## **Supporting Information for**

## Ligand-field Dependence of the Excited State Dynamics of Hangman Bisporphyrin Dyad Complexes

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Index	Page
Förster energy transfer calculation	S2-S3
Absorption spectra of (HPX)Fe <sup>III</sup> -OH and (HPX)Fe <sup>III</sup> -OH(1-MeIm) and	S4
emission spectra of (E-P) $Zn^{II}$ and (E-P) $Zn^{II}$ (1-MeIm)	

## **Förster Energy Transfer Calculation**

Förster EET requires resonant coupling between the emitting dipole of the donor and the absorption dipole of the acceptor, therefore the spectral overlap integral  $(J(\lambda))$  is the most important rate-determining parameter. Equation 1 was used to estimate the rate of Förster EET.

$$k_{EET} = C \left( \frac{\Phi_D \kappa^2}{\tau_D r^6 \eta^4 N} \right) J(\lambda), \qquad (1)$$

where 
$$J(\lambda) = \int_{0}^{\infty} F_{D}(\lambda) \varepsilon_{A}(\lambda) \lambda^{4} d\lambda$$
, (2)

and 
$$C = \frac{9000 \ln(10)}{128\pi^5}$$
 (3)

In Equation 1,  $\Phi_D$  and  $\tau_D$  are the emissive quantum yield and lifetime, respectively, of the donor, r is the D–A distance,  $\kappa^2$  is a factor that accounts for the relative orientation of D and A transition dipole moments ( $0 < \kappa^2 < 4$ ),  $\eta$  is the medium refractive index, and N is Avogadro's number. Equation 2 defines the spectral overlap integral,  $J(\lambda)$ , where  $F_D(\lambda)$  is the normalized emission spectrum of the donor and  $\varepsilon_A(\lambda)$  is the absorption spectrum of the acceptor (with intensities plotted as molar extinction coefficients), both as a function of wavelength ( $\lambda$ ).

The absorption spectrum of (HPX)Fe<sup>III</sup>–OH, and the normalized emission spectrum of (E-P)Zn<sup>II</sup> (Figure S1) are used to calculate the spectral overlap integral ( $J(\lambda) = 3.59 \times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$ ). Taking an emission quantum yield of  $\Phi_D = 0.045$  for (E-P)Zn<sup>II</sup> and an unquenched lifetime of  $\tau_D = 1.8$  ns (vide supra), a D–A center-to-center distance of r = 17 Å, an angular factor of  $\kappa^2 = 2/3$  (assuming that the absorption/emission dipoles in both porphyrins have planar symmetry, and the two porphyrins are freely rotating relative to each other), and using a solvent refractive index of n = 1.5 (toluene), a resonant EET rate of  $k_{\text{EET}} = 4.3 \times 10^9 \text{ s}^{-1}$  results for **1**. On the basis of this  $k_{\text{EET}}$ , the observed lifetime of S<sub>1</sub> may be calculated from,

$$\tau = 1 / (k_0 + k_{\text{EET}}) \tag{4}$$

and is it predicted to be  $\tau \sim 200$  ps, based on a natural lifetime of  $\tau_0 = 1.8$  ns (where  $\tau_0 = 1 / k_0$ ), as determined from the fluorescence lifetime of the (E-P)Zn<sup>II</sup> monomer.

The Förster calculation was repeated for dyad **1** with 1-MeIm bound, since ligation of 1-MeIm was found to perturb the electronic spectra of both components of the dyad (Figure S1). A pronounced red-shift in the emission spectrum of (E-P)Zn<sup>II</sup>(1-MeIm) ( $\lambda_{em,max} = 584$  and 639 nm) combined with an attenuated fluorescence quantum yield ( $\Phi_D = 0.03$ ; estimated based on

quantitative comparison with unbound (E-P)Zn<sup>II</sup>, and consistent with that observed for pyridine binding to (OEP)Zn<sup>II</sup>)), and shorter unquenched lifetime ( $\tau_D = 1.6$  ns) translates to a slower calculated rate of EET and longer S<sub>1</sub> lifetime ( $k_{EET} = 3.5 \times 10^9 \text{ s}^{-1}$ ,  $\tau \sim 250 \text{ ps}$ ). The Förster calculation for dyad **2** uses the same input quantities as for dyad **1** but with the D–A distance reduced to r = 13 Å. The shorter distance corresponds to a faster rate constant of EET of ( $k_{EET} = 2.2 \times 10^{10} \text{ s}^{-1}$ , and a shorter S<sub>1</sub> lifetime of  $\tau \sim 45 \text{ ps}$ .



**Figure S1.** Spectral overlap between the emission of  $(E-P)Zn^{II}$  (blue dashed) and the electronic absorption of  $(HPX)Fe^{III}$ –OH (blue solid) compared with the emission of  $(E-P)Zn^{II}(1-MeIm)$  (red dashed) and the absorption of  $(HPX)Fe^{III}$ –OH(1-MeIm) (red solid).