Synergistic "Ping-Pong" Energy Transfer For Efficient Light Activation in a Chromophore-Catalyst Dyad

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SUPPORTING INFORMATION

- 1. Cyclic voltammetry
- 2. Room temperature emission spectra in chloroform and acetonitrile/acetone (50:50) solvent mixture of the compounds studied
- 3. Description of the method used to estimate the triplet excited state energy for Ru_{cat} .
- 4. Low temperature phosphorescence spectra for H_2TPP and ZnTPP
- 5. NMR spectra of all the synthesized compounds
- 1. Cyclic voltammetry



Figure S1: Cyclic and square wave voltammograms of H₂-P (left) and Zn-P(right).



Figure S2: Cyclic and square wave voltammograms of Ru_{cat} .



Figure S3: Cyclic and square wave voltammograms of H_2 -P-Ru_{cat} (left) Zn-P-Ru_{cat} (right).

2. Room temperature emission spectra of the compounds studied



Figure S4. Emission spectra in chloroform (acetonitrile for Ru_{cat}) of compounds investigated. Excitation wavelength: 590 nm for H_2 -P and H_2 -P-R u_{cat} (left), 555 nm for Zn-P and Zn-P-R u_{cat} (right) and 515 nm for R u_{cat} .



Figure S5. Emission in acetonitrile/acetone (50:50) solvent mixture. Excitation wavelength: 555 nm for $Zn-P-Ru_{cat}$, and 595 nm for H_2 -P- Ru_{cat}

3. Description of the method used to estimate the triplet excited state energy of Ru_{cat}

The MLCT spectral region was assumed to consist of overlapping bands for spin-allowed and spin-forbidden transitions. The onset for spin-forbidden transitions was assumed to be around 550 nm.³² The luminescence spectrum was modified according to:

$$L(v)dv = \frac{L(v)}{v^3}dv$$

Where L(v) refers to the luminescence intensity at wavenumber v and normalized to the maximum of the modified absorption MLCT band:

$$A(v)dv = \frac{A(v)}{v}dv$$



Figure S6. Normalized MLCT absorption band for \mathbf{Ru}_{cat} (blue) weighted on wavenumber (ν) and luminescence spectrum (red) weighted on ν^3 . The intersection point of the two curves has been used to estimate the triplet excited state energy of \mathbf{Ru}_{cat} .



Figure S7. Phosphorescence spectrum of **Zn-P** in degassed ethanol:methanol (4:1) rigid matrix at 77 K. Excitation wavelength: 565 nm.



Figure S8. Phosphorescence spectrum of H_2 -P in degassed ethanol:methanol (4:1) rigid matrix at 77 K. Excitation wavelength: 600 nm.

5. NMR spectra all the synthesized compounds



Figure S9. ¹H NMR spectrum of compound H₂-P-terpy in CDCl₃.



Figure S10. Aromatic region of ¹H NMR spectrum of compound H₂-P-terpy in CDCl₃.



Figure S11. ¹³C NMR spectrum of compound H₂-P-terpy in CDCl₃.



Figure S12. Aromatic region of ¹³C NMR spectrum of compound H₂-P-terpy in CDCl₃.



Figure S13. ¹H NMR spectrum of compound H₂-P-Ru_{cat} in CDCl₃.



Figure S14. Aromatic region of ¹H NMR spectrum of compound H_2 -P-Ru_{cat} in CDCl₃.



Figure S15. ^{13}C NMR spectrum of compound $H_2\text{-}P\text{-}Ru_{cat}$ in CDCl3.



Figure S16. Aromatic region of 13 C NMR spectrum of compound H_2 -P-Ru_{cat} in CDCl₃.



Figure S17. ¹H NMR spectrum of compound **Zn-P-Ru**_{cat} in DMSO-*d*₆.



Figure S18. Aromatic region of ¹H NMR spectrum of compound Zn-P-Ru_{cat} in DMSO-d₆.



Figure S19. ¹³C NMR spectrum of compound **Zn-P-Ru**_{cat} in DMSO- d_6 .



Figure S20. Aromatic region of ¹³C NMR spectrum of compound **Zn-P-Ru**_{cat} in DMSO- d_6 .



Figure S21. ¹H NMR spectrum of compound H_2 -P in CDCl₃.



Figure S22. Aromatic region of ¹H NMR spectrum of compound H₂-P in CDCl₃.



Figure S23. ¹³C NMR spectrum of compound H₂-P in CDCl₃.



Figure S24. Aromatic region of 13 C NMR spectrum of compound H₂-P in CDCl₃.



Figure S25. ¹H NMR spectrum of compound Zn-P in CDCl₃.