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Communication

Supporting Information

Fixed Distance Photoinduced Electron Transfer between Fe and Zn Porphyrins Encapsulated within the Zn HKUST-1 Metal Organic Framework

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Sample Preparation and Loading

All solvents as well as 1,3,5 benzene tricarboxylic acid (BTCA), aniline and $Zn(II)(NO_3)_2 \bullet 6H_2O$ were obtained from Sigma-Aldrich and used without further purification. Zn4SP and Fe4SP were obtained from Frontier Scientific (Logan, Utah) and used without further purification.

The Zn4SP and the Zn4SP:Fe4SP encapsulated ZnHKUST-1 were prepared by carefully layering a 5 ml of a solution containing 0.115 g of 1,3,5 benzene tricarboxylate, 0.058 g of $Zn(II)(NO_3)_2 \bullet 6H_2O$ and 30 mg of the porphyrin of interest (or total weight of 30 mg for mixed bed materials) over 5 ml of toluene containing 120 µl of pyridine in a 25 ml scintillation vial. After ~ 4 days dark crystals appeared on the side of the vial. The solution was then decanted and the crystals collected by centrifugation. The crystals were washed extensively with ethanol.

Porphyrin loading into the cavities of the ZnHKUST-1 was determined spectroscopically (Fig. S1). The spectroscopic method involves dissolving a known weight of Zn4SP@ZnHKUST-1(Zn) or Zn4SP:Fe4SP@HKUST-1(Zn) in water containing 0.5 M HCl. Under these conditions the material is completely solubilized and the resulting solution concentration of Zn4SP and Fe4SP are determined spectrophotometrically. The number of porphyrin complexes per cavity can then be determined.
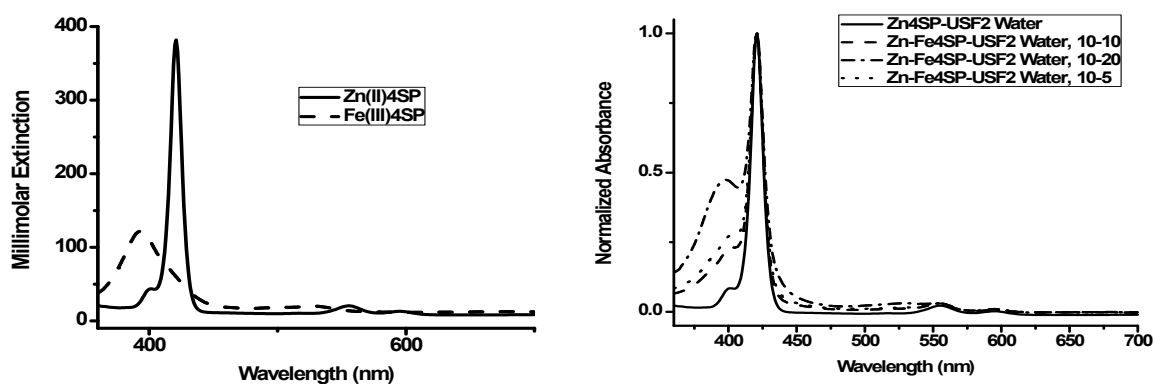

Figure S1: Left panel: Millimolar extinction spectra of Fe4SP and Zn4SP in water. Right Panel: Normalized absorption spectra of mixed bed Zn4SP:Fe4SP@USF2 with various loading ratios solubilized in water.

Transient Absorption and Steady State Emission

Transient absorption (TA) and fluorescence data were obtained using particle suspensions in ethanol. For TA, samples were subjected to 532 nm excitation from a frequency doubled Nd:YAG laser (Continuum MiniLite I, 7 ns FWHM, ~ 1 mJ/pulse) while being probed with white light from an Xe arc lamp (Oriel) filtered through a ¼ m single monochrometer (Yvon-Jobin) and detected with a photomultiplier tube (R928, Hamamatsu). The signal was amplified using a Mels Griot 3AMP005 pre-amplifier followed by a Stanford Instruments SR445A 350 post amplifier and digitized using a Tektronix TDS7404 4 GHz digitizer. Spectra were the average of 25 pulses. Samples were deaerated using an Ar purge. Curve fitting was accomplished through Origin™. The quality of the fit is judged using χ^2 analysis, residuals and autocorrelation. Steady-state emission data were obtained using an ISS PC1 spectrofluorometer (Champaign, IL). The steady state emission spectra of Zn4SP@HKUST-1(Zn) and Zn4SP:Fe4SP@HKUST-1(Zn) are displayed in figure S1. Emission lifetimes were ~1.2 ns for both Zn4SP@HKUST-1 (Zn) and all loadings of Fe4SP:Zn4SP@HKUST-1 (Zn) (J. Miksovska, Florida International University, personal communication).
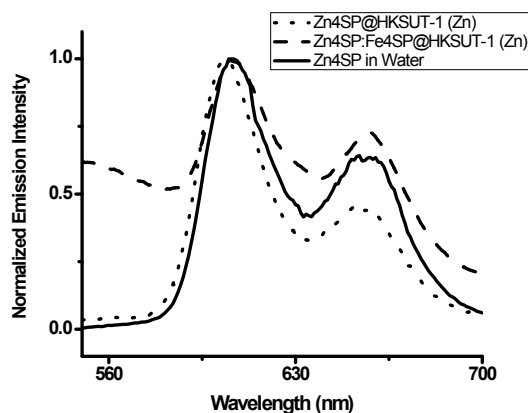

Figure S2: Steady state emission spectra of Zn4SP in water (solid line), Zn4SP@USF2 (dotted line) and Zn4SP:Fe4SP@USF2, 1:1 loading ratio (dashed line).

X-Ray Diffraction

All crystalline phases have been identified using Single Crystal X-Ray diffraction method to have very similar unit cell parameters and space group symmetry as previously published structure of HKUST-1 with encapsulated porphyrin moieties [S1] [a=26.5252(6)Å, Fm-3m for Zn4SP:Fe4SP@HKUST-1(Zn) and a=26.5108(4)Å, Fm-3m for published Fe4SP-HKUST-1(Zn) structure. The X-ray diffraction data were measured on Bruker D8 Venture PHOTON 100 CMOS diffractometer equipped with a Cu Kα INCOATEC Imus micro-focus source (λ = 1.54178 Å). The crystal was kept at 100(2) K during data collection. Indexing was performed using APEX2 [S2] and final unit cell parameters have been determined based on the global refinement of 8122 reflections within 5.7-137 2Theta range [S3]. As porphyrin moieties, Zn4SP and Fe4SP would occupy the same position (with partial occupancy) in the model of the crystal structure the refinement has not been attempted due to low loading and inability to distinguish between those two metals in this case.

[1]Zn4SP to Fe4SP Photoinduced ET

An evaluation of the Marcus parameters for [1]Zn4SP to Fe4SP intercavity ET is presented in Fig. S3. The plotted k_{ET} values fall in the range of ~$1x10^9$ s^{-1} (1 ns) to $1.5x10^{10}$ s^{-1} (0.2 ps) for reasonable values of β and λ. These values are near the limit of resolution of the phase and modulation fluorescence lifetime measurements for turbid samples (J. Miksovska, personal communication). The data also demonstrates that intercavity ET can only take place between porphyrins in adjacent cavities. The probability of having adjacent porphyrins in the MOF that is 60% loaded is given by:

$$P = o.6(0.6N-1)/[N(N^2-1)] \qquad \text{Eq. S1}$$
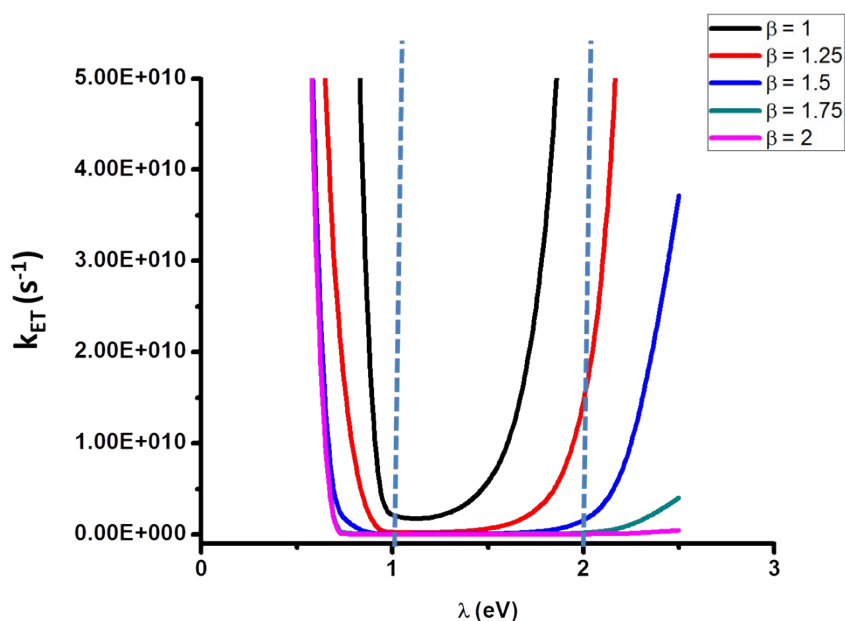
Where N is the total number of cavities per mg of MOF.

Figure S3: Plots of calculated k_{ET} versus λ for differing β values using d = 19 Å , k0 = $1x10^{13}$ s^{-1}, R_0 = 9.7 Å (for Fe4SP/Zn4SP), ΔG° = -1.08 eV (-25 kcal mol^{-1}) and T = 300K. The dashed lines designates the region of expected k_{ET} values for [1]Zn4SP to Fe4SP photoinduced intercavity ET.

S1. R. W. Larsen, L. Wojtas, J. Perman, R. K. Musselman, M. J. Zaworotko, and C. M. Vetromile J. Am. Chem. Soc. 2011, 133, 10356.

S2. Bruker (2013). APEX2 (Version 2013.6-2). Bruker AXS Inc., Madison, Wisconsin, USA.

S3. Bruker (2013). SAINT-V8.32A. Data Reduction Software.