My research focuses on the design of new synthetic strategies to obtain novel materials. By carefully controlling the conditions that determine the atomic structure of a material, materials with specific or enhanced properties may be prepared. Because the synthetic conditions control the structure that in turn directs the properties of the material, I have chosen to introduce my projects by the structural motif or arrangement of metal atoms followed by the general synthetic strategy commonly employed to obtain that motif. I have broadly classified the four structural motifs that I study as: single particles, discrete molecules, coordination polymers, and metal-organic frameworks and the structures are depicted in Figure 1. Please contact me if you are interested in learning more about these structures and how to prepare them.

![Figure 1. Four basic structural motifs for inorganic materials.](image)

**Single (nano)particles of metals or metal oxides, borides, nitrides**

The refinement of grain sizes down to the nanometer size regime has been demonstrated to strongly influence the mechanical, electrical, or magnetic properties of a material. Therefore, special consideration has been given to develop syntheses that control the growth of the particles AND to produce monodisperse particles.

Two methods employed to control particle growth and size are solution-phase processing and reverse micelles. Solution-phase processing utilizes commercially available precursors which are thermally or reductively decomposed in organic solvents. The resulting amorphous powders consist of fine particulates from which nanocrystalline particles nucleate and grow during solid-state annealing. Reverse micelles are water-in-oil droplets formed when mixtures of water, surfactants, and non-polar solvents are combined at the appropriate concentrations. Generally, the overall solution is observed as homogeneous and visibly clear. The size of the aqueous pools within the organic solvent is linearly dependent on the $w$ value ($w = [H_2O]/[\text{surfactant}]$); however, there are many factors that affect crystal growth within the aqueous pools including: the $w$ value, the nature of the surfactant, the concentration of reactants, the size of the counterions, the presence of co-surfactants, the reaction time, and the pH of solution.
**Coordination Compounds**

Coordination compounds (or coordination complexes when the overall structure has a charge) contain a metal center that accepts electron pairs from organic molecules or anions called ligands to form coordinate covalent bonds. Coordination compounds or complexes may have one or more metal centers (dimers, trimers, etc.); however, the structure is a distinct unit.

Ligand design is a very important aspect of coordination chemistry. The structure of the ligand and how it coordinates to the metal center can affect the overall properties (such as stability, solubility, spectroscopy) of the compound. In my research, we have designed, synthesized, and characterized many organic molecules that can serve as ligands. Once they are purified and fully characterized the ligand is coordinated to a metal center and the resulting coordination compounds or complexes are characterized. A gadolinium(III) coordination complex that we have prepared with the triethylenetetramine hexacetate-bis(3-hydroxytyramide) ligand is shown in Figure 2.

![Figure 2. Coordination complex of [GdTTHA(HTA)\(_2\)]\(^{1-}\)](image)

**1-D Coordination Polymers**

Self-assembly of discrete complexes into higher ordered structures based on coordination polymers utilize stable coordinate covalent bonds. However, a variety of different noncovalent interactions such as hydrogen bonding and \(\pi-\pi\) stacking can also be employed. One method to produce a coordination polymer is to design the ligand such that it can complex with one metal center and bridge and coordinate to a different metal center producing a metal containing polymer. For example, the TTHA(HTA)\(_2\) ligand that was use to make the Gd(III) complex in Figure 1 contains two catechol moieties that are available to bridge and coordinate and a different metal center extending into a coordination polymer (see Figure 3).

![Figure 3. Synthesis of the gadolinium(III)-iron(III) heterobimetallic coordination polymer.](image)
Metal-Organic Framework Solids

Metal-organic framework solids are synthetic analogues to natural aluminosilicate (aluminum and silicon cations bridged by oxygen anions) minerals, such as clays and zeolites. While clays are layered solids that may swell or shrink when water is absorbed or removed, zeolites are rigid three dimensional framework structures consisting of interconnected tunnels and/or cavities. These rigid, porous aluminosilicate frameworks have been used commercially as absorbents (vermiculite packing material, kitty litter), ion-exchange supports (in the water-softening process), and catalysts (in the 'cracking' of petroleum to form gasoline). Scientists have tried to mimic the synthetic tricks of Nature by using heat, pressure, pH, and more elements from the Periodic Table to produce porous metal-organic framework solids. Metal-organic framework solids employ organic substituents (ligands) to link multiple metal centers together. By adjusting the length of the organic ligand, one can control the size of the formed cavity or pore. [Think about Tinker Toys™ and arranging them in a cube--the wood spools with holes represent the metal centers that are connected together with organic ligands, or the dowels. By changing the length of the dowels, the cavity increases or decreases in size.] Not only can the pore size be controlled with chemical synthesis, but the shape of the pore and/or the interconnecting tunnels can also be specifically designed by employing different metal centers or ligands. Metals have preferred coordination geometries (octahedral, tetrahedral, square planer, etc.); therefore, they "direct" the assembly of the framework. Metal-organic zeolite analogues have a distinct advantage over aluminosilicate zeolites because they can be custom-tailored for specific purposes such as small molecule (H₂, CO₂, or CH₄) storage and transport, size or shape-selective (chiral) separation, and catalysis.

We are currently investigating synthetic strategies to produce chiral ligands that are capable of coordinating to two different metal centers. The molecule, N, N’-bis(3,4-dihydroxybenzoyl)-trans-1,2-diaminocyclohexane (Figure 4), may be able to serve as a ligand that bridges two metal centers to produce a metal organic framework with chiral channels or cavities.

![Figure 4. N, N’-bis(3,4-dihydroxybenzoyl)-trans-1,2-diaminocyclohexane](image)

Summary of Synthetic Strategies and Characterization

The syntheses of discrete complexes, 1-D coordination polymers, or MOFs have many similarities so the general approach can be broken down into three nontrivial steps:

1. **Synthesis, purification, and characterization of the ligands.**
2. **Metal complexation.** This step entails finding the ideal conditions (namely reaction stoichiometry, time, pH, temperature, sensitivity to oxygen, etc.) to form the desired product.
3. **Characterization of the material.** This step includes a variety of techniques and instrumentation including: quantitative inorganic analysis, NMR, FT-IR, UV-visible spectroscopy, microscopy, thermogravimetric analysis, single crystal and powder x-ray diffraction.