

Electronic Supplementary Information for:

**Photophysics and halide quenching of a cationic metalloporphyrin
in water**

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Absorption Data

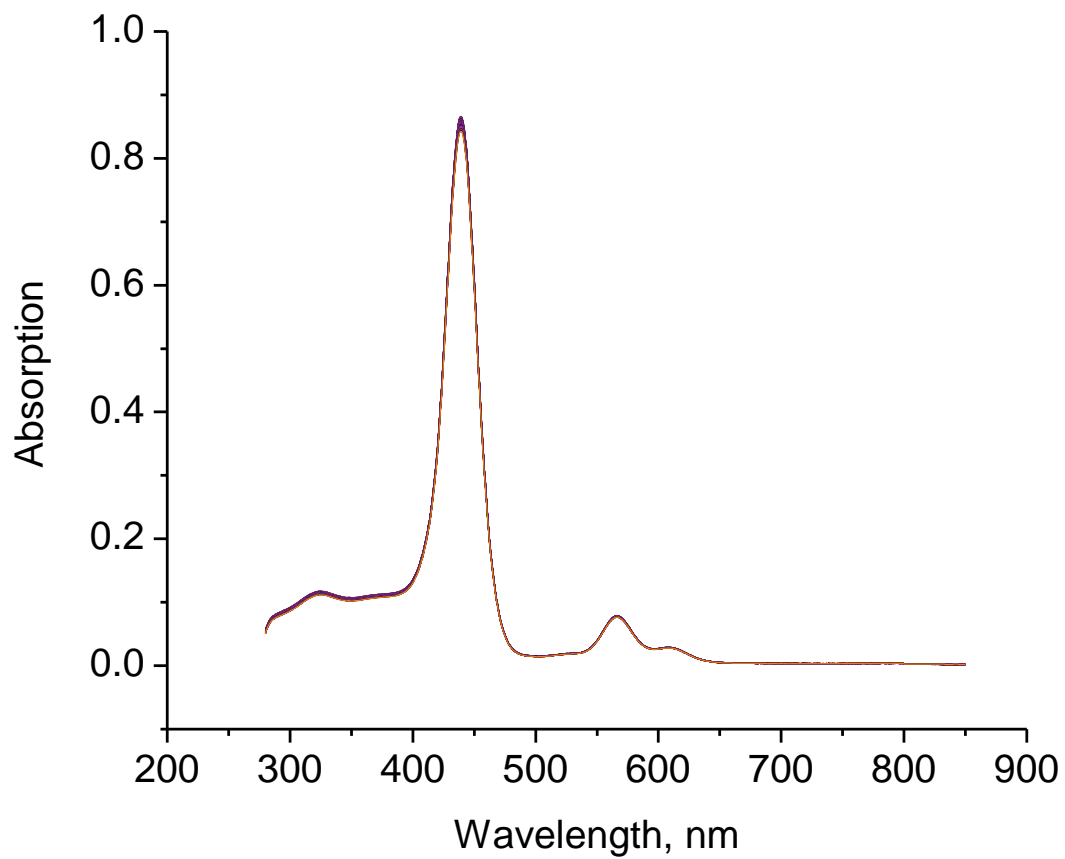


Figure S1. Absorption spectra of 5×10^{-6} M ZnTMPyP in the presence of 1.0M of NaI in a constant ionic strength of 1.0 M collected forty times at 2 min per cycle.

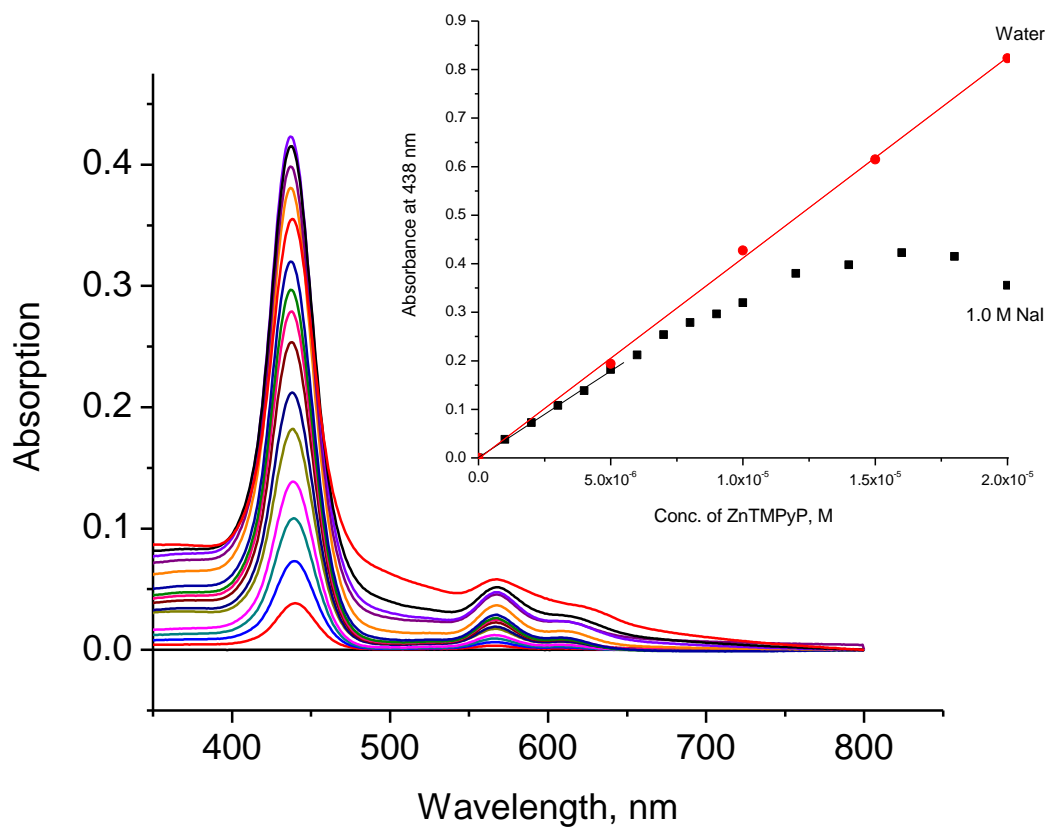


Figure S2. Absorption spectra of 0-20 x 10⁻⁶ M ZnTMPyP in the presence of 1.0M of NaI in a constant ionic strength of 1.0 M. Inset: Beer's law plot of ZnTMPyP in water (circles). Note that ZnTMPyP in aqueous 1.0 M NaI solution (squares) follows Beer's Law at the concentration range of 0-7x10⁻⁶ M but deviates from it at higher ZnTMPyP concentrations.

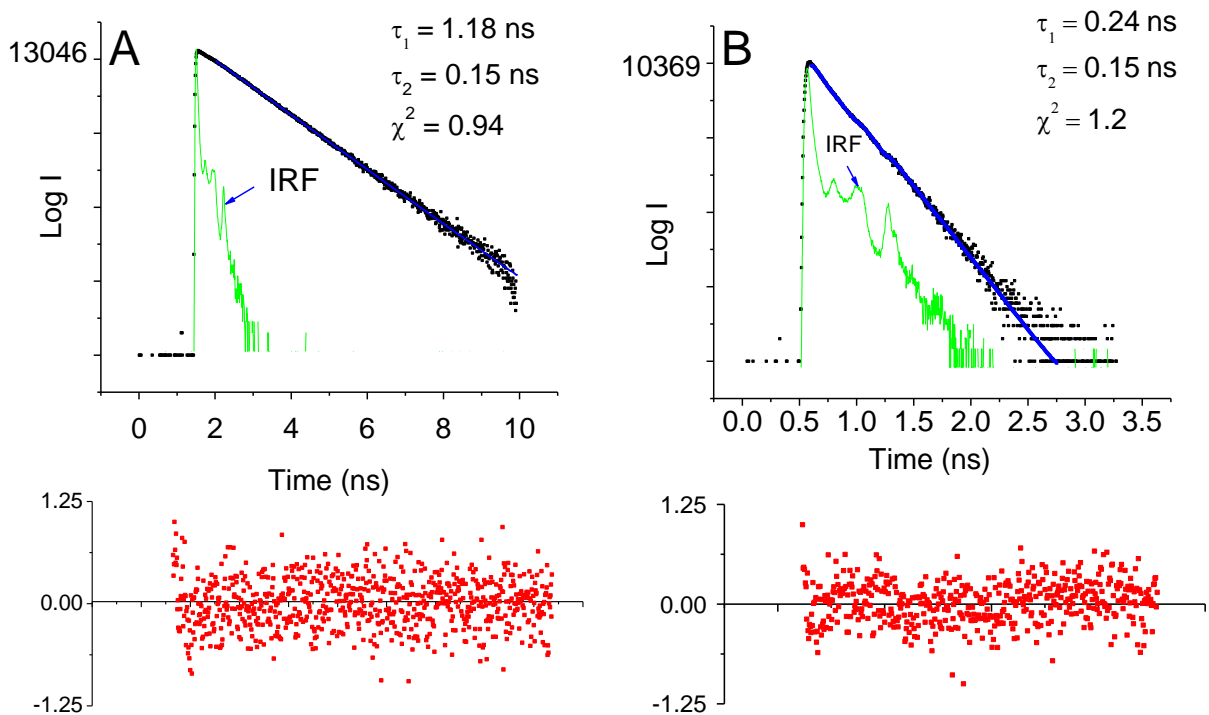


Figure S3. Time-correlated single-photon counting data for the S_1 fluorescence decay of ZnTMPyP in A) 1.0 M NaCl and B) 0.5 M NaI at constant ionic strength of 1.0 M collected at room temperature with the excitation wavelength set at 430 nm and the emission observed at 630 nm. The solid line gave the best fit of a convolution of a biexponential decay function with the instrument response function (IRF). Plot below the decay curve is the distribution of residuals for the biexponential fit. Note that the two panels are in different time scales.

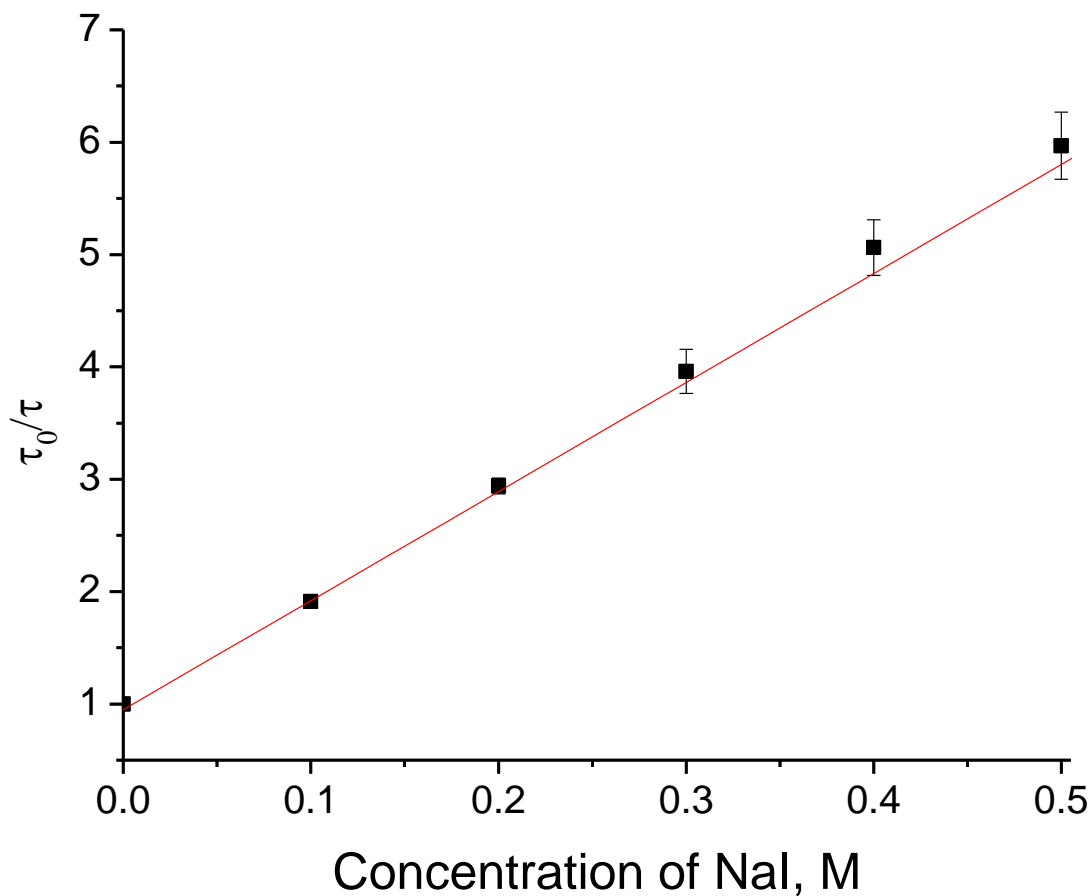


Figure S4. Stern-Volmer plots for the iodide quenching of the S_1 state of 5 μM aqueous ZnTMPyP solution, obtained from the ratio of the weighted average of fluorescence lifetimes of the dye without quencher to that with quencher. The K_{SV} from the slope of the line is 10.09 M^{-1} . Error bars are the standard deviation of duplicate measurements.

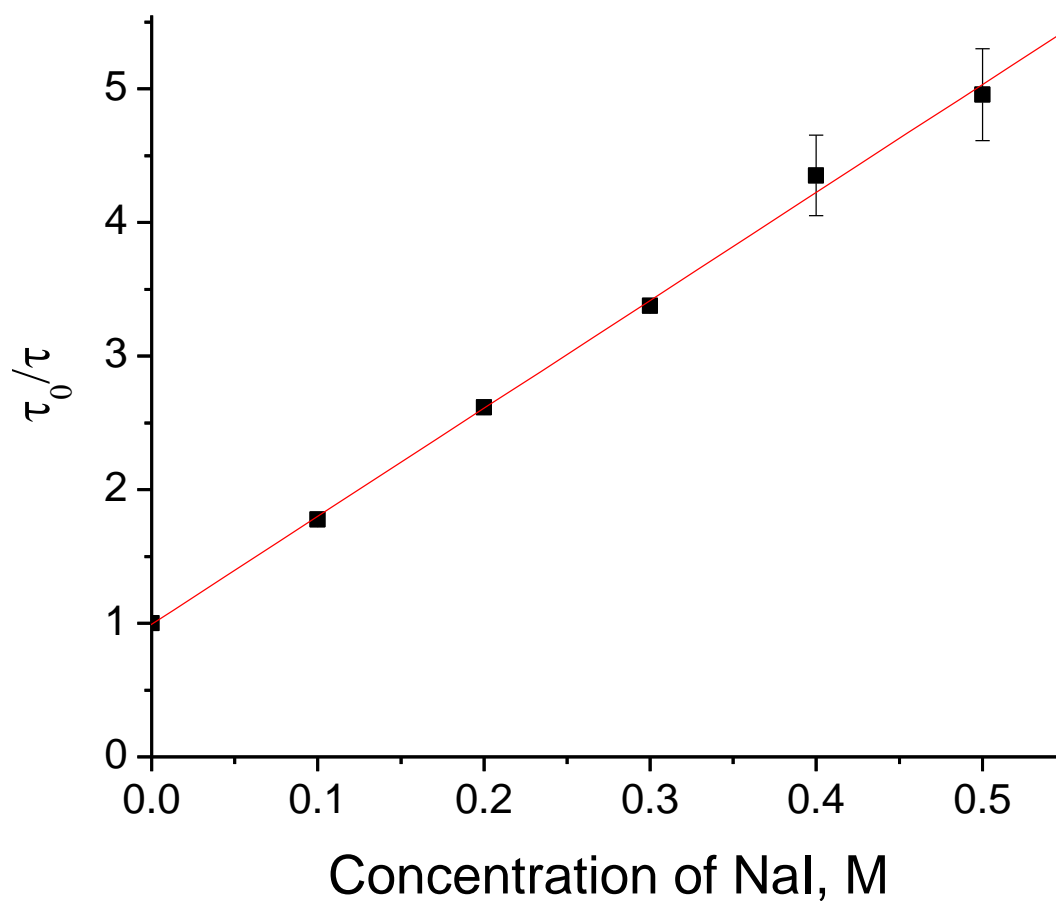


Figure S5. Stern-Volmer plots for the iodide quenching of the S_1 state of 5 μM aqueous ZnTMPyP solution, obtained from the ratio of fluorescence lifetimes of the dye without quencher to that with quencher. K_{SV} from the slope of the line is 8.08 M^{-1} . Error bars are the standard deviation of duplicate measurements.

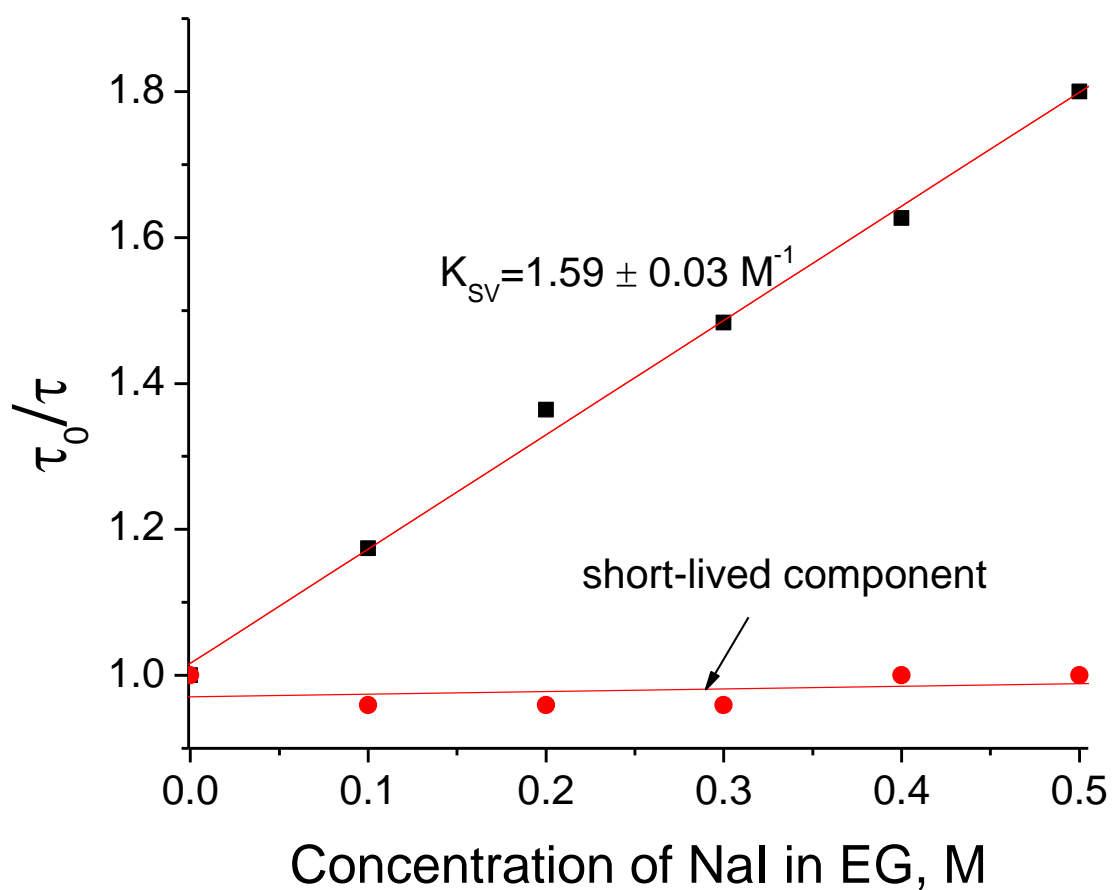


Figure S6. Stern-Volmer plots for the iodide quenching of the S_1 state of 5 μM ZnTMPyP in ethylene glycol solution, obtained from the ratio of fluorescence lifetimes of the dye without quencher to that with quencher.

The theoretical rate constant for diffusion-limited bimolecular interaction between ZnTMPyP and iodide ions in solution, k_{DS} , is calculated from the Debye-Smoluchowski equation:

$$k_{DS} = k_S \frac{r_c/R}{\exp\left(\frac{r_c}{R}\right) - 1} \quad (\text{S1})$$

where k_S is the Smoluchowski diffusional rate constant, R is the sum of the radii of ZnTMPyP which is equal to 7 \AA and iodide which is equal to 2.2 and r_c is the Onsager length and is given by

$$r_c = \frac{Z_1 Z_2 e^2}{4\pi\epsilon k_B T} \quad (\text{S2})$$

Where $Z_1 e$ is the charge of the fluorophore (ZnTMPyP⁴⁺), $Z_2 e$ is the charge of the quencher (I⁻).

The Smoluchowski diffusional rate constant can be calculated using

$$k_S = 1000 \times 4\pi N R (D_{ZnTMPyP^{4+}} + D_{I^-}) \quad (\text{S3})$$

where N is the Avogadro's number, R is as defined above and $D_{ZnTMPyP^{4+}}$ and D_{I^-} are the diffusion coefficients of ZnTMPyP⁴⁺ and I⁻, respectively¹⁻³. Values of the diffusion coefficients were calculated from the Stokes-Einstein equation. Equations 5-7 return a value of $2.95 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for the diffusion-limited bimolecular interaction rate constant, k_{DS} , between ZnTMPyP⁴⁺ and I⁻ in solution. This value is 20 times higher than the k_{DS} calculated for the interaction between ZnTPPS⁴⁻ and I⁻. This is not surprising since the interaction in the former system is attractive while it is repulsive in the latter. However, the experimentally determined bimolecular quenching rate constant augments only by a factor of 4 when replacing repulsive interactions between ZnTPPS⁴⁻ and iodide to the attractive interactions between ZnTMPyP⁴⁺ and iodide.

For the static contribution to quenching, we examined the steady state emission data for contributions from a non-fluorescent ground state complex between porphyrin and iodide using the modified Stern-Volmer equation shown below:

$$\frac{I_0}{I} = (1 + K'_{SV}[Q])(1 + K_{SV}[Q]) \quad (\text{S4})$$

where the first term is the dynamic contribution and the second term is the static contribution to quenching. Solving for the roots of the quadratic equation gives 6.92 M^{-1} and 1.91 M^{-1} . Since, we already know that K'_{SV} is $8.08 \pm 0.19 \text{ M}^{-1}$ from fluorescence lifetime measurements, we assign the higher value to the dynamic contribution and the lower value to the static contribution to quenching. A static quenching constant of 1.91 M^{-1} indicates a weak association and supports the earlier hypothesis that the ZnTMPyP and iodide do not form ground state aggregates.

We, thus examine the static contribution to quenching that arises from the close proximity of fluorophore and quencher at the moment of excitation. We use the equation given below to determine the effective quenching sphere, where V is the quenching sphere volume and N_A is Avogadro's number.

$$\frac{I_0}{I} = (1 + K'_{SV}[Q])\exp(VN_A[Q]) \quad (\text{S5})$$

We used Grace plotting tool to fit eq. S5 on the experimental data fitting only from 0.00 M to 0.50 M concentrations of quencher since our time resolved measurements were done at this range only. Our best fit returned an equation: $\frac{I_0}{I} = (1 + 10.7386[Q])\exp(0.1619[Q])$ and calculated the quenching radii for iodide to be 4.0 \AA which is smaller than 9.2 \AA , the sum of the radii of the porphyrin and iodide. Eq. S5 did not give meaningful results when fitted beyond 0.50 M concentration of iodide.

References

1. T. P. Lebold, E. K. L. Yeow and R. P. Steer, Fluorescence quenching of the S1 and S2 states of zinc meso-tetrakis(4-sulfonatophenyl)porphyrin by halide ions, *Photochemical & Photobiological Sciences*, 2004, **3**, 160.
2. J. Szmytkowski, S. M. K. Brunet, U. Tripathy, J. A. O'Brien, M. F. Paige and R. P. Steer, Photophysics and halide quenching of Soret-excited ZnTPPS⁴⁻ in aqueous media, *Chemical Physics Letters*, 2010, **501**, 278.
3. D. M. Togashi and S. M. B. Costa, Excited state quenching kinetics of zinc meso-tetrakis (N-methylpyridinium-4-yl) porphyrin by methyl viologen in AOT reverse micelles, *Physical Chemistry Chemical Physics*, 2002, **4**, 1141.