Part I: Building chiral mesoporous metal-organic frameworks with predesigned achiral ligands (30 minutes)

Part II: Heterobimetallic Paddlewheel Complexes: Progress and Promise (20minutes)

Hong-Cai Zhou, Daofeng Sun, Yanxiong Ke, Tracy M. Mattox, and David J. Collins

Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio, 45056 USA.

Part I:

A predesigned achiral trigonal-planar ligand, 4,4′,4″-triazine-2,4,6-triyl-tribenzoate (TATB), has been synthesized as a means to stabilize chiral Metal-Organic Frameworks (MOFs) against thermal decomposition and guest removal without sacrificing porosity. Four chiral MOFs have been constructed using TATB and an hourglass secondary building unit (SBU): $Zn_3(TATB)_2(H_2O)_2{\cdot}4DMF{\cdot}6H_2O$ (**1**), $Cd_3(TATB)_2(H_2O)_2{\cdot}7DMA{\cdot}10H_2O$ (**2**), $Zn_3(TATB)_2(HCOO){\cdot}[H_2N(CH_3)_2]{\cdot}[HN(CH_3)_2]{\cdot}3DMF{\cdot}3H_2O$ (**3**), and $Cd_3(TATB)_2(CH_3COO){\cdot}[H_2N(CH_3)_2]{\cdot}[HN(CH_3)_2]{\cdot}3DMA{\cdot}4H_2O$ (**4**). Complexes **1** and **2** are isostructural and possess three-dimensional (10,3)-a nets with chiral mesoporous channels of 20.931 and 21.230 Å, respectively, but are thermally unstable due to the easy removal of coordinated water molecules on the SBU. Replacement of these water molecules by formate or acetate leads to **3** and **4**, respectively. Formate or acetate links SBUs to form infinite helical chains bridged by TATB to create three-dimensional anionic networks. Thermal gravimetric analysis shows that solvent-free **3** is thermally stable to 410°C and possesses permanent porosity with a large Langmuir surface area of 1558 m^2/g.

Part II:

Paddlewheel complexes have been studied extensively in the past 30 years; however, the majority of such research has focused on homometallic complexes, and very

little research has addressed the synthesis, properties, and potential applications of heterobimetallic complexes. One of our research focuses has been the synthesis and characterizations of heterometallic paddlewheels. This endeavor has yielded heterobimetallic complexes of platinum (II) with many of the first-row transition metals in +2 and +3 oxidation states: Pt-V, Pt-Cr, Pt-Mn, Pt-Fe, Pt-Co, and Pt-Ni species have been synthesized and characterized. These complexes exhibit only weak metal-metal interactions. As a result, the MN_4 end of the paddlewheel closely resembles proximally-blocked porphyrin complexes: the square-planar transition metal center has nonbonding atomic orbitals extending axially at the open coordination site with the opposite end of the paddlewheel being blocked by the Pt atom. These unsaturated metal centers can capture small molecules and may be useful for catalysis.