Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Photoinduced Inter-Cavity Electron Transfer between Ru(II)tris(2,2'-bipyridne) and Co(II)tris(2,2'-bipyridine) Co-Encapsulated within a Zn(II)-Trimesic Acid Metal Organic Framework

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Supplementary Information

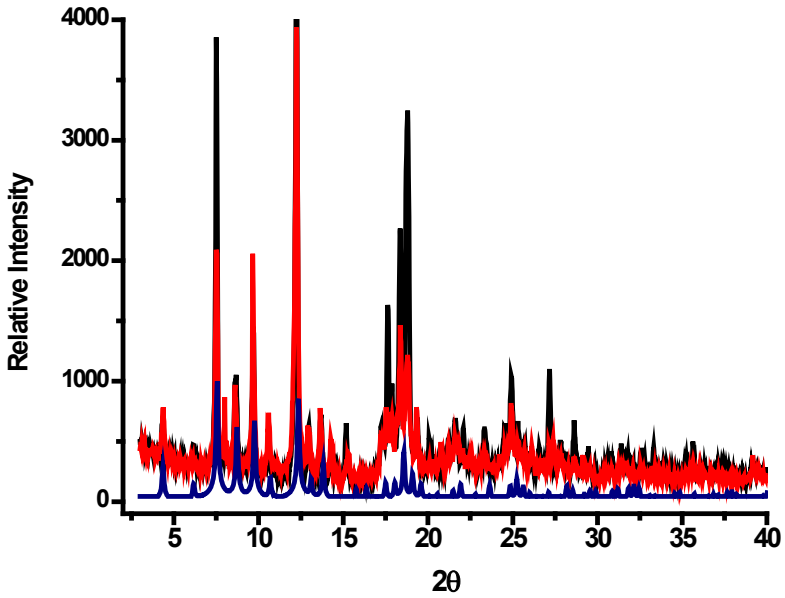

Fig. S1: Overlay of the X-ray powder diffraction pattern of USF2 (black trace) RuBpy@USF2 (red trace) and XRD simulated from the single crystal unit cell (blue trace). Powder X-Ray diffraction patterns were measured on a Bruker D8 Advance diffractometer using Cu-Kα radiation (λ = 1.5418 Å) at room temperature. Coupled θ/2θ scans between 3° and 50° with a step size of 0.02° were performed with time per step of 0.5 sec. The XRD for the corresponding RuBpy:CoBpy@USF2 materials are identical to that shown for the RuBpy@USF2. The additional diffraction peaks at 8°, 12.0°, 14.3°, 15.3°, 20.7°, 26.1°, 27.5° ... 2Θ) observed in the experimental PXRD spectra in comparison with the calculated one belong to an impurity that has been identified as UQUVOS CSD Refcode containing Zn cations, trimesate anions and water molecules. Small, colorless crystals have been observed under the microscope and the unit cell has been determined using single crystals X-ray diffraction method. As these crystals do not contain RuBpy or CoBpy they did not contribute to the observed emission.

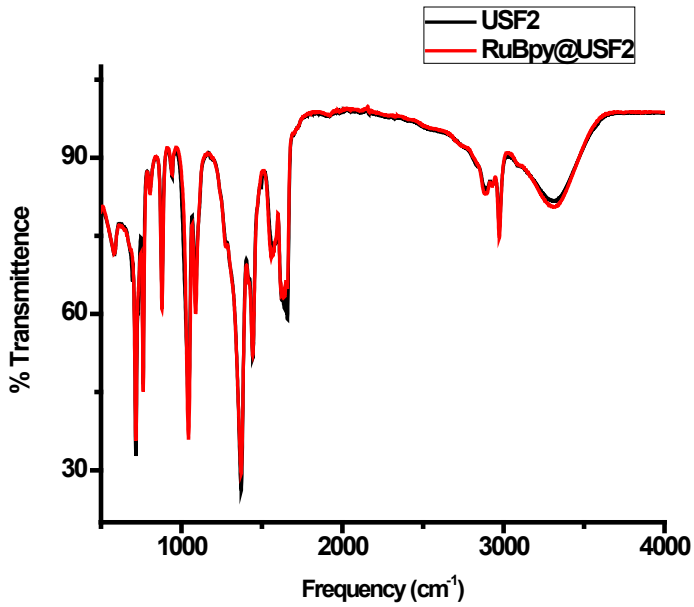

Fig. S2: Overlay of the FTIR spectra of USF2 and RuBpy@USF2. The FTIR spectra were recorded on a Perkin-Elmer Spectrum Two spectrometer and were background corrected. The XRD for the corresponding RuBpy:CoBpy@USF2 materials are identical to that shown for the RuBpy@USF2.

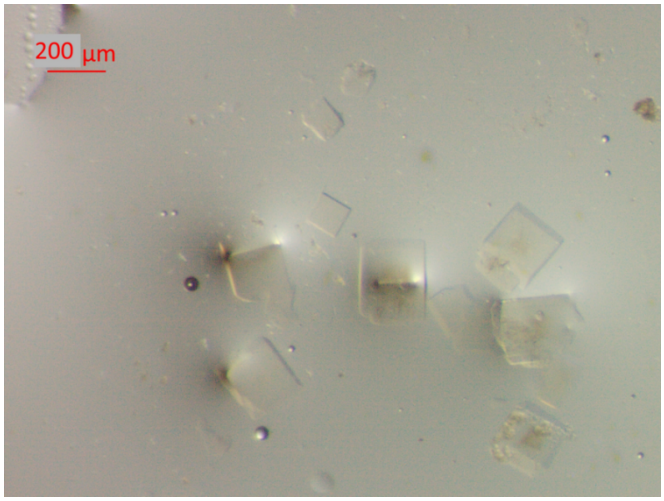

Fig. S3: Microscope photograph of USF2 crystals that have been soaked in ethanol saturated with RuBpy for three days and then washed in ethanol. Ethanol washes were performed by letting the crystals soak in ethanol for ~8 hours and centrifuged. This was repeated for three cycles. The same process was repeated for RuBpy@USF2. No changes were observed in either the crystal images, XRD patterns, FTIR or photophysical properties.

RuBpy Loading

The loading of RuBpy into USF2 was determined spectrophotimetrically. In this method, ~7mg of dried RuBpy@USF2 was dissolved in 1 mL of water. The concentration of Zn^{2+} was determined using Zinconc (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene)[S1,S2]. Briefly, 50 µL of Zincon stock solution (~ 2mM) in methanol was added to 2 mL of 10 mM CAPS buffer, pH 9.1. The Zn^{2+} concentration was determined using the absorbance at 620 nm (maximum for the Zincon-Zn^{2+} complex) and an $\varepsilon_{620\ nm}$ of 25,050 $M^{-1}cm^{-1}$. The corresponding RuBpy concentration was determined by diluting the solubilized RuBpy@USF2 material into neat water and using the $\varepsilon_{452\ nm}$ of 14,600 $M^{-1}cm^{-1}$. Using the RuBpy to Zn^{2+} ratio of the solubilized RuBpy@USF2 and the fact that one unit cell contains one large cavity and 22 Zn^{2+} ions, the loading of RuBpy per cavity could be determined. The loading was found to average 0.63 RuBpy complexes per cavity (63% loading). Similar loading values were obtained for the CoBpy:RuBpy mixed bed USF2 material.

S1: Sabel, C.E.; Neureuther, J.M.; Sieman, S. *Anal. Biochem.* **2010**, 397, 218-226.
S2: Platte, J.A.; Marcy, V.M., *Anal. Chem.* **1959**, 31, 1226-1228.