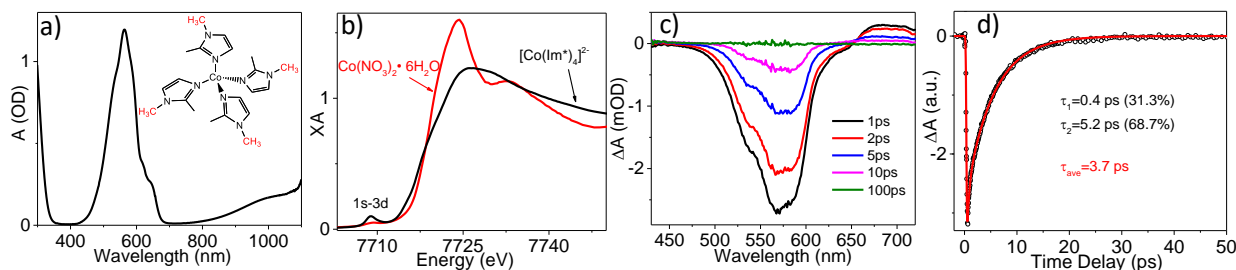


- 57503-DNI6
- Developing the Photocatalytic Properties of Zeolitic Imidazolate Frameworks
- Jier Huang, Marquette University

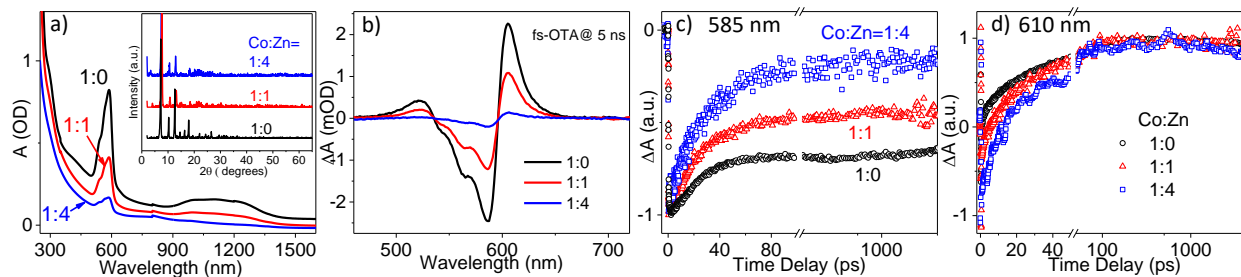
*In the first year of the grant, we have made progress in the following projects:*

1) We investigated the effect of dimension on excited state dynamics by comparing the optical transient absorption (OTA) spectra of ZIF-67 with a model compound which only includes a single unit of  $\text{Co}[\text{im}^*]_2$  ( $\text{im}^* = 1,3\text{-dimethylimidazolate}$ ) (Figure 1). This model complex shows similar  $T_d$  geometry as that in ZIF-67 (Figure 1). However, the excited state (ES) lifetime of this compound ( $\sim 3$  ps) is orders of magnitude shorter than that of ZIF-67 ( $\sim 2.9 \mu\text{s}$ ), suggesting that the porous framework in ZIF-67 plays a central role in the formation of long-lived excited state.



**Figure 1.** (a) UV-visible-near IR absorption spectrum of  $\text{Co}[\text{im}^*]_2$ . The inset shows and the molecular structure of  $\text{Co}[\text{im}^*]_2$ . (b) the XANES spectra of  $\text{Co}[\text{im}^*]_2$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at Co K edge. (c) Femtosecond OTA spectra of  $\text{Co}[\text{im}^*]_2$  following 1000 nm excitation. (d) The kinetic trace at 580 nm representing GS bleach recovery of  $\text{Co}[\text{im}^*]_2$  following 1000 nm excitation.

2) We recently synthesized mixed-metal ZIF films with different ratios of Co/Zn and Co/Cu. We carried out the studies on their ES dynamics (Figure 2). We found that the ES lifetime becomes shorter in the sample with larger concentration of Zn. We also observed direct electron transfer from excited Co center to Cu center. These results imply that the presence of  $\text{Zn}^{2+}$  may have inhibited charge transportation in the mixed-metal films, while the presence of Cu centers have facilitated charge transport through ZIF framework. These initial results have been published in *J. Am. Chem. Soc.* **2018**, *140*, 11573-11576.



**Figure 2.** (a) UV-visible-near IR absorption spectra of mixed-metal ZIFs with different Co:Zn ratios. The inset shows their XRD patterns. (b) The comparison of femtosecond OTA spectra at 5 ns time delay for ZIF films with different ratios. The comparison of kinetics of ground state bleach at 585nm (c) and excited charge separated state absorption at 610 nm (d) for ZIFs with different Co:Zn ratios.

3) We examined the intrinsic light harvesting and charge separation properties of ZIF-67 in the presence of photosensitizers or electron acceptors. The initial results for charge separation dynamics to methylene blue is published in *Phys. Chem. Chem. Phys.* **2018**, 14884-14888.

*The impact of research on PI's career and the students*

- 1) This award allows the PI and her research group to perform the fundamental studies on the optical properties of ZIFs and supports her participating professional activities including mentoring graduate and undergraduate students, participating outreach program and community service, scientific meetings etc. The PI has given 7 invited talks in scientific conferences including Fusion Conference of Frontiers in Photochemistry (Cancun, Mexico, February 18-22, 2018) and 2018 Fall ACS meeting (Boston, MA, August 19-23, 2018), and presented posters in Solar Fuel GRC (Ventura, CA, January 28-February 2, 2018) and Donor-Acceptor GRC (New Port, RI, August 5-10, 2018).
- 2) Two graduate students (Brian Pattengale and Sizhuo Yang) have been trained on this project and published a few peer-reviewed papers. They have presented their work at the Gordon Research Seminar (July 21-22, 2017) and Conference on Photochemistry (Lewiston, ME, July 23-28, 2017). Sizhuo has presented his work as poster in the Gordon Research Conference on Donor-Acceptor Interaction (New Port, RI, August 5-10, 2018).
- 3) One undergraduate student (Sir Lawrence Tender) has been trained on this project. Sir Lawrence Tender has presented his work at Marquette Summer Poster Session on July 29, 2017.
- 4) One postdoc researcher (Peilei He) has been trained on this project since April 1<sup>st</sup>, 2018.

Publications that acknowledged this grant

- 1) Pattengale, B.; SantaLucia, D.; Yang, S.; Hu, W.; Liu, C.; Zhang, X.; Berry, J.\*; **Huang, J.\*** "Direct Observation of Node-to-Node Communication in Zeolitic Imidazolate Frameworks", *J. Am. Chem. Soc.* **2018**, *140*, 11573-11576.
- 2). Pattengale, B.; **Huang, J.\*** "Photoinduced Interfacial Charge Separation Dynamics in Zeolitic Imidazolate Framework." *Phys. Chem. Chem. Phys.* **2018**, *20*, 14844-14888.