Electronic Supporting Information for:

Near-IR Phosphorescent Metalloporphyrin as a Photochemical Upconversion Sensitizer

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Experimental Section

General. Rubrene and spectroscopic grade toluene were purchased from Aldrich and used without further purification. PtTPTNP was synthesized according to the published procedure.[1] N,N'-*bis*(1-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic diimide (PDI) was synthesized starting from commercially available dihexylketone via the adopted literature procedures.[2, 3]

Spectroscopic Measurements. Static absorption spectra were measured with a Cary 50 Bio UV-Vis spectrophotometer from Varian. Steady-state luminescence spectra were obtained with a PTI instruments spectrofluorimeter. A Ti:Sapphire laser (Chameleon Ultra II, Coherent) was utilized as the excitation light source providing 690 nm nJ laser pulses at 80 MHz. Incident laser power was varied using a series of neutral density filters. All luminescence samples were prepared in specially designed 1 cm^2 optical cells bearing a sidearm roundbottomed flask and were subjected to a minimum of three freeze-pump-thaw degas cycles prior to all measurements. The incident laser power was measured using either a Molectron Power Max 5200 power meter or an Ophir Nova II/PD300-UV power meter.

Quantum Yield Measurements. The sensitized upconverted fluorescence quantum yield measurements of rubrene and PDI in toluene were measured relative to [Os(phen)$_3$](PF$_6$)$_2$ in acetonitrile using 690 nm excitation, measured under identical conditions utilizing equation 1,[4]

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{A_{std}}{A_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right)\left(\frac{\eta_{UC}}{\eta_{std}}\right)^2 \qquad (1)$$

where Φ_{uc}, A_{uc}, I_{uc} and η_{uc} represents the quantum yield, absorbance, integrated photoluminescence intensity, and refractive index of the upconversion sample at the excitation wavelength. The corresponding terms for the subscript "std" are for the reference quantum counter at the corresponding excitation wavelength. The QY standard was $[Os(phen)_3](PF_6)_2$ in acetonitrile, whose $\Phi_{std} = 0.03 \pm 0.002$ determined using an absolute photoluminescence quantum yield system (Hamamatsu, C11347). The refractive index of the solvents used were $\eta_{acetonitrle}=1.344$ and $\eta_{toluene}=1.496$ as obtained from Sigma-Aldrich solvent properties. The integrated intensity of the upconverted fluorescence was analyzed in the region 500-680 nm while that of $[Os(phen)_3](PF_6)_2$ was analyzed in the region 600-850 nm. Quantum yield values reported herein represent an average of five independent measurements. Even though the emission profile of the standard sample does not overlap the upconverted photoluminescence evident at shorter wavelengths, not that the experimentally determined quantum yields were reproducible using this relative actinometric method.

Stern-Volmer Quenching. The Stern-Volmer (K_{SV}) constants were obtained according to the Stern-Volmer relation, equation 2,

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (2)$$

where I_0 and I represent the PtTPTNP photoluminescence intensities in the absence and presence of the quencher respectively. K_{SV} is the Stern-Volmer constant, and $[Q]$ is the molar concentration of the rubrene and PDI energy transfer acceptor.

References

1. J. R. Sommer, R. T. Farley, K. R. Graham, Y. Yang, J. Xue, J. R. Reynolds and K. S. Schanze *ACS Applied Materials & Interfaces*, 2009, **1**, 274.

2. Y. W. Huang, J. C. Hu, W. F. Kuang, Z. X. Wei and C. F. Fual *Chem. Commun.* 2011, **47**, 5554.

3. H. Langhals *Helv. Chim. Acta.* 2005, **88**, 1309.

4. J. N. Demas and G. A. Crosby *J. Phys. Chem.* 1971, **75**, 991.
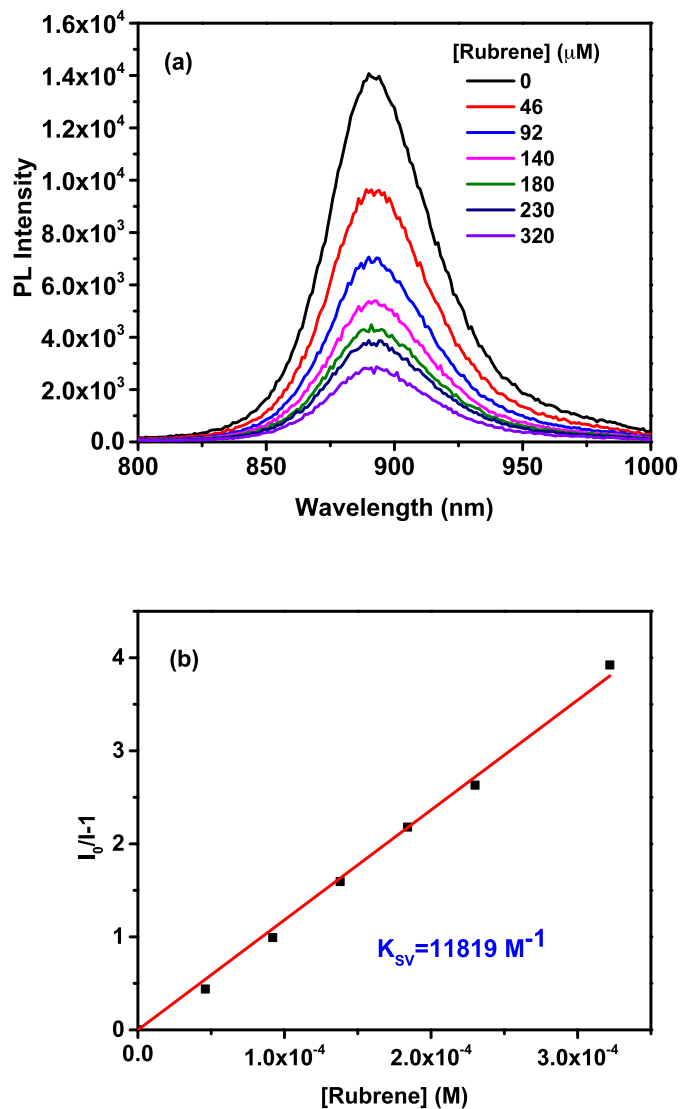
Figure S1. (a) Photoluminescence intensities of the quenching of 4 µM PtTPTNP measured as a function of rubrene concentration in deaerated toluene. (b) Stern-Volmer plot generated from photoluminescence quenching of PtTPTNP with rubrene in deaerated toluene.
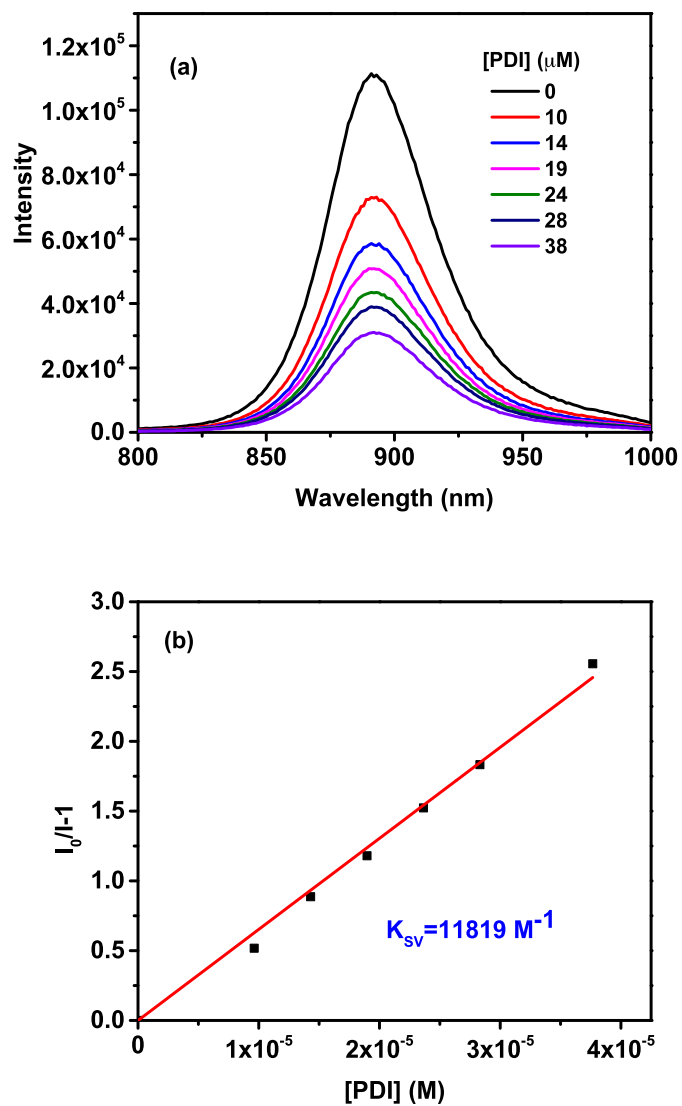
Figure S2. (a) Photoluminescence intensity quenching of 4 μM of PtTPTNP measured as a function of PDI concentration in deaerated toluene. (b) Stern-Volmer plot generated from photoluminescence quenching of PtTPTNP with PDI in deaerated toluene.
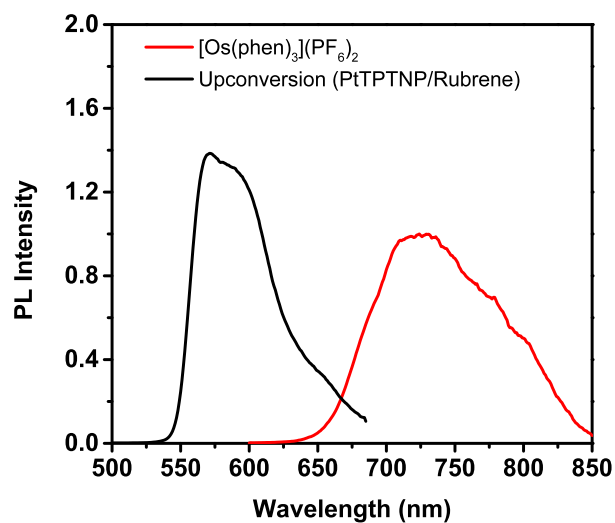
Figure S3. Photoluminescence intensity of [Os(phen)$_3$](PF$_6$)$_2$ in deaerated acetonitrile and upconverted PtTPTNP/rubrene in deaerated toluene with 690 nm excitation at a power density of 26 W/cm^2.
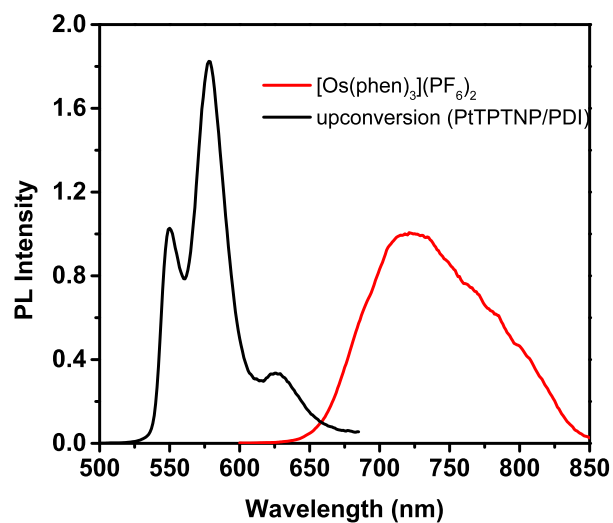
Figure S4. Photoluminescence intensity of $[Os(phen)_3](PF_6)_2$ in deaerated acetonitrile and upconverted PtTPTNP/PDI in deaerated toluene with 690 nm excitation at a power density of 20 W/cm^2.
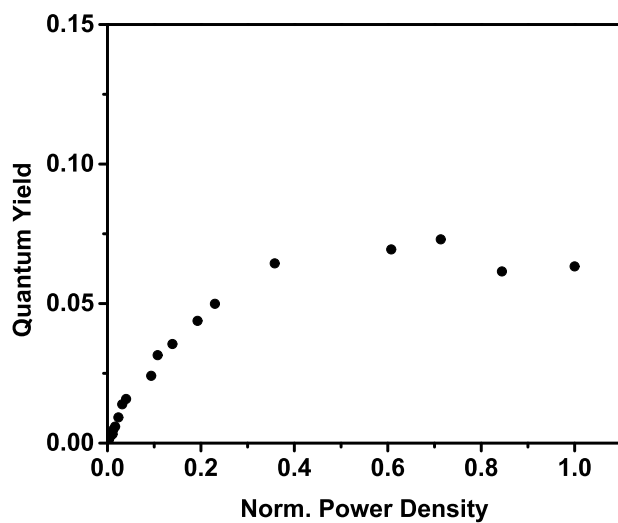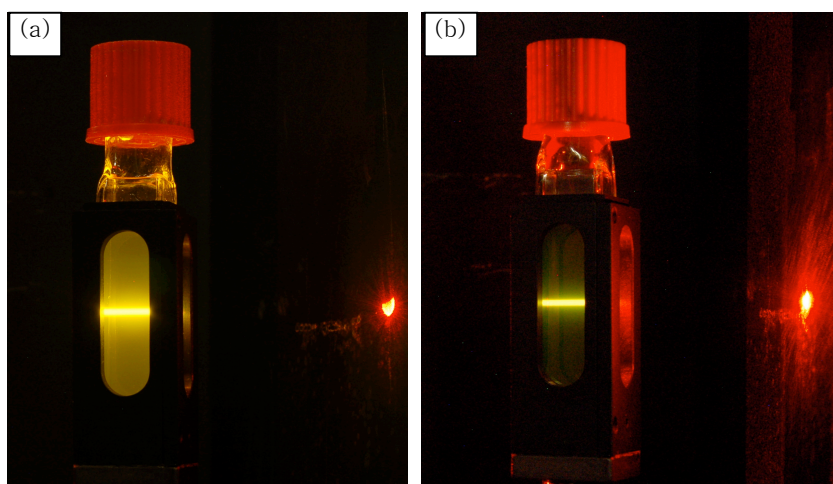
Figure S5. Upconversion quantum yields in the 1.7 μM PtTPTNP and 0.8 mM rubrene solution composition in deaerated toluene measured as a function of 690 nm incident light power density.
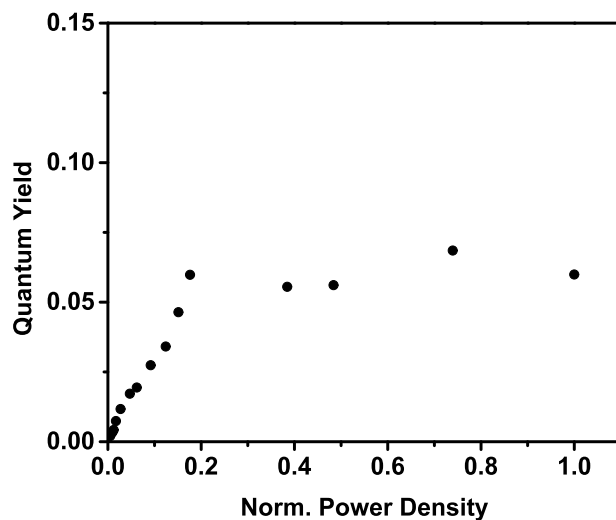
Figure S6. Upconversion quantum yields in the 1.7 μM PtTPTNP and 0.14 mM PDI solution in deaerated toluene measured as a function of 690 nm incident light power density.

Figure S7. Photograph of red-to-yellow photon upconversion (a)PtTPTNP/rubrene, (b)

PtTPTNP/PDI in toluene with 690 nm excitation.
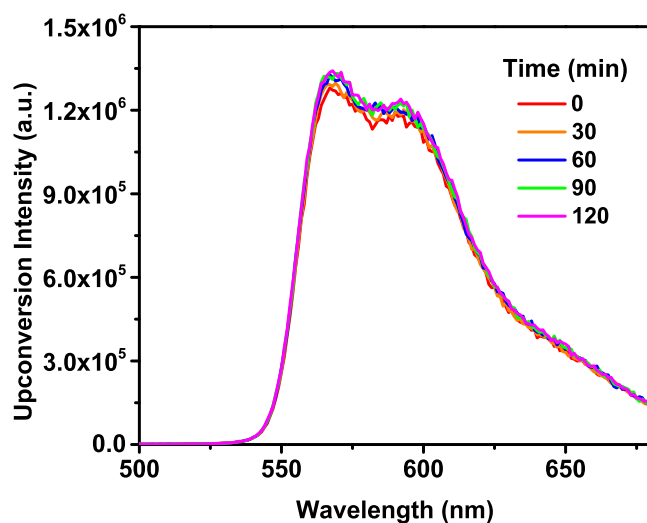
Figure S8. Upconverted emission spectra of 1.7 μM PtTPTNP and 0.8 mM rubrene solution recorded in deaerated toluene. The emission spectra were monitored over a 2 h period upon continuous 690 nm laser irradiation at 30 W/cm^2.

1.   H. Langhals, *Helv. Chim. Acta*, 2005, **88**, 1309–1343.