

Department of Chemistry

Graduate Student Seminar – Summer 2020

**A Solid-Solution Approach to Multivariate Metal-Organic Frameworks  
and their Interactions with Light**

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The goal of this research is to prepare tunable organic-based emissive materials, utilizing a substitutional solid solution (SSS) approach to multivariate metal-organic frameworks (MTV-MOFs). This approach uses high symmetry and stable zirconia-based MOFs as a platform to embed dilute organic molecules in a crystalline matrix. The first study aimed to understand how multiple fluorophores would behave when incorporated alone and at varied concentrations, or incorporated into the same framework. Phenanthroimidazole based links were prepared which took advantage of an excited state proton transfer (ESPT) to allow single wavelength excitation while emitting varied colors from blue to green to red. Incorporation of multiple dilute fluorophores into a single framework resulted in an emission profile which was the linear combination of the fluorophores, while increasing the fluorophore concentration resulted in phenomena related to concentrated solution-based systems, ie. inner filtering and FRET. Further investigation into these phenomena led to the use of a more  $\pi$ -rich fluorophore, which forms aggregates in solution with increasing concentration. This molecule contains a 9,10 Bis-(phenylethynyl)-anthracene core which under dilute conditions emits green light, but in the solid state emits red light. A similar, albeit more controlled, trend was observed when incorporated into an MTV-MOF matrix where the emission profile was modeled with respect to the anthracene concentration. This model indicates that the observed process was due to a dimeric species and that the MOF was preventing trimers and other larger aggregates from forming. Throughout this presentation it is demonstrated how an SSS approach can be applied to MTV-MOFs to allow the fine control of spectroscopic properties and increase the tunability of organic functional materials.