Coordination Modulation as an Alternative Pathway to UiO-66 Electronic Structure Engineering for Photocatalytic Oxidative Desulfurization

*Reihaneh Najafzade, Ruhollah Khajavian, Masoud Mirzaei **

**Email: mirzaeesh@um.ac.ir*

Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad,

Mashhad 9177948974, Iran

Nowadays, one of the most important challenges in petroleum industry is to remove sulfur compounds from liquid fuels in simple and low-cost ways [1]. Among desulfurization processes, the newly emerged photocatalytic oxidative desulfurization (PODS) has the advantages of milder operating conditions, lower energy consumption, and higher efficiency, holding great prospect to achieve deep desulfurization [2].

After the initial reports on capability of metal-organic frameworks (MOFs) in producing charge separation in the mid-2000s [3,4], research on photoactive MOFs have gained considerable interest. However, the photocatalytic activity of the MOFs-based photocatalysts is still low. Many strategies have been used to overcome this limitation including; 1) doping suitable guest molecules; 2) modification of metallic node (mixed-metal MOF); 3) functionalized organic linker; 4) incorporation of chromophoric struts (antenna effect). These approaches however; are often hard to practice, involve multiple synthetic procedures and sophisticated structures.

In this work, we propose defect engineering [5] as a simple strategy in order to induce photoactivity in UiO-66, as a model MOF with zirconium-oxo cluster node, by using modulating agent bearing enediol units, which are able to form inner-sphere charge transfer (CT) complexes, through a one-pot synthetic method. This results in a red shift of the MOF absorption and provide harvesting of solar photon and improves the separation and migration performance of photogenerated electron-hole pairs. In addition, using this method not only altered electronic structure of the MOF, but also changed its porous structure. Compared to pristine UiO-66, the experimental results showed a 35% improvement in the photocatalytic activity of modulated UiO-66 under visible light irradiation.

REFERENCES:

[1] Srivastava, V. C. An Evaluation of Desulfurization Technologies for Sulfur Removal from Liquid Fuels. *RSC Adv.* **2012**, 2, 759-783.

[2] Zhou, X.; Wang, T.; Liu, H.; Gao, X.; Wang, C.; Wang, G. Desulfurization through Photocatalytic Oxidation: A Critical Review. *ChemSusChem.* **2021**, 14, 492-511.

[3] Alvaro, M.; Carbonell, E.; Ferrer, B.; Llabrés i Xamena, F. X.; Garcia, H. Semiconductor Behavior of a Metal-Organic Framework (MOF). *Chem. Eur. J.* **2007**, 13, 5106-5112.

[4] Llabrés i Xamena, F. X.; Corma, A.; Garcia, H. Applications for Metal-Organic Frameworks (MOFs) as Quantum Dot Semiconductors. *J. Phys. Chem. C* **2007**, 111, 80-85.

[5] Fang, Z.; Bueken, B.; De Vos, D. E.; Fischer, R. A. Defect-Engineered Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **2015**, 54, 7234-7254.