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# Luminescent Metal-Organic Frameworks

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# Luminescent Metal-Organic Frameworks: Zinc and Zirconium-based MOFs Doped with Emissive Osmium Complexes

Lucas Stehle, Kaitlyn Mercado, Kristi Kneas, Jeffrey Rood

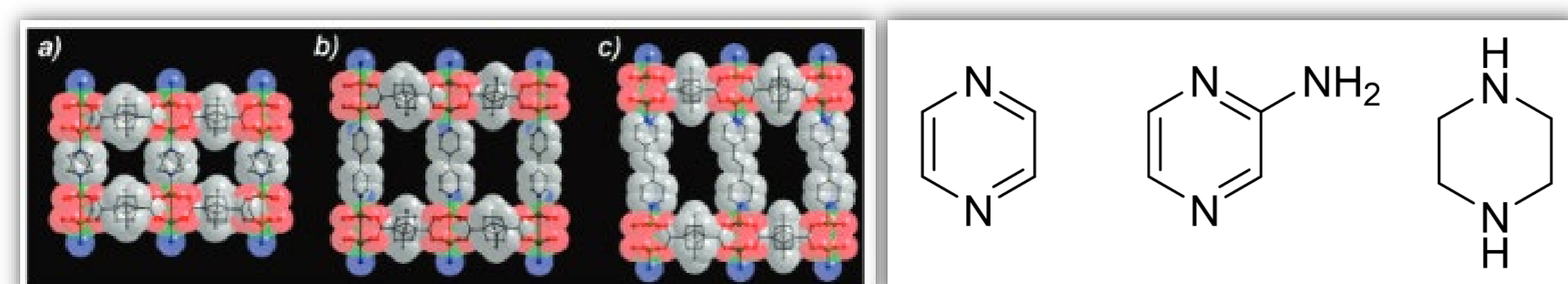
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## Abstract

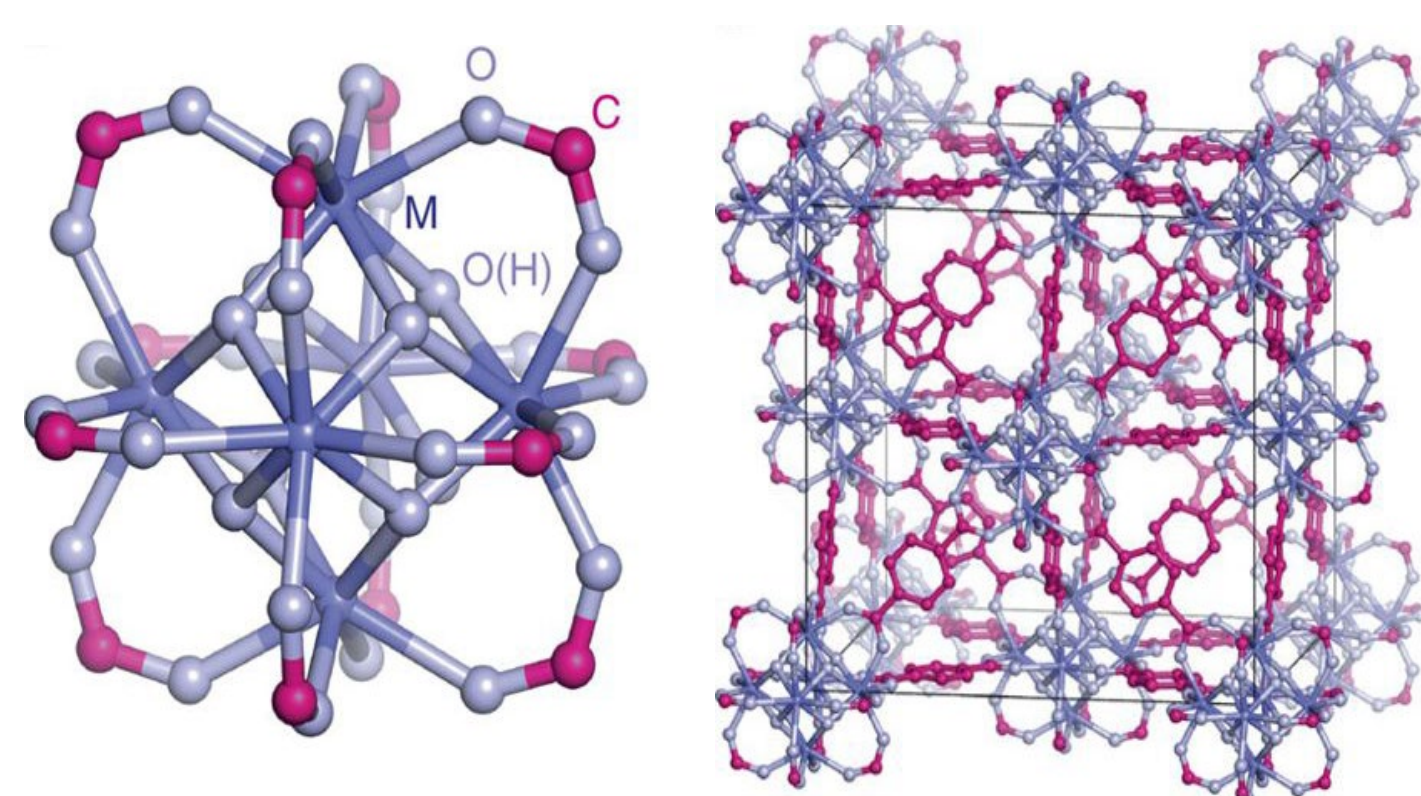
Metal-organic frameworks (MOFs), porous materials composed of metal ions and organic linkers, have broad applications in separation, small molecule storage, and catalysis. Luminescent metal-organic frameworks (LMOFs) hold great potential in the development of sensors, and, with their relatively straightforward 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.



**Figure 1:** Crystal structures of different Zn MOFs that can vary by organic ligand.  $[Zn_2(\text{camph})_2L]$  L= an N-donor organic pillar.<sup>1</sup>

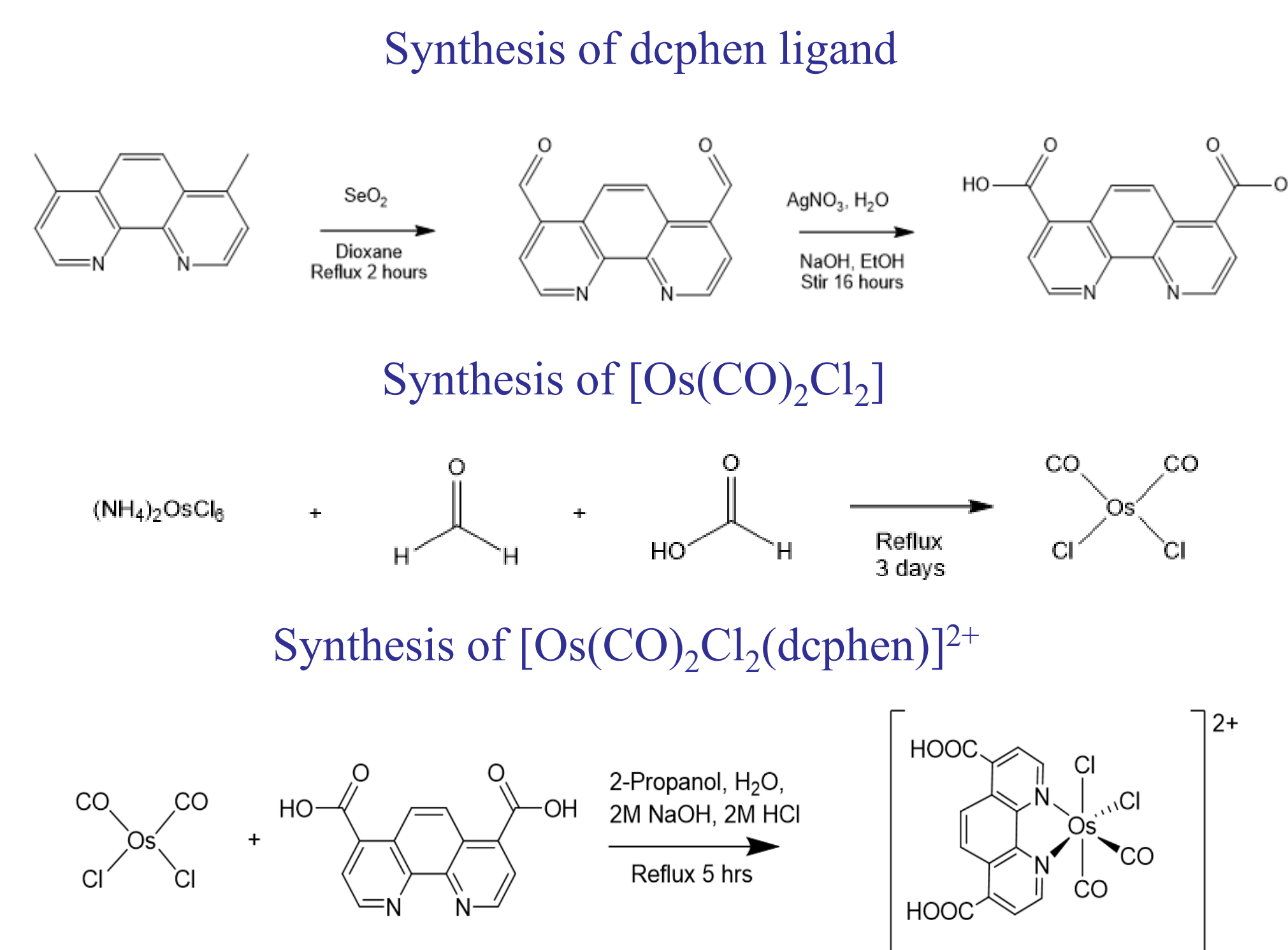


**Figure 2:** Crystal structure of Zr MOF, UiO-66.<sup>2-3</sup> Shown left is the  $Zr_6O_4(\text{OH})_4(\text{BDC})_{12}$  building unit and shown right is the resulting face-centered arrangement of the extended MOF structure. White space indicates accessible porosity within the lattice.

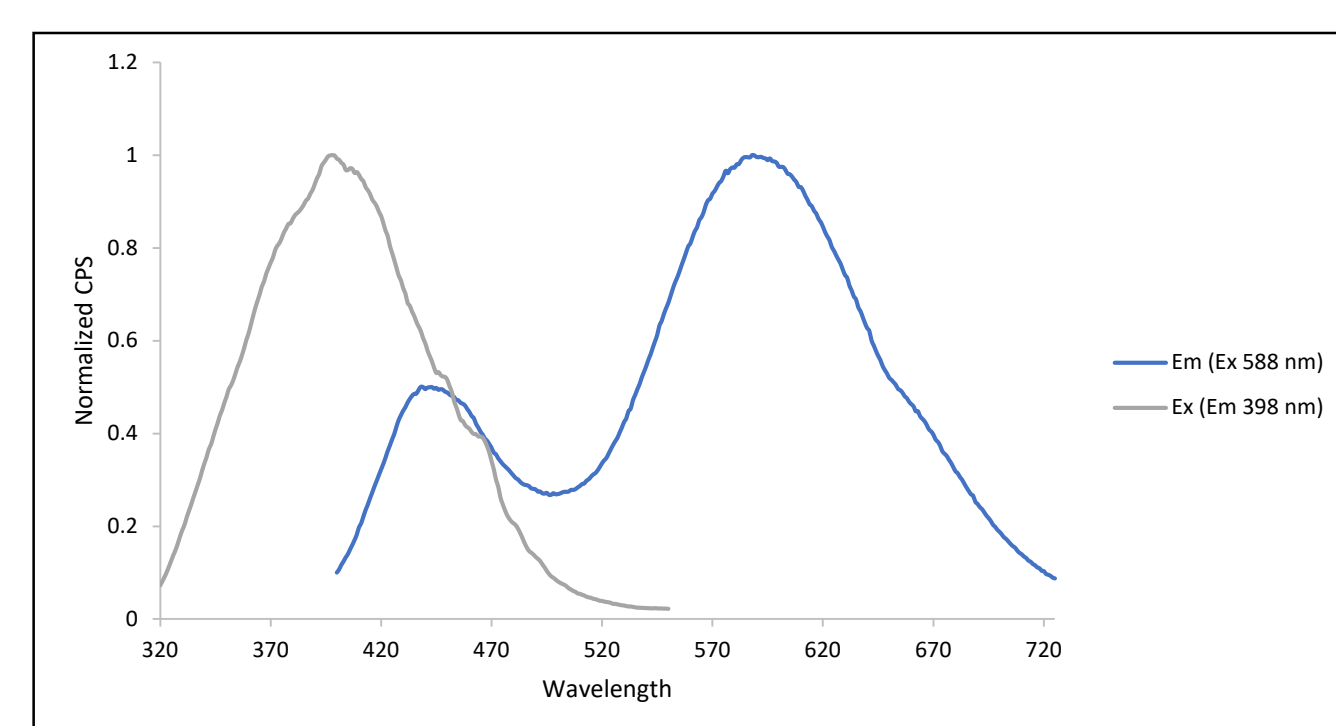
## Approach to LMOF Formation

- Osmium complexes containing 1,10-phenanthroline-4,7-dicarboxylic acid (dcphen) were incorporated into each LMOF due to the  $\pi$ -system conjugation exhibited by dcphen. The carboxylic acid groups serve to replace some of the organic carboxylate linkers within the MOF.
- Previous work in this research group supports the use of dcphen when synthesizing LMOFs. In such cases, the overall structure of the extended MOF lattice and the desired porosity was retained.

## Preparation of Osmium Complex<sup>4-5</sup>



IR	CO Stretches	Wavenumbers ( $\text{cm}^{-1}$ )
$[\text{Os}(\text{CO})_2\text{Cl}_2]$	2 - Sharp	2008, 1928
$[\text{Os}(\text{CO})_2\text{Cl}_2(\text{dcphen})]$	2 - Sharp	2042, 1966

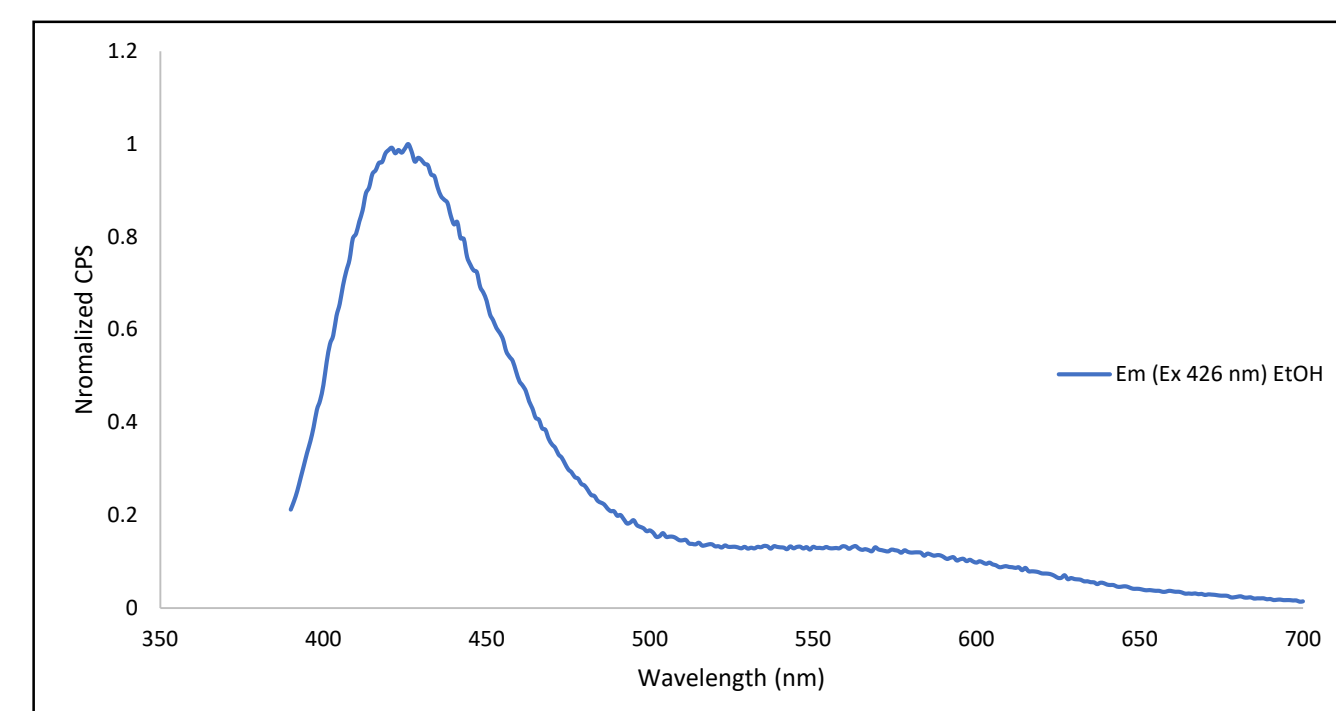


Max Ex/Em $\lambda$ (nm)	398/588
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**Figure 3:** Excitation and emission of  $[\text{Os}(\text{CO})_2\text{Cl}_2(\text{dcphen})]^{2+}$  in EtOH.

## Photoluminescence Measurements - LMOFs

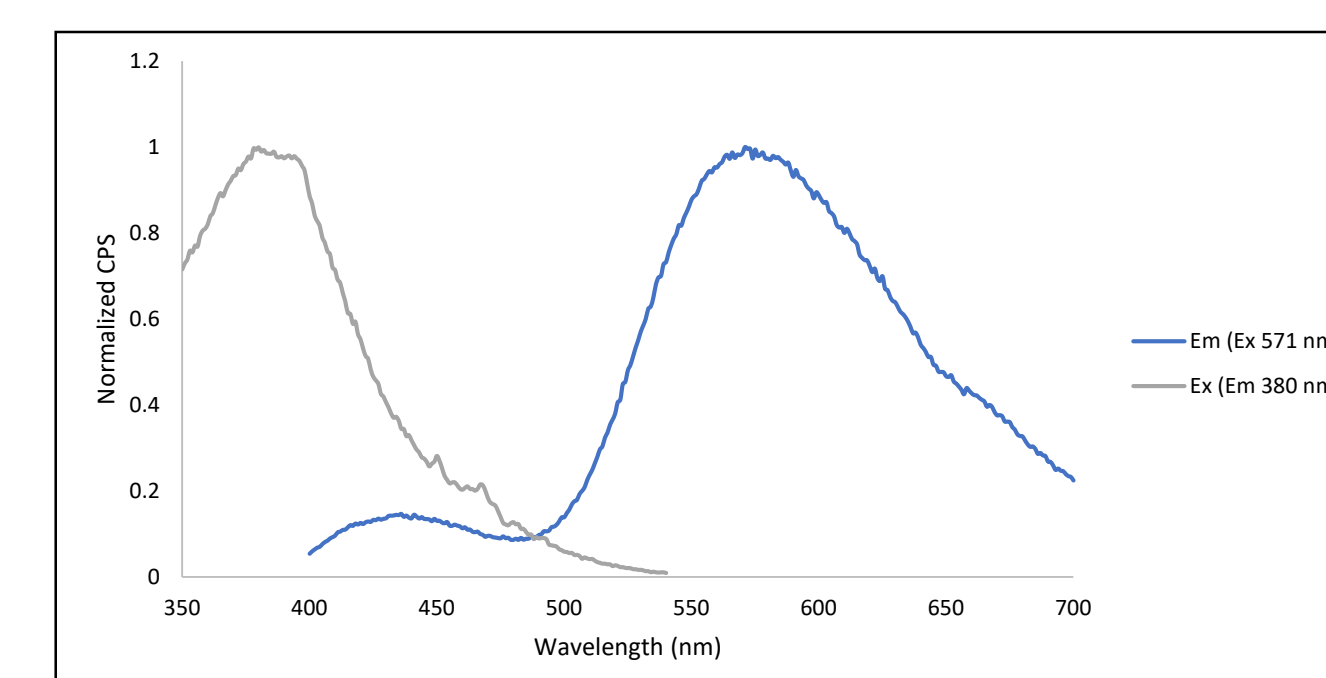
### Zn-MOF



Solvent	Max Ex/Em $\lambda$ (nm)
Ethanol	426/352

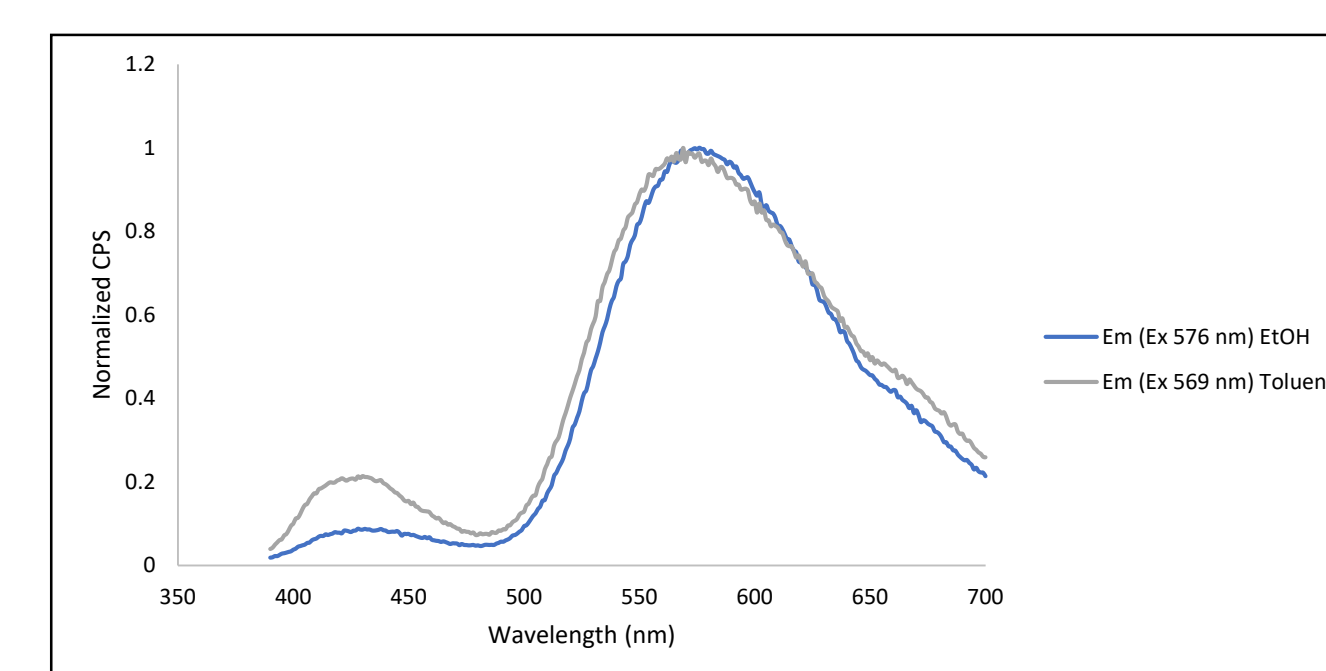
**Figure 4:** Emission spectra of  $[Zn_2(\text{camph})_2(4,4'\text{-bpy})]$  (undoped) after EtOH soak.

## Photoluminescence Measurements – LMOFs, Continued



MLCT Ex/Em $\lambda$ (nm)	571/381
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**Figure 5:** The emission and excitation spectra shows  $[Zn_2(\text{camph})_2(4,4'\text{-bpy})]$  doped with  $[\text{Os}(\text{CO})_2\text{Cl}_2(\text{dcphen})]$  after activation.

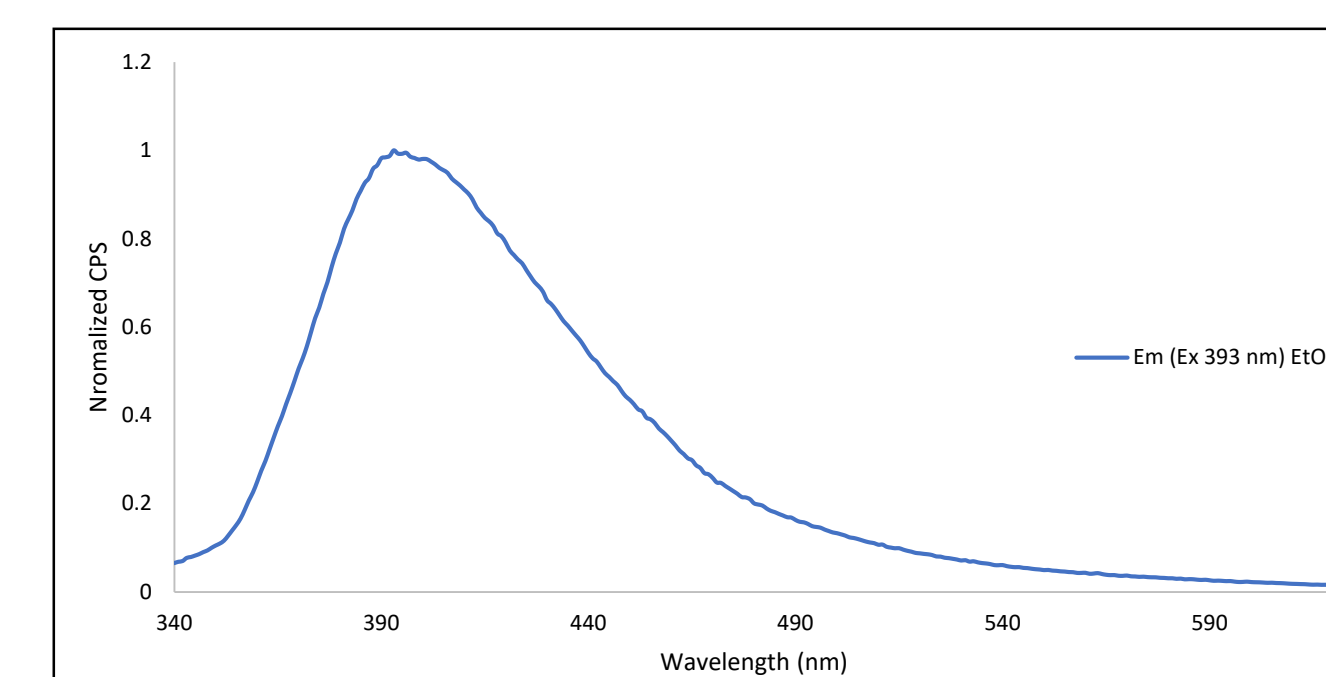


Solvent	MLCT Ex/Em $\lambda$ (nm)
Toluene	569/382
Ethanol	576/382

**Figure 6:** The excitation and emission spectra shows doped  $[Zn_2(\text{camph})_2(4,4'\text{-bpy})]$  soaked in toluene and EtOH.

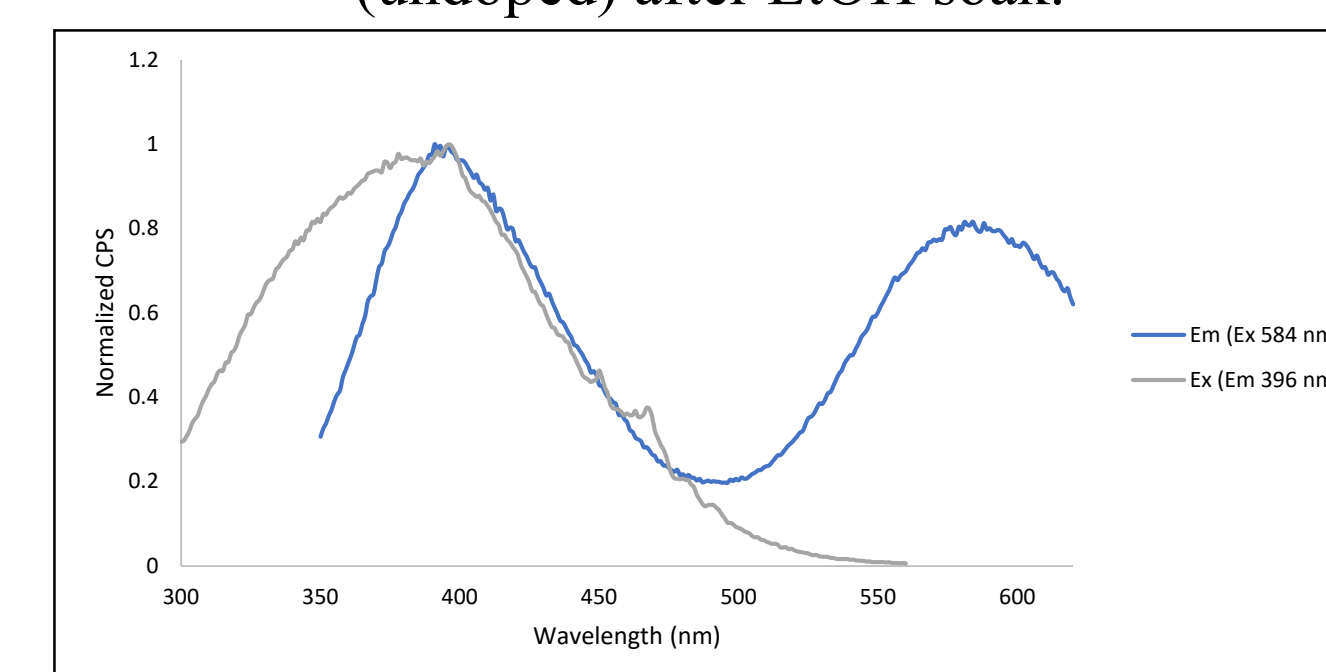
- The Zn-LMOF displayed emission peaks at 436 and 571 nm when excited at 381 nm in the presence of air.
- The short wavelength emission is attributed to ligand-localized emission from the MOF itself, while the longer wavelength emission is due to MLCT and support the incorporation of the osmium complex into the MOF.
- No significant changes in emission behavior were noted upon soaking the LMOF in toluene or ethanol.

### UiO-66



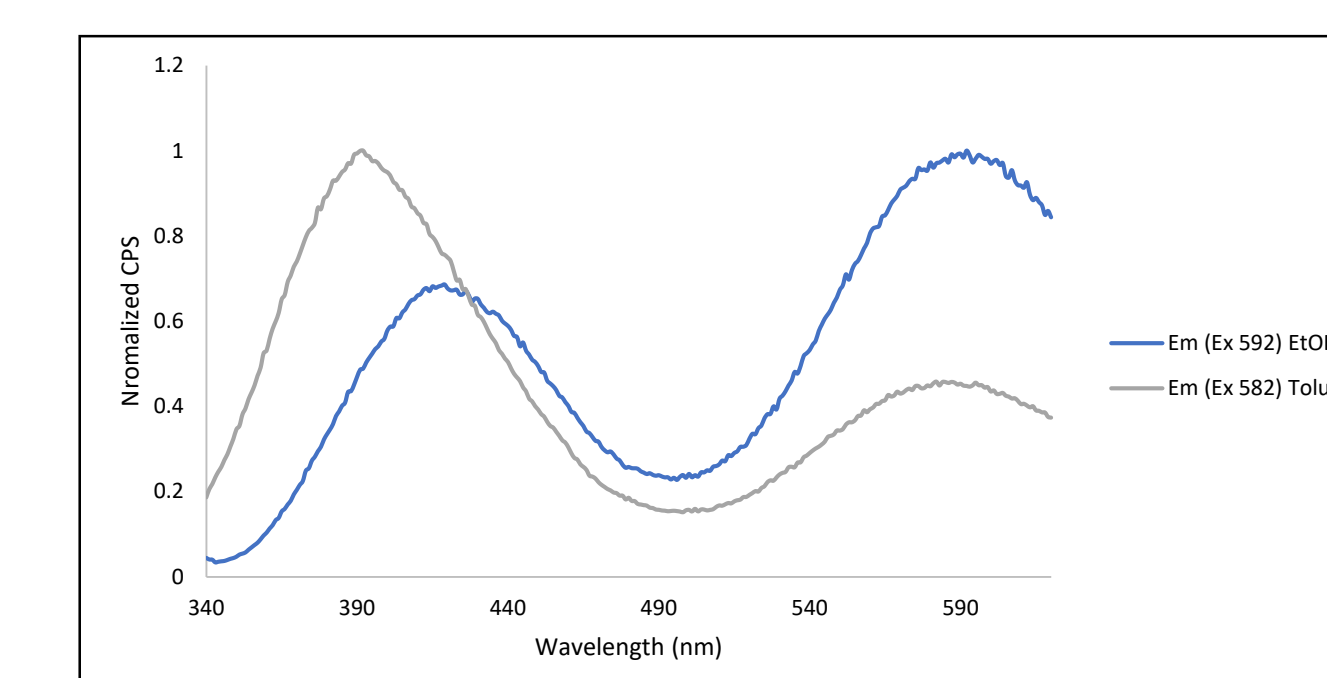
Solvent	Max Ex/Em $\lambda$ (nm)
Ethanol	393/396

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



MLCT Ex/Em $\lambda$ (nm)	584/320
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**Figure 8:** The excitation and emission spectra shows doped UiO-66 after activation.



Solvent	MLCT Ex/Em $\lambda$ (nm)
Toluene	582/378
Ethanol	592/394

**Figure 9:** The excitation and emission spectra shows UiO-66 doped with  $[\text{Os}(\text{CO})_2\text{Cl}_2(\text{dcphen})]$  in toluene and EtOH.

- 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.

## Summary

- 1,10-phenanthroline-4,7-dicarboxylic acid is useful in incorporating the osmium complex into MOF structures in order to analyze luminescent properties.
- Our doping approach has been extended to the UiO-66 and zinc camphorate systems. Emissive materials have been isolated containing  $\text{Os}(\text{dcphen})(\text{CO})_2\text{Cl}_2$  for both MOF systems.

## 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.

## Acknowledgements

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