

Porous Anionic Metal-Organic Frameworks: Exhibiting Photocatalytic Activity for Diels-Alder reactions by Encapsulating Ru(II) Complexes

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Today's standard of living has resulted into high energy demand and put increased strain on the environment. It has therefore become important to look into different types of energy sources in general and nature's process of photocatalysis in particular. Through this process, energy and materials are obtained based on the sun's influx of sustainable energy. This strategy has proved advantageous to catalyze useful organic transformation for synthesizing pharmaceuticals as well as to eliminate organic pollutants and resolve environmental issues. The development of heterogeneous photocatalysts allows us to easily separate the photocatalyst from the reaction mixture and reuse it multiple times. The unique features of Metal-Organic Frameworks (MOFs), including structural diversity and tailorability as well as high surface area, etc., enable them to be a highly versatile platform for photocatalysis catalysis. ^[1]

In this project, an anionic MOF $[(\text{H}_2\text{NMe})^+][\text{In}_{48}(\text{HImDC})_{96}]^{2-}$ and three $[\text{Ru}(\text{bpy})_3]^{2+}@[(\text{H}_2\text{NMe})^+][\text{In}_{48}(\text{HImDC})_{96}]$ with different $[\text{Ru}(\text{bpy})_3]^{2+}$ loading (named Ru@InMOF-1, Ru@InMOF-2, Ru@InMOF-3) were solvothermally synthesized and well characterized. PXRD profiles demonstrate that the successful $[\text{Ru}(\text{bpy})_3]^{2+}$ loading does not influence the crystalline integrity of $[(\text{H}_2\text{NMe})^+][\text{In}_{48}(\text{HImDC})_{96}]$. The results of inductively coupled plasma (ICP) show that the $[\text{Ru}(\text{bpy})_3]^{2+}$ loading of Ru@InMOF-1, -2, -3 are 15.92, 31.14, 72.28 mg($[\text{Ru}(\text{bpy})_3]^{2+}$)/g($[\text{Ru}(\text{bpy})_3]^{2+}@[(\text{H}_2\text{NMe})^+][\text{In}_{48}(\text{HImDC})_{96}]$), respectively. The EDX maps of TEM indicate that the Ru concentration is homogeneously distributed through the MOF nanoparticle. Since the Ru molecules neither form a core-shell structure nor are agglomerated at the surface of the InMOF nanoparticle; they are most probably located inside the framework of InMOF. UV-Vis diffuse reflectance spectroscopy (DRS) was further used to investigate the light response properties of as-prepared samples. The pure anionic MOF has no ability to respond under visible light; however, the absorption of the Ru@InMOFs extends significantly into visible region, which makes them promising photocatalysts. Thus, the electronically mismatched Diels-Alder reactions (trans-Anethole and isoprene) chosen as a probe reaction to investigate their photocatalytic properties.

Reference

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- [2] F. Nouar, J. Ecket, J. F. Eubank, P. Forster, M. Eddaoudi, *J. Am. Chem. Soc.*, **2009**, 131, 2864-2870.