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

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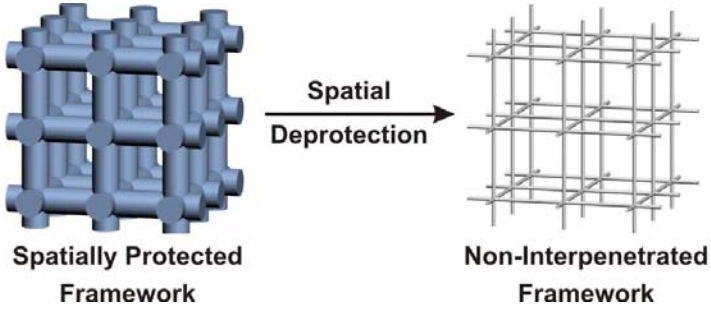
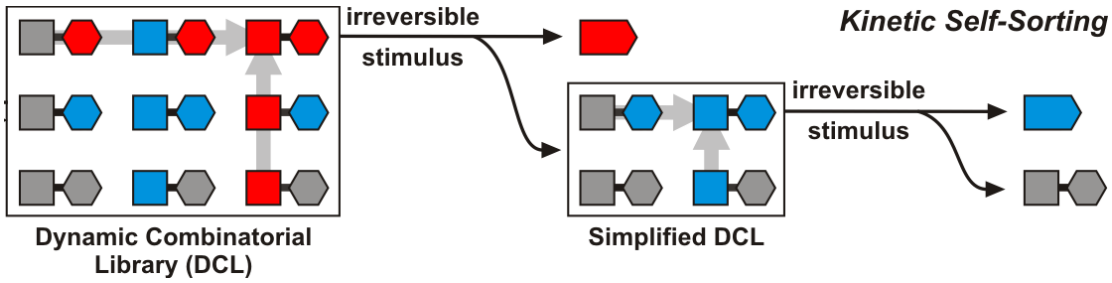
Ordered porous materials known as *metal-organic frameworks* (MOFs) witnessed explosive growth in the past two decades. These robust and modular structures offer new possibilities for studies of physisorption (relevant to gas storage and separation) and chemical compartmentalization (of importance to catalysis) of molecular species within their ordered pores. Objectives of our research are to (*a*) engineer MOFs with ultra large pores by avoiding the interpenetration of multiple copies of the same MOF, and (*b*) investigate the influence of MOF encapsulation and other irreversible processes on the chemical ordering of complex mixtures of equilibrating compounds.

First goal is pursued through the use of organometallic chromium-based spatial protecting groups (SPGs), which block large regions of space during MOF synthesis—thus preventing interpenetration. SPGs will be oxidatively removed once the synthesis of the MOF is complete, to reveal large pores that could not have been introduced into the structure directly.





In equilibrating mixtures of compounds, size- and shape-selective inclusion of individual species within the pores of a MOF can influence the distribution of equilibrating compounds in solution. Sequential application of this process leads to self-sorting behaviors, wherein complex (messy) mixtures of precursors spontaneously simplify during the course of one irreversible physical or chemical transformation.