

Supporting Information

Strong Inhibition of Singlet Oxygen Sensitization in Pyridylferrocene–Fluorinated Zinc Porphyrin Supramolecular Complexes

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Synthesis

Benzyl Ferrocenylcarboxylate (2b). Oxalyl chloride (3.0 mL, 35 mmol) was added to a stirred solution of ferrocenylcarboxylic acid (1.5 mg, 7.0 mmol) in dry CH₂Cl₂ (100 mL) and pyridine (0.03 mL). The resulting solution was stirred for 10 h at room temperature and refluxed for 6 h. Excess oxalyl chloride and solvents were removed under reduced pressure and the residue was redissolved in dry CH₂Cl₂ (50 mL) and pyridine (2 mL). Benzyl alcohol (7.5 mL, 73 mmol) was added to the resulting solution, and the solution was stirred for 12 h. The reaction mixture was washed with saturated NaHCO₃ aqueous solution and water. The organic layer was dried over anhydrous Na₂SO₄, and then the solvent was evaporated. Column chromatography on silica gel with CHCl₃-NEt₃ (19 : 1) as an eluent and subsequent reprecipitation from ethyl acetate afforded **2b** as a yellow solid (1.10 mg, 3.4 mmol, 49% yield). mp 106.5-107.0 °C; ¹H NMR (270 MHz, CDCl₃) δ 7.3-7.5 (m, 5H), 5.27 (s, 2H), 4.83 (t, *J* = 2 Hz, 2H), 4.39 (t, *J* = 2 Hz, 2H), 4.10 (s, 5H); UV-vis (CH₂Cl₂) λ_{max} (log ε) = 446.4 (1.39), 310.1 (2.05); Anal. Calcd for C₁₈H₁₆FeO₂: C, 67.49; H, 5.04. Found: C, 67.48; H, 5.04.

Ferrocenylamido-4-pyridine (3a). Oxalyl chloride (3.0 mL, 35 mmol) was added to a stirred solution of ferrocenylcarboxylic acid (1.5 mg, 7.0 mmol) in dry CH₂Cl₂ (50 mL) and pyridine (0.03 mL). The resulting solution was stirred for 18 h at room temperature and refluxed for 6 h. Excess oxalyl chloride and solvents were removed under reduced pressure and the residue was redissolved in dry CH₂Cl₂ (50 mL). A CH₂Cl₂ solution of 4-aminopyridine (3.00 g, 31.8 mmol) was added to the resulting solution, and the solution was stirred for 12 h. The reaction mixture was washed with saturated NaHCO₃ aqueous solution and water. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated. Column chromatography on silica gel with CHCl₃-NEt₃ (19 : 1) as an eluent and subsequent

reprecipitation from CHCl₃-hexane afforded **3a** as a orange-colored solid (264 mg, 0.86 mmol, 12% yield). mp 220 °C (dec.); ¹H NMR (270 MHz, CDCl₃) δ 8.53 (dd, *J* = 7 Hz and 2 Hz, 2H), 7.57 (dd, *J* = 7 Hz and 2Hz, 2H), 7.45 (br s, 2H), 4.80 (t, *J* = 2 Hz, 2H), 4.49 (t, *J* = 2 Hz, 2H), 4.27 (s, 5H); UV-vis (CH₂Cl₂) λ_{max} (log ε) = 448.0 (1.62), 323.8 (2.37); EI MS *m/z* 306 (M⁺). Anal. Calcd for C₁₆H₁₄FeN₂O: C, 62.77; H, 4.61; N, 9.15. Found: C, 62.77; H, 4.54; N, 9.14.

Ferrocenylamido-4-benzene (3b). Thionyl chloride (0.73 mL, 10 mmol) was added to a stirred solution of ferrocene-carboxylic acid (1.15 mg, 5.0 mmol) and aniline (0.91 mL, 10 mmol) in dry CH₂Cl₂ (5 mL) at room temperature. The resulting solution was stirred for 16 h at room temperature. The reaction mixture was washed with saturated NaHCO₃ aqueous solution and water. The organic layer was dried over anhydrous Na₂SO₄, and the solvent was evaporated. Column chromatography on silica gel with CHCl₃ as an eluent and subsequent reprecipitation from acetone-water afforded **3b** as an yellow solid (298 mg, 0.98 mmol, 20% yield). ¹H NMR (300 MHz, CDCl₃) δ 7.60 (d, *J* = 8 Hz, 2H), 7.36 (dd, *J* = 8 Hz, 2H), 7.13 (dd, *J* = 8 Hz, 1H), 4.78 (t, *J* = 2 Hz, 2H), 4.43 (t, *J* = 2 Hz, 2H), 4.26 (s, 5H); UV-vis (CH₂Cl₂). Anal. Calcd for C₁₇H₁₅FeNO: C, 66.91; H, 4.95; N, 4.59. Found: C, 66.79; H, 4.81; N, 4.63.

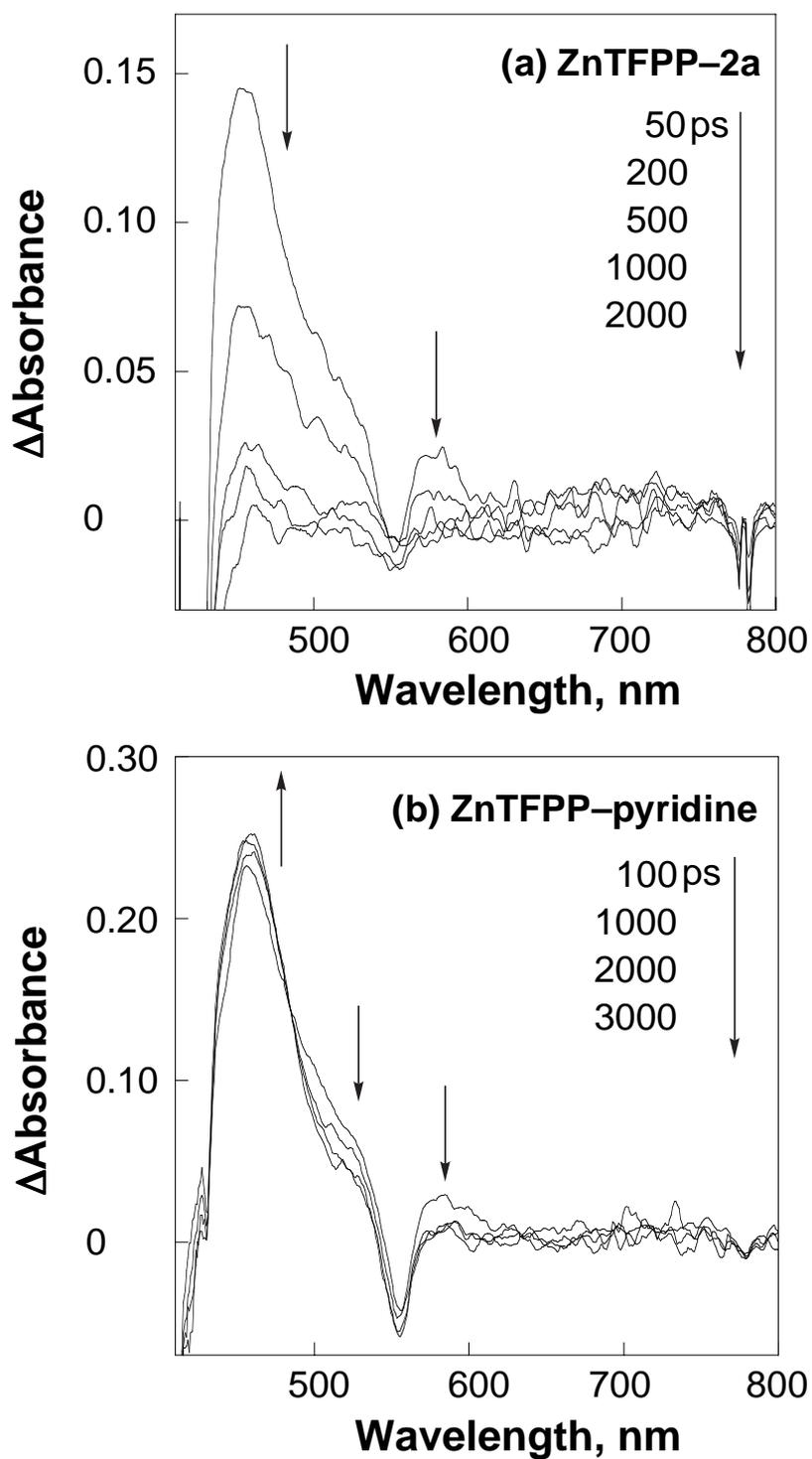


Figure S3. Picosecond transient absorption spectra of (a) ZnTFPP-2a complex, (b) ZnTFPP-pyridine complex excited at 388 nm in deaerated CH₃CN. [ZnTFPP] = 8.0×10^{-5} M, [2a] = 1.0×10^{-2} M, [pyridine] = 2.0×10^{-1} M.

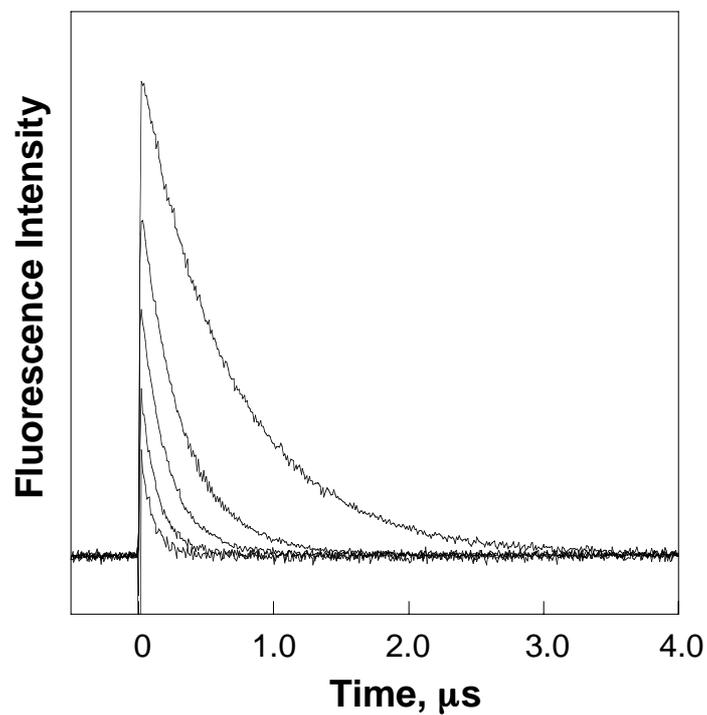


Figure S4. The photodynamics of the triplet excited state ${}^3\text{ZnTFPP}^*$ in the presence of **2a** at 460 nm in CH_3CN . $\lambda_{\text{ex}}=555$ nm. $[\text{ZnTFPP}]=1.0 \times 10^{-5}$ M, $[\mathbf{2a}]=0-2.8 \times 10^{-2}$ M.

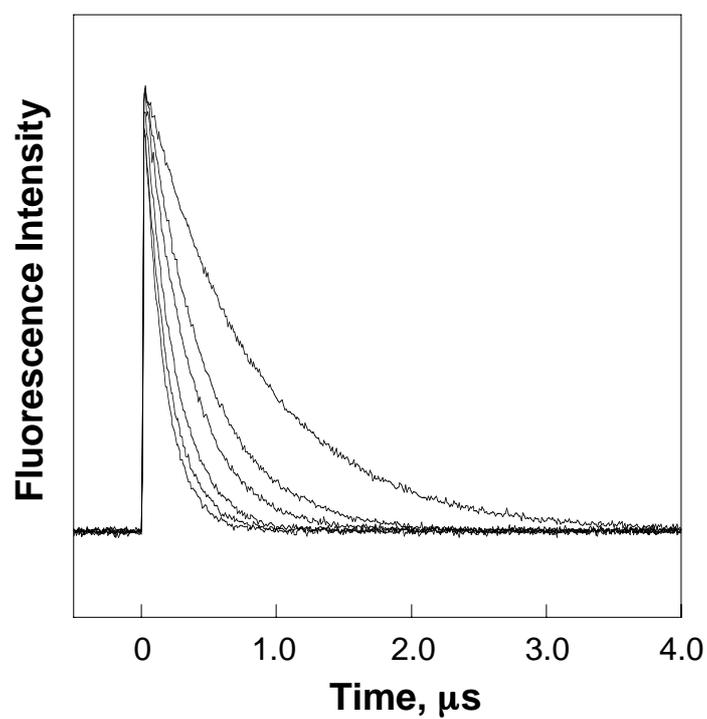


Figure S5. The photodynamics of the triplet excited state ${}^3\text{ZnTFPP}^*$ in the presence of pyridine and **2b** at 460 nm in CH_3CN . $\lambda_{\text{ex}}=555$ nm. $[\text{ZnTFPP}]=1.0 \times 10^{-5}$ M, $[\text{pyridine}]=1.0 \times 10^{-3}$ M, $[\mathbf{2b}]=0-3.0 \times 10^{-2}$ M.