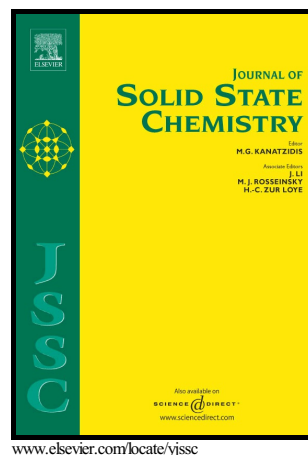


# Author's Accepted Manuscript

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# Photophysical Properties of $[\text{Ru}(2,2'\text{-bipyridine})_3]^{2+}$ Encapsulated within the Uio-66 Zirconium Based Metal Organic Framework.

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**KEYWORDS:** Ruthenium, Metal organic framework, Uio-66, Ru(II) tris(2,2'-bipyridine), photophysics.

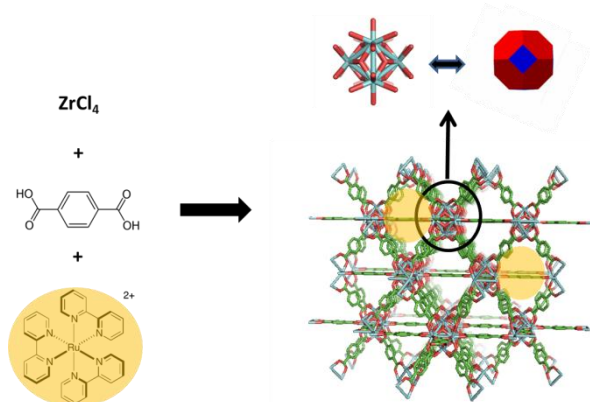
Supporting Information Placeholder

**ABSTRACT:** The ability to encapsulate photo-active guest molecules within the pores of metal organic frameworks (MOFs) affords the opportunity to develop robust photocatalysts as well as solar energy conversion systems. An important criteria for such systems is stability of the new materials towards moisture, high temperatures, etc which preclude the use of many MOF frameworks. Here, the ability to encapsulate  $[\text{Ru}(\text{II})(2,2'\text{-bipyridine})_3]^{2+}$  ( $[\text{Ru}(\text{bpy})_3]^{2+}$ ) into the cavities of the zirconium based MOF Uio-66 as well as the photophysical properties of the complex are reported. The X-ray powder diffraction data of the orange Uio-66 powder are consistent with the formation of Uio-66 in the presence of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . The steady state emission exhibits a significant bathochromic shift from 603 nm in ethanol to 610 nm in Uio-66. The corresponding emission decay of the encapsulated  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex is biexponential with a fast component of 128 ns and a slower component of 1,176 ns (20 deg C). The slow component is consistent with encapsulation of  $[\text{Ru}(\text{bpy})_3]^{2+}$  into cavities with restricted volume that prevents the population of a triplet ligand field transition that is anti-bonding with respect to the Ru-N bonds. The origin of the fast component is unclear but may involve interactions of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  encapsulated within large cavities formed through missing ligand defect sites within the Uio-66 materials. Co-encapsulated quenchers contained within these larger cavities gives rise to the reduced lifetimes of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complexes.

## Introduction

The development of photo-active materials involving metal organic frameworks (MOF) has been of increasing interest over the past decade with a focus on light harvesting and photocatalytic applications.<sup>1-5</sup> A particularly useful strategy for producing photocatalytic MOFs involves the encapsulation of a photoactive guest molecule within the pores of the MOF. In these systems the target reactants diffuse through available channels and cavities within the MOF, encounter the photoexcited catalyst, undergo photochemical transformation and subsequently diffuse back through the pores/channels eventually exiting the material. This type of photocatalytic MOF offers a number of advantages including the fact that a wide array of existing photocatalysts can be exploited, reactant molecules must enter the pores of the MOF in order to react with the photocatalyst thus allowing for selective chemistry to take place at specific sites within the MOF and the large library of existing MOFs can be targeted with little need for new MOF designs or exotic ligands. Examples of this type of photocatalyst have been reported in which the encapsulated guest include a Keggin type polyoxometalate complex encapsulated within an HKUST-1(Cu) framework<sup>6,7</sup>, free base and metalloporphyrin encapsulated within both rhoZMOF and HKUST-1 framework<sup>8-10</sup> and  $[\text{Ru}(\text{bpy})_3]^{2+}$  encapsulated in pillard 2-D sheet materials, polyhedral Zn based MOFs and Zr based MOFs.<sup>11-18</sup>

Ruthenium(II)polypyridyl complexes are of specific interest as guests in the development of photocatalytic MOFs due to the fact that the excited states of  $\text{Ru}(\text{II})(\text{L})_3$  complexes exhibit favorable reduction/oxidation potentials in the excited state as well as relatively long lifetimes (allowing for greater excited state reactivity) and the complexes have excellent photostability.<sup>19</sup> In addition, a wide array of functionalized bipyridine ligands are available which can be utilized to further tune the excited state properties of the  $\text{Ru}(\text{II})(\text{L})_3$ -type complexes.



**Fig. 1:** General assembly of the Uio-66 MOF from Zr-O clusters and 1,4 BDC. The illustration indicates the cavities likely to contain the  $[\text{Ru}(\text{bpy})_3]^{2+}$  complex.

Here the 'one-pot' method is employed to encapsulate  $[\text{Ru}(\text{bpy})_3]^{2+}$  into the cavities of the water stable Uio-66 MOF. Uio66 is formed from octahedral  $\text{Zr}_6\text{O}_4(\text{OH})_4$  clusters connected through 1,4-benzene dicarboxylate (BDC) ligands and contains octahedral cavities of ~11 Å in diameter and tetrahedral cavities of ~8 Å in diameter.<sup>20-22</sup> The structure of Uio66 is displayed in Fig. 1. This MOF displays exceptional stability towards water, temperature and mechanical stress. In addition, Uio-66 exhibits an affinity towards  $\text{CO}_2$  with uptake being improved through functionalization of the BDC ligand.<sup>22</sup> The results

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