

# Fluorescent Detection of Carbon Disulfide with an Isoreticular Series of Interpenetrated Zr-based LMOFs

Yuki Osumi, Ever Velasco, Jing Li

Department of Chemistry and Chemical Biology, Rutgers, the State University of New Jersey, Piscataway, NJ 08854

## Background and Introduction

Metal-Organic Frameworks (MOFs) are an extremely versatile class of crystalline and porous inorganic-organic materials that have gained significant attention in gas storage, separation and purification, catalysis, luminescent sensing, energy efficient lighting, etc.<sup>1,2,3</sup>. We herein present the synthesis and characterization of two iso-reticular interpenetrated Zr-based luminescent MOFs  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(tcbpe)_8(H_2O)_4(OH)_4(1)$  and  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4(tcbpe-f)_8(H_2O)_4(OH)_4(2)$  for the selective detection and capture of carbon disulfide. These two materials demonstrate a calorimetric bathochromic shift in the optical bandgap and quench in luminescent intensity upon exposure to carbon disulfide. The interaction between carbon disulfide and the frameworks were investigated by in-situ FTIR measurements and computational (DFT) modeling. These results reveal that the oxygen and hydrogen atoms from linker in addition to the Zr node contribute to the preferential binding site of carbon disulfide.

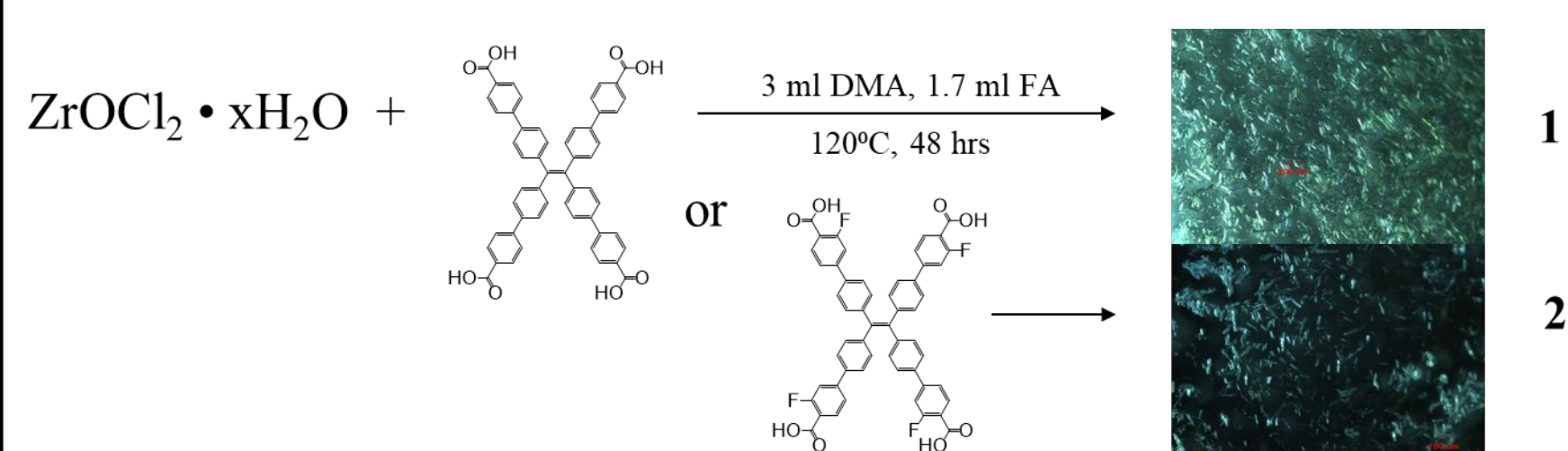


Figure 1: Synthesis scheme for the two Zr-based LMOFs.

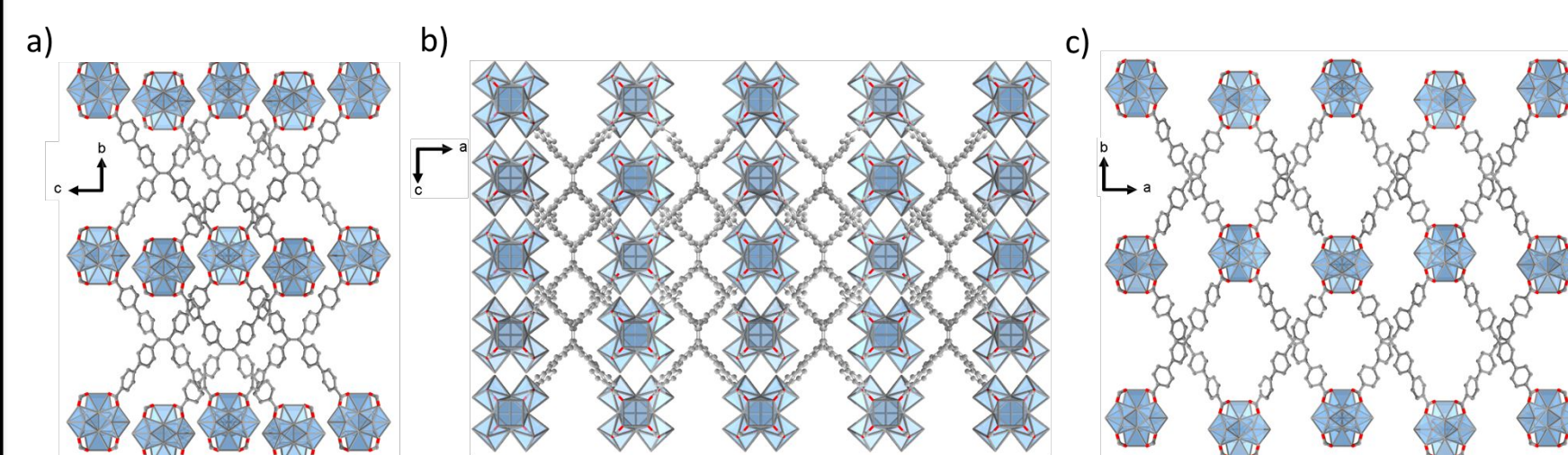


Figure 2: Structure of 1 as viewed along the a-axis (a), b-axis (b), and c-axis (c)

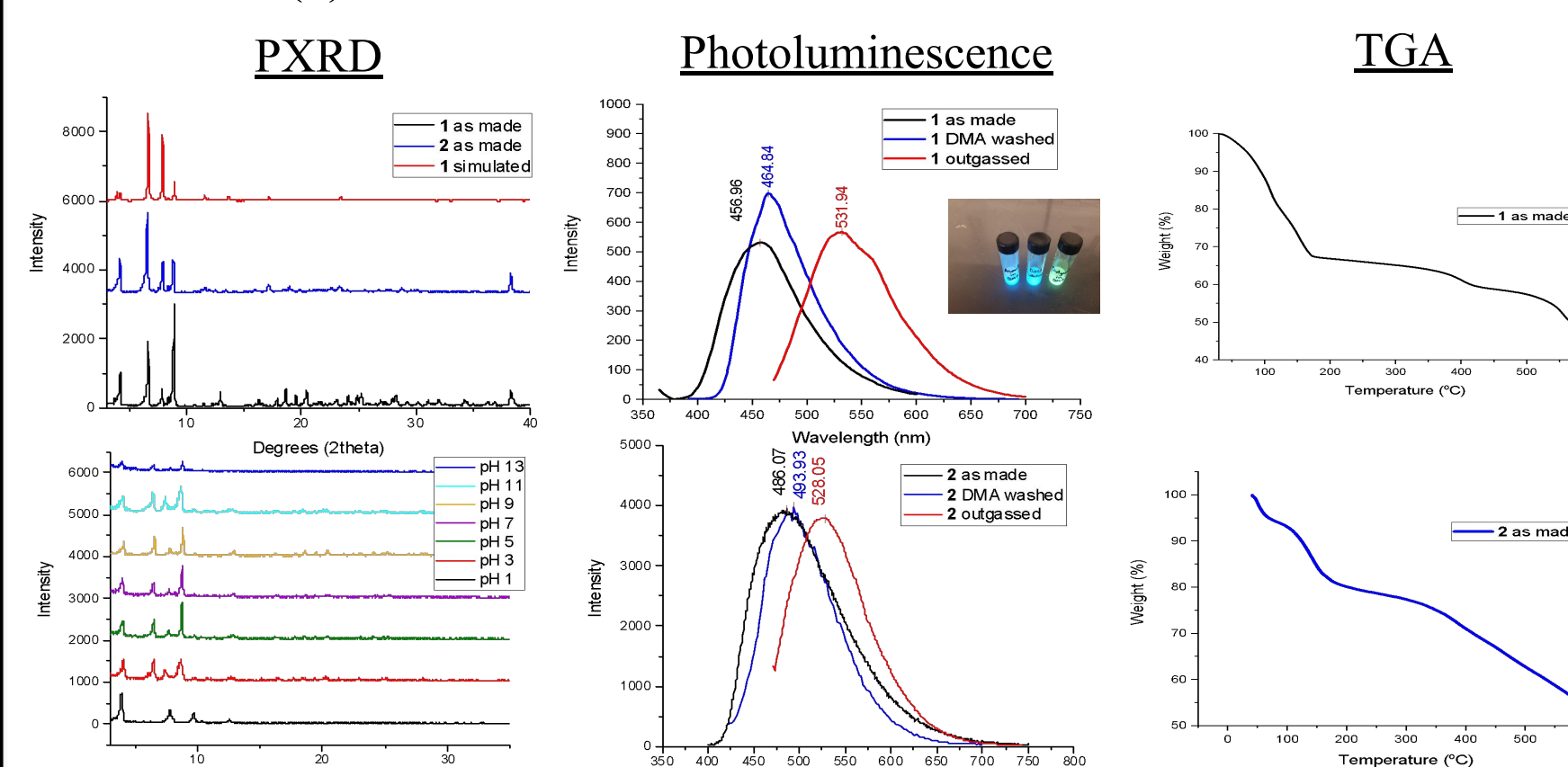


Figure 3: PXRD patterns of Zr-MOFs (top-left) and Zr-MOFs at various pH values (bottom-left). Photoluminescence of 1 (top-middle) and 2 (bottom-middle). TGA of 1 (top-right) and 2 (bottom-right).

## Molecular Interactions between Zr-MOF and CS<sub>2</sub>

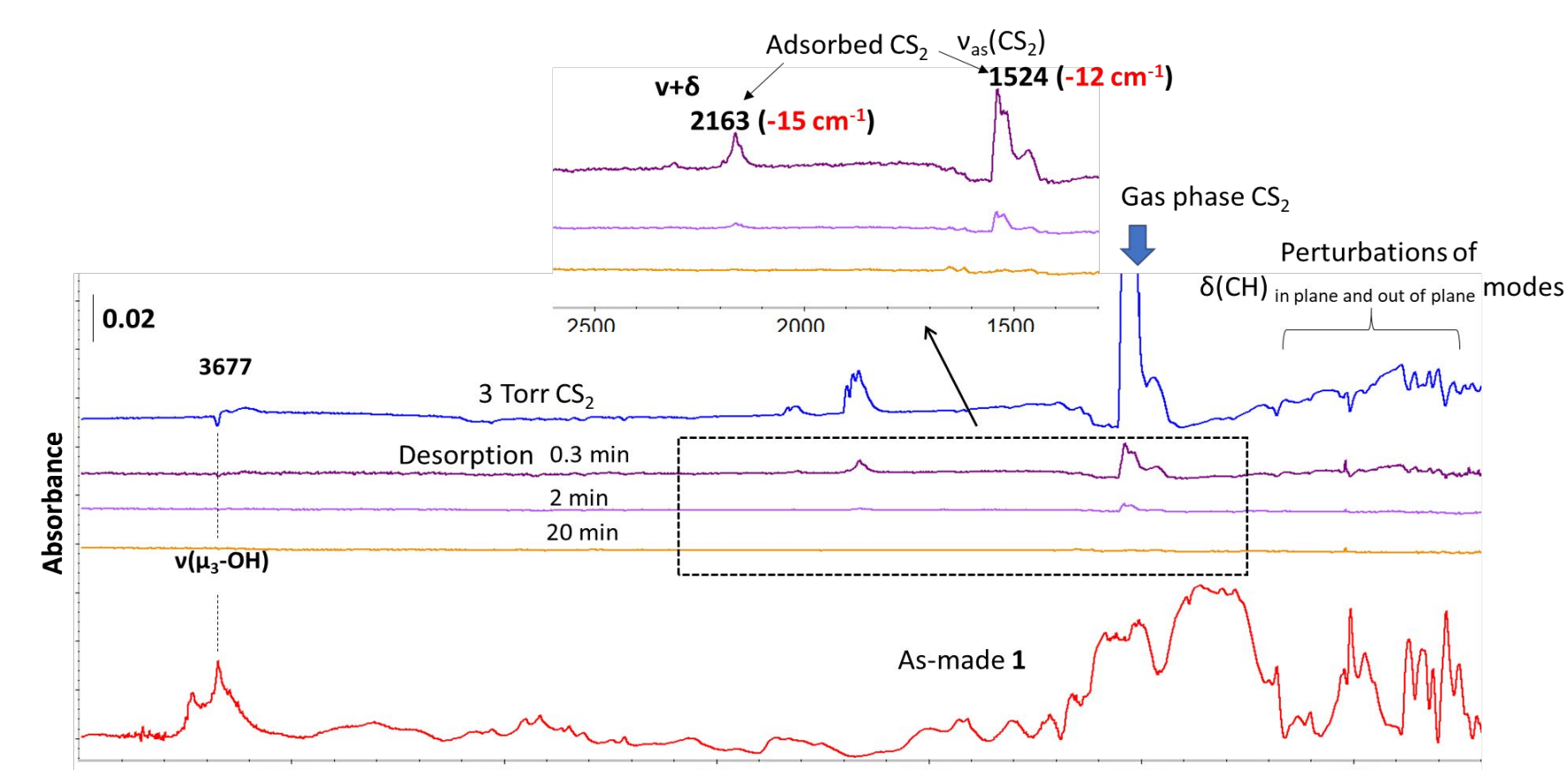


Figure 4: In-situ FTIR of 1 placed within 3 torr CS<sub>2</sub> system. Special thanks to Kui Tan from Department of Materials Science and Engineering at University of Texas at Dallas

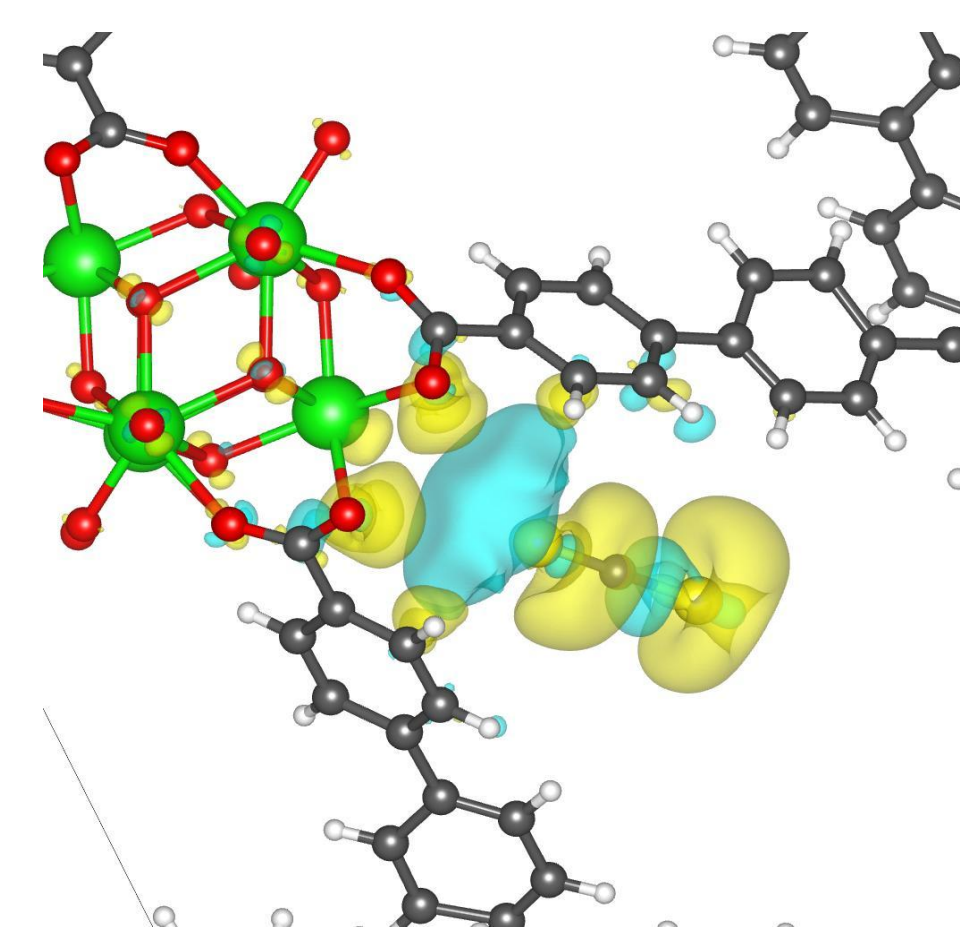


Figure 5: Results from DFT Calculations showing charge rearrangement of Zr - CS<sub>2</sub> interactions. Special thanks to Stephanie Jensen and Timo Thonhauser from the Center for Functional Materials Wake Forest University.

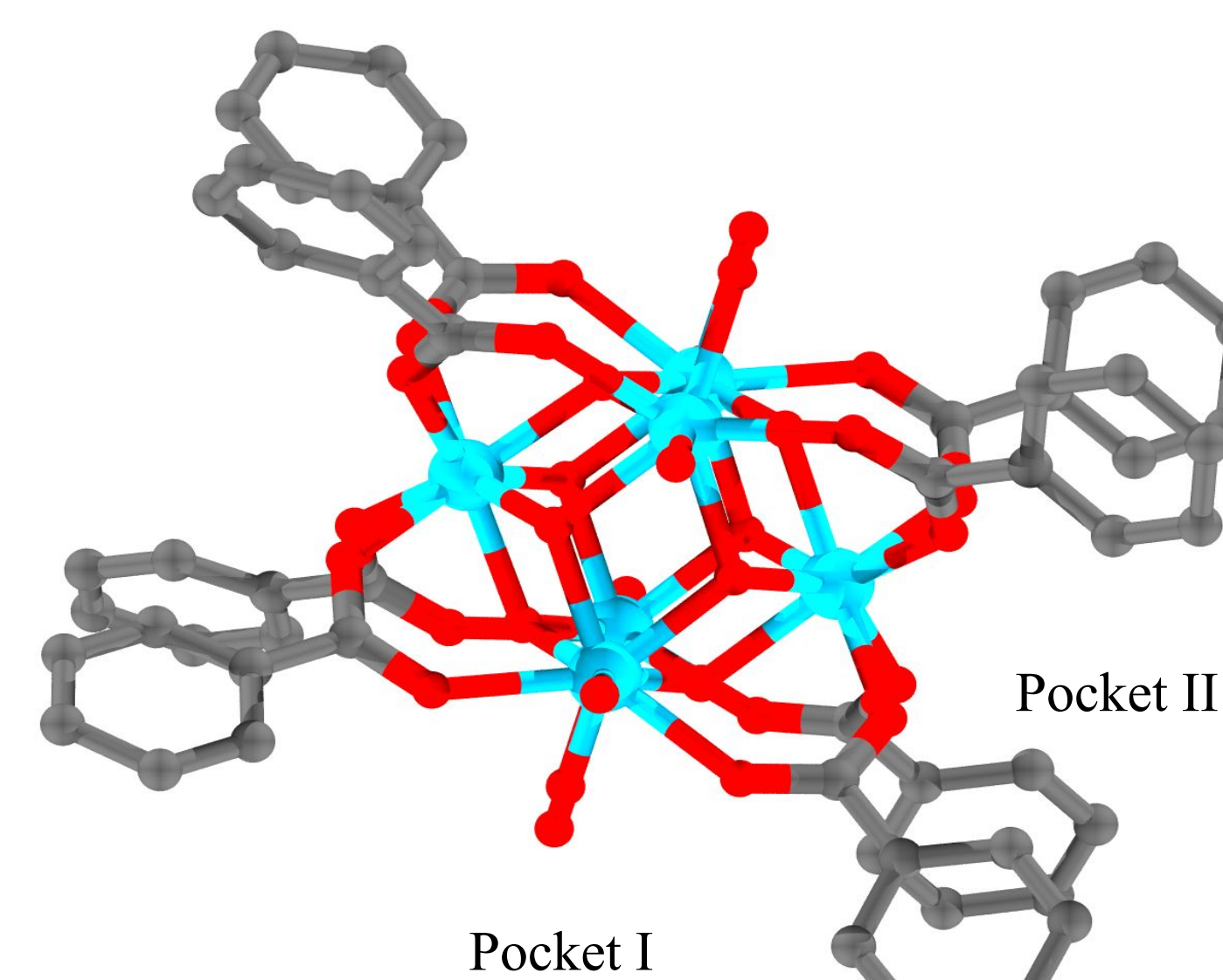


Figure 6:  $Zr_6O_4(OH)_8(H_2O)_4$  secondary building unit (SBU)  
 □ Pocket I: Predominantly Zr-OH bonds  
 □ Pocket II: Predominantly Zr-O-C that comprise the coordination bonds between the SBU and linker  
 □ CS<sub>2</sub> most preferential binding site occurs within pocket II

## Effect upon Exposure to CS<sub>2</sub>

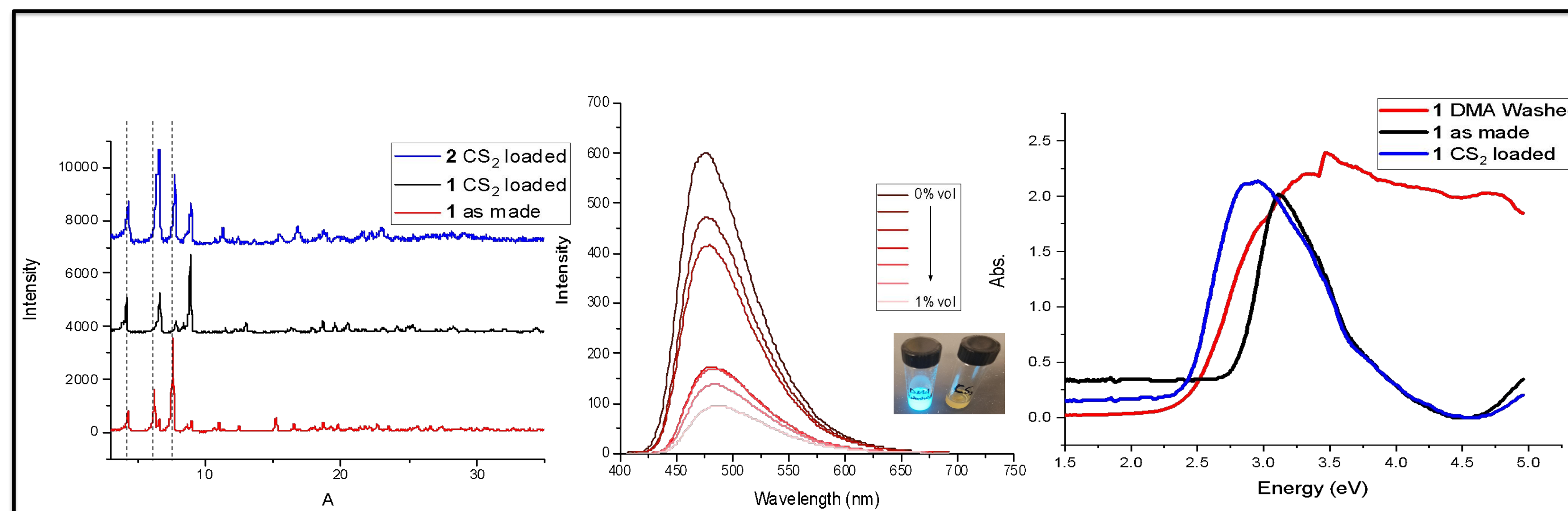


Figure 7: PXRD patterns of 1 and 2 loaded with CS<sub>2</sub> compared to the as made sample (left). Photoluminescence spectra of 1 as a function of CS<sub>2</sub> concentration (middle). UV-Vis spectra of as-made, washed, and CS<sub>2</sub> loaded 1.

## Stern-Volmer Analysis

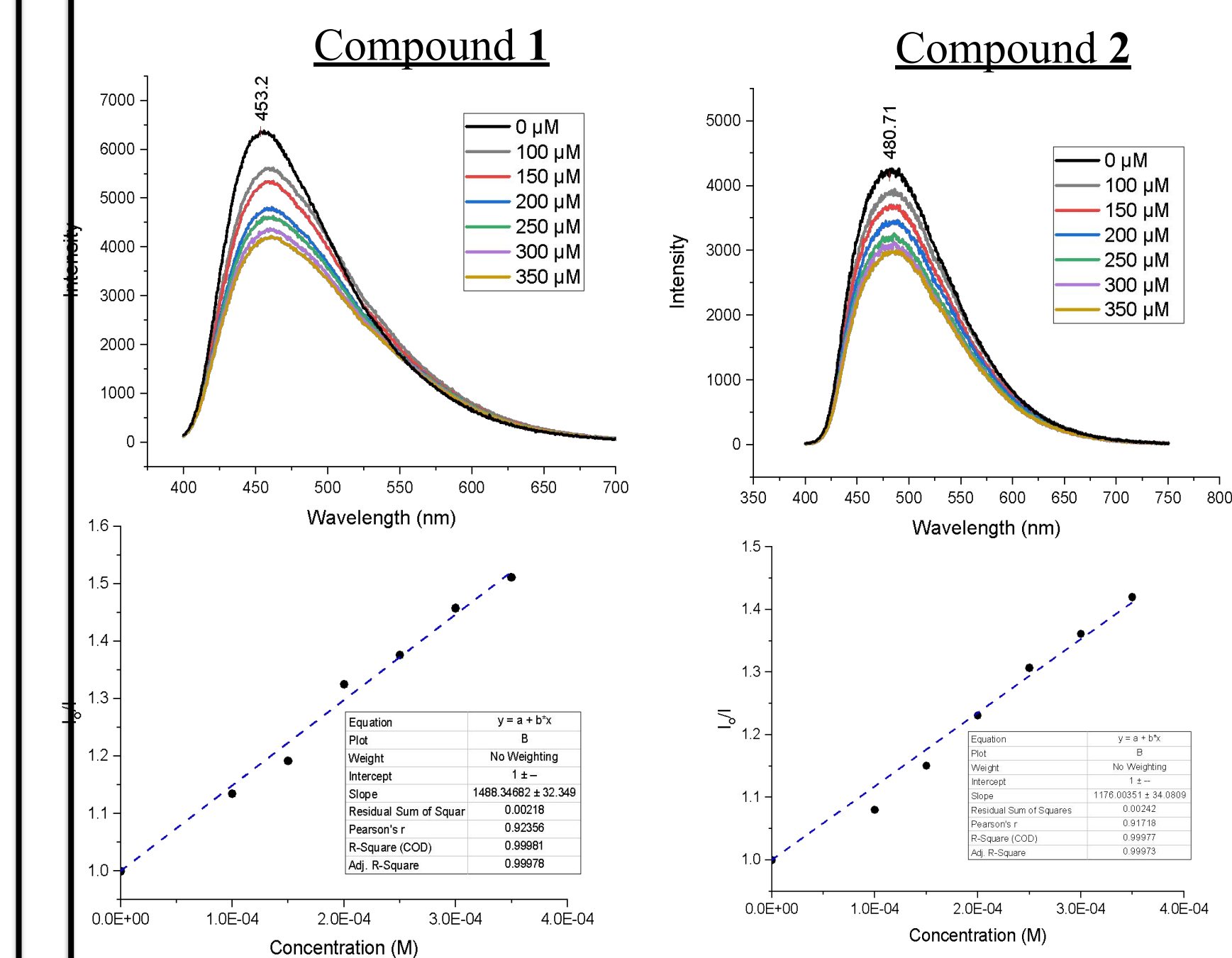


Figure 8: Stern-Volmer Analysis and data fitting for the luminescence quenching of 1 and 2 upon CS<sub>2</sub> exposure to calculate the limit of detection

## Recyclability

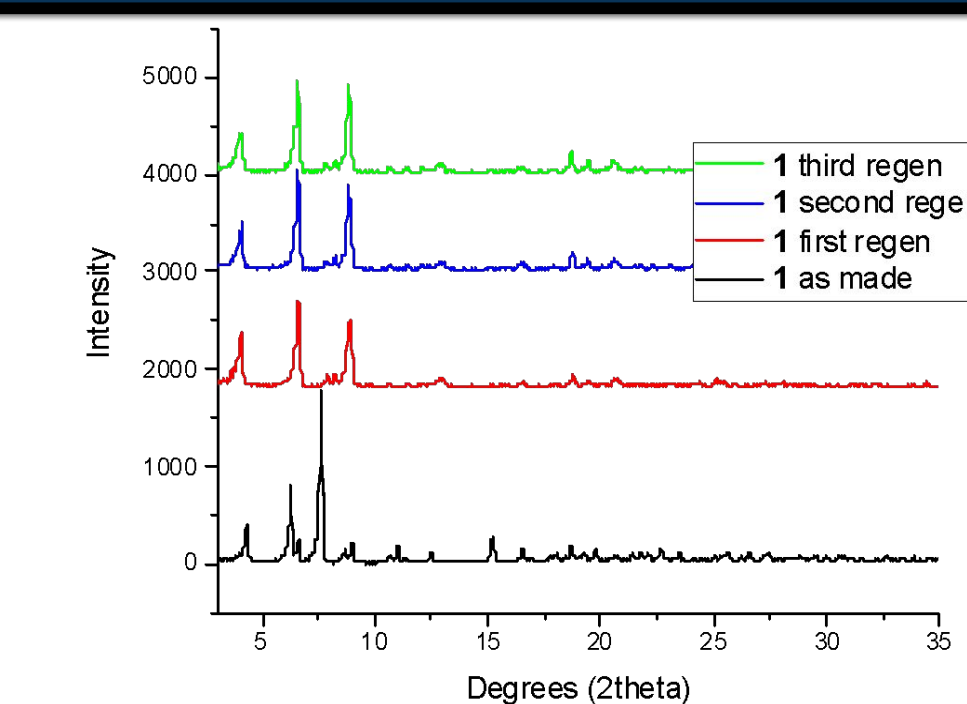


Figure 9: The PXRD patterns of 1 after the exposure to CS<sub>2</sub> and subsequent washing with 1M HCl and DMF

## Conclusion

In conclusion, we have synthesized two interpenetrated Zr-MOFs for the luminescent detection of CS<sub>2</sub> and studied the molecular interactions between CS<sub>2</sub> and the framework.

## References

- H. Wang and J. Li, *Acc Chem Res*, 2019, **52**, 1968-1978.
- W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li and S. K. Ghosh, *Chem Soc Rev*, 2017, **46**, 3242-3285.
- W. P. Lustig and J. Li, *Coordination Chemistry Reviews*, 2018, **373**, 116-147

## Acknowledgements

Special thanks to Ever Velasco and Dr. Jing Li as well as all of the Jing Li Research Group members for all their continued help and support. All authors in this work as grateful for the financial support from the Department of Energy (Grant No. DE-SC0019902).