

Singlet Oxygen Generation via Two Photon Excited FRET

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Supporting Information

General. THF was distilled from Na / benzophenone before use. All other solvents used were anhydrous and reagent grade. Absorption spectra were recorded on a Cary 50 UV-vis spectrometer in chloroform. Fluorescence emission and excitation spectra were obtained using an ISA/SPEX Fluorolog 3.22 equipped with a 450W Xe lamp, double excitation and double emission monochromators and a digital photon-counting photomultiplier. Slit widths were set to 3.0 nm band-pass on both excitation and emission monochromators. Correction for variations in lamp intensity over time and wavelength was achieved using a reference silicon photodiode. The spectra were further corrected for variations in photomultiplier response over wavelength and for the path difference between the sample and the reference by multiplication with emission and excitation correction curves generated on the instrument. Samples for fluorescence experiments were dissolved in chloroform in standard 1 cm quartz cells. The optical density was kept below 0.1. All measurements were performed at room temperature. The synthesis of **2** and **3** has previously been reported.^{12, 14} Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a PerSeptive Biosystems Voyager-DE spectrometer using delayed extraction mode and with an acceleration voltage of 20 keV. Samples were prepared from a solution of THF using *trans*-indole acrylic acid as the matrix.

Synthesis of tetrakis(3',5'-di(AF-343)phenyl)porphyrin (1): AF-343¹² (300 mg, 465 μmol), tetrakis(3',5'-dihydroxyphenyl)porphyrin¹⁴ (35 mg, 47 μmol), K_2CO_3 (100 mg, 719 μmol), and 18-crown-6 (12 mg, 45 μmol) were dissolved in 4 mL of dry DMF and stirred under argon at 70 $^\circ\text{C}$ for 4 days. The reaction was cooled to rt, and the mixture was poured in a separatory funnel containing 50 mL of CH_2Cl_2 and washed with water (100 mL) twice, and brine (100 mL). The organic phase was dried over Na_2SO_4 and

evaporated *in vacuo*. The residue was taken up in a minimum amount of CHCl_3 and precipitated into 200 mL of 8:2 hexanes:ethyl acetate. The residue was filtered, collected, and further purified by column chromatography on silica gel (CHCl_3) to yield 144 mg of a dark purple solid (58 %). ^1H NMR (300 MHz, CDCl_3): δ = -2.81 (s, 2H), 0.34 (t, J = 7 Hz, 48H), 1.86-2.07 (m, 32H), 4.25 (br s, 16H), 4.36 (br s, 16H), 6.63 (d, J = 8 Hz, 8H), 6.71 (d, J = 8 Hz, 8H), 6.76 (br s, 8H), 6.95-7.03 (m, 20H), 7.10-7.15 (m, 32H), 7.17-7.24 (m, 16H), 7.33-7.39 (m, 16H), 7.45-7.50 (m, 24H), 7.83-7.89 (dd, 16H), 8.04-8.07 (m, 16H), 8.91 (br s, 8H). MS (MALDI) m/z = 5260.69 ($\text{M}+\text{H}^+$), calcd m/z = 5261.70; m/z = 5299.04 ($\text{M}+\text{K}^+$), calcd m/z = 5299.79. HSMS (MALDI) m/z = 5261.81 ($\text{M}+\text{H}^+$), calcd m/z = 5261.70.