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Luminescent Metal-Organic Frameworks

Lucas Stehle  
*Elizabethtown College*, stehlel@etown.edu

Kaitlyn Mercando  
*Elizabethtown College*, mercandok@etown.edu

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Abstract
Metal-organic frameworks (MOFs), porous materials composed of metal ions and organic linkers, have broad applications in separation, small molecule storage, and catalysis. Luminescent metal-organic frameworks (LMOFs) hold great potential in the development of sensors, and, with their relatively straightforward syntheses that produce predictable, homogeneous, extended structures, should result in good sensor-to-sensor reproducibility and uniform response. In addition, subtle differences in overall LMOF structure, metal ion coordination, pore surfaces, and host-guest interactions within pores should have significant impact on observed photoluminescence and provide numerous strategies for analyte detection. Highlighted here is the development of LMOFs composed of zinc or zirconium ions that incorporate luminescent osmium complexes into the framework structure and the excitation and emission spectra of these materials in the presence of small molecules of varying polarity.

Luminescent Metal Organic Frameworks
- MOFs have a very large surface area and the size of their pores can be manipulated easily, making them attractive for small molecule uptake.
- The pore size within a MOF can be changed by varying the type or size of the metal center or the organic ligand used in synthesis.
- LMOFs can be synthesized by incorporating a luminescent osmium complex into the MOF lattice by replacing a small amount of the organic linker with the complex.
- Currently, two LMOF systems are being developed in order to examine the photophysical properties of environment-sensitive complexes within a host lattice. Shown below are the two MOF lattices of interest for this study.

Preparation of Osmium Complex
· Os complexes containing 1,10-phenanthroline-4,7-dicarboxylic acid (dcphen) were incorporated into each LMOF due to the β-system conjugation exhibited by dcphen. The carboxylic acid groups serve to replace some of the organic linkers within the MOF.
· Previous work in this research group supports the use of dcphen for the Zn-MOF, UiO-66. Shown left is the centered arrangement of the extended MOF structure. White space indicates accessible porosity within the lattice.

Photoluminescence Measurements – LMOFs, Continued
Figure 5: The emission and excitation spectra shows [Zn2(camph)(4,4'-bpy)] doped with [Os(CO)2Cl2(dcphen)] after activation.

Figure 6: The excitation and emission spectra shows UiO-66 doped with [Os(CO)2Cl2(dcphen)] in toluene and EIOH.

Figure 8: The excitation and emission spectra shows UiO-66 doped with [Os(CO)2Cl2(dcphen)] after activation.

Figure 7: The emission spectra shows UiO-66 (undoped) after EIOH soak.

Figure 9: The excitation and emission spectra shows UiO-66 doped with [Os(CO)2Cl2(dcphen)] in toluene and EIOH.

Summary
- The UiO-66-LMOF displayed emission peaks at 391 and 584 nm when excited at 320 nm in the presence of air, attributed to the MOF and MLCT, respectively.
- Upon soaking in solvents, a decrease in the intensity of the 584 nm emission was noted, with toluene producing a lower emission intensity than ethanol. This is tentatively attributed to solvent quenching effects.

Future Work
- Obtain further emission and excitation data for both doped LMOF systems and test the effects of different solvent systems on emission wavelength.
- For UiO-66, explore a wider range of solvents to further probe the solvent quenching effects.
- Investigate the stability and emissive properties of the UiO-66 LMOFs in an aqueous environment.
- For the Zn-MOF, examine the emission behavior via anisotropy measurements. The chiral nature of the MOF backbone could produce a useful response when examined this way.

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References

Lucas Stehle, Kaitlyn Mercando, Kristi Kneas, Jeffrey Rood
Department of Chemistry and Biochemistry, Elizabethtown College, Elizabethtown, PA  17022