conjugated molecules that have highly predictable HOMO–LUMO gaps and can be used to sense analytes of energy and environmental interest—including small inorganic anions, phenols, and organic amines and ureas.

Our studies of complex mixtures of equilibrating compounds have demonstrated that chemical (oxidation) and physical (distillation, precipitation, encapsulation within MOF pores) irreversible stimuli can be used to reduce these mixtures in complexity from $n^2$ to just $n$ components. These findings are of potential industrial interest, as they show that complex precursor mixtures can be used to achieve highly selective synthesis of well-defined molecular products through kinetic self-sorting.