Accessory Materials

A1

For the formation of a 1:1 stoichiometric complex between ZnTPP and a ligand:

$$[ZnTPP] + [Ligand] \rightleftharpoons [Complex]$$

The following equations apply if the ligand does not absorb at the analyzing wavelength:

$$K_{a} = \frac{[\text{Complex}]}{[\text{ZnTPP}][\text{Ligand}]} \qquad \dots (1.1)$$

$$[ZnTPP]_{T} = [ZnTPP] + [Complex] \qquad ...(1.2)$$

$$[Ligand]_{T} = [Ligand] + [Complex] \qquad ...(1.3)$$

$$Abs = \varepsilon_{ZnTPP}[ZnTPP]l + \varepsilon_{Complex}[Complex]l \qquad ...(1.4)$$

where K_a is the association constant, the subscript T denotes the total solution concentration, Abs is the measured solution absorption, ε is the molar absorption coefficient, and l is the path length (set as 1 cm at all times). Combining Eqns (1.2) and (1.4) gives:

$$[\text{Complex}] = \frac{\text{Abs} - \varepsilon_{\text{ZnTPP}} [\text{ZnTPP}]_{\text{T}}}{\varepsilon_{\text{Complex}} - \varepsilon_{\text{ZnTPP}}} = \frac{\Delta \text{Abs}}{\Delta \varepsilon} \qquad \dots (1.5)$$

Combining Eqns (1.1), (1.2), and (1.3) gives a function that is quadratic in [Complex]:

$$K_{a}[\text{Complex}]^{2} - (1 + K_{a}([\text{ZnTPP}]_{T} + [\text{Ligand}]_{T}))[\text{Complex}] + K_{a}[\text{ZnTPP}]_{T}[\text{Ligand}]_{T} = 0$$
...(1.6)

Combining Eqn (1.5) with the minimum solution of Eqn (1.6) gives:

$$\Delta Abs = \frac{\Delta \varepsilon \left(a - \sqrt{a^2 - 4K_a^2 [ZnTPP]_T [Ligand]_T} \right)}{2K_a} \qquad \dots (1.7)$$

$$a = 1 + K_{a} ([ZnTPP]_{T} + [Ligand]_{T}) \qquad \dots S1.8$$

If $[ZnTPP]_T$ is known and constant throughout the titration, then fitting Eqn (1.7) to a plot of ΔAbs versus $[Ligand]_T$ allows the parameters $\Delta \varepsilon$ and K_a to be extracted (Fig. 3 inset). Curve fitting was conducted using a non-linear least-squares regression analysis in the *KaleidaGraph* program.

The fluorescence quantum yield (Φ_f) and fluorescence lifetime (τ_f) of ZnTPP and 4mpy·ZnTPP in deaerated solvents are presented in Table A2.1. Solutions of 4mpy·ZnTPP were ~10⁻⁵ M ZnTPP and ~10⁻² M 4-methylpyridine, ensuring >99% complexation. The ligand did not absorb at the visible excitation wavelengths used, while time-resolved fluorescence spectroscopy studies detected no diffusional quenching of porphyrin fluorescence by unbound 4-methylpyridine at these concentrations. Thus the fluorescence of 4mpy·ZnTPP could be studied without interference from the large excess of unbound 4-methylpyridine in solution.

While the $\Phi_{\rm f}$ of ZnTPP was only slightly reduced upon complexation, the $\tau_{\rm f}$ was decreased by 10-30%. The radiative rate ($k_{\rm rad}$) and non-radiative rate ($k_{\rm nr}$) of photoexcited ZnTPP and 4mpy·ZnTPP are also included in Table A2.1. These rates are strongly affected by pyridyl ligation in the noncomplexing solvents toluene, CHCl₃, and CH₂Cl₂. In PhCN, $k_{\rm rad}$ and $k_{\rm nr}$ are not as strongly affected by complexation, suggesting that the nitrile can bind weakly to the central metal of ZnTPP.

Solvent	${{{{{\varPhi}}_{\rm{f}}}^{\rm{A}}}}$	$arPsi_{ m f}$	$ au_{ m f}$	$ au_{ m f}$	$k_{\rm rad}$ ^B	$k_{ m rad}$	$k_{\rm nr}{}^{\rm C}$	$k_{ m nr}$
	ZnTPP	4mpy·ZnTPP	[ns]	[ns]	$[s^{-1}\times 10^{-}$	$[s^{-1} \times 10^{-7}]$	$[s^{-1}\times 10^{-}$	$[\text{s}^{-1}\times 10^{-8}]$
			ZnTPP	4mpy·ZnTPP	7]	4mpy·ZnTPP	8]	4mpy·ZnTPP
					ZnTPP		ZnTPP	
PhCN	0.036	0.034	1.82	1.62	1.98	2.10	5.30	5.96
CH_2Cl_2	0.028	0.027	1.75	1.43	1.60	1.89	5.55	6.80
CHCl ₃	0.028	0.025	1.75	1.33	1.60	1.88	5.55	7.33
Toluene	0.033	0.032	2.05	1.64	1.61	1.95	4.72	5.90

Table A2.1: Photophysical parameters for ZnTPP and its complex with 4-methylpyridine (4mpy·ZnTPP) in de-aerated solvents.

^A Reference for $\Phi_{\rm f}$ measurements was ZnTPP in de-aerated benzene ($\Phi_{\rm f}$ 0.033): *J. Am. Chem. Soc.* **1975**, 97, 5111. ^B Calculated as $k_{\rm rad} = \Phi_{\rm f} \cdot \tau_{\rm f}^{-1}$. ^C Calculated as $k_{\rm nr} = (1 - \Phi_{\rm f}) \cdot \tau_{\rm f}^{-1}$. Figure A3.1 Transient Absorption Spectra of (a) $4mpy \cdot ZnTPP$ in toluene (porphyrin triplet-triplet absorption) and (b) $1 \cdot ZnTPP$ in toluene, transient lifetime 6.9 µs.



The driving force for charge separation (ΔG_{CS}) was calculated using the Weller equation:

$$\Delta G_{\rm CS} = \exp\left(E^{\rm OX}({\rm D}) - E^{\rm RED}({\rm A})\right) - E_{00} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_S R_{\rm C-C}} - X$$
(4.1)

where $E^{\text{ox}}(D)$ is the one-electron oxidation potential of the donor, $E^{\text{red}}(A)$ is the one-electron reduction potential of the acceptor, $R_{\text{C-C}}$ is the centre-to-centre inter-chromophore separation, *e* is the charge of an electron, ε_0 is the permittivity of a vacuum, E_{00} is the relevant excited state energy of the donor, and ε_8 is the dielectric constant of the solvent of interest. *X* is a correction factor required if the redox potentials were measured in a solvent other than the solvent of interest:

$$X = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{r^+} + \frac{1}{r^-}\right) \left(\frac{1}{\varepsilon_{\text{REF}}} - \frac{1}{\varepsilon_{\text{S}}}\right)$$
(4.2)

where r^+ and r^- are the radii of the cationic form of the donor and the anionic form of the acceptor respectively, and ε_{REF} is the dielectric constant of the solvent in which the redox potentials were measured.

The reduction potentials of **1** and **2** were determined as -1.06 V and -0.94 V respectively vs Fc⁺/Fc in CH₂Cl₂. The oxidation potential of ZnTPP ligated with pyridine in CH₂Cl₂ (0.22 V vs Fc⁺/Fc) has been reported (J. Otsuki, K. Harada, K. Toyama, Y. Hirose, K. Araki, M. Seno, K. Takatera, T. Watanabe, *Chem. Commun.* **1998**, 1515). The ionic radii of the donor and acceptor were estimated as 4.3 Å and 4.2 Å respectively from the energy-minimized structure of **1**·ZnTPP. *R*_{C-C} was predicted to be 12.1 Å and 10.0 Å for **1**·ZnTPP and **2**·ZnTPP respectively. For electron transfer from the excited singlet state of the porphyrin in **1**·ZnTPP, E₀₀ was 2.04 eV in all solvents. This value is the average of the energy of the lowest energy absorption band and highest energy fluorescence band of 4mpy·ZnTPP. For electron transfer from the excited triplet state of the porphyrin in **1**·ZnTPP, *E*₀₀ was taken as 1.58 eV in all solvents.^[19b] The ΔG_{CS} value for electron transfer from the excited singlet state of the porphyrin in **1**·ZnTPP is included in Table 1. The ΔG_{CS} value for electron transfer from the excited triplet state of **1**·ZnTPP is predicted to less negative by 0.46 eV compared to the ΔG_{CS} from the singlet state.

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