

Supporting Information

Dendritic Molecular Assemblies for Singlet Oxygen Generation: *meso*-Tetraphenylporphyrin-Based Biphotonic Sensitizers with Remarkable Luminescence

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1. General Experimental Details

General. Solvents used for reactions were distilled using common purification methods, except DMF and $^i\text{Pr}_2\text{NH}$ which were dried by molecular sieves (3 Å). ^1H and ^{13}C NMR spectra were recorded on BRUKER Ascend 400 at 298K, respectively. High-resolution mass spectra were recorded on two different spectrometers: Bruker MicroTOF-Q II (for compounds **1** in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (8:2) + 0.1% formic acid and **3** in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (8:2) + 0.1% formic acid) and a Thermo Fisher Scientific Q-Exactive (for compounds **2** and **3** in CH_2Cl_2 + 0.1% formic acid) in ESI positive mode at the Centre Régional de Mesures Physique de l'Ouest (CRMPO) in Rennes. The aldehydes **a-d** (Chart S1) have been synthesized from commercial reagents according to usual synthetic approaches and fully characterized when new. Their synthesis will be reported elsewhere. Pyrrole and other starting reagents were purchased from commercial suppliers. The silica used for the chromatographic separations was of SI 60 (63-200 μm) and TLC 60 H (15 μm) grade.

Spectroscopic Measurements: All photophysical properties have been performed with freshly-prepared air-equilibrated solutions at room temperature (298 K). UV/Vis absorption spectra were recorded on a Jasco V-570 spectrophotometer. Fluorescence measurements were performed using an Edinburgh Instruments (FLS920) spectrometer in photon-counting mode. Fully corrected emission spectra were obtained, for each compound, under excitation at the wavelength of the absorption maximum, with $A_{\lambda_{\text{ex}}} < 0.1$ to minimize internal absorption.

Measurements of singlet oxygen quantum yield (Φ_{Δ}): Measurements were performed on a Fluorolog-3 (Horiba Jobin Yvon), using a 450 W Xenon lamp. The emission at 1272 nm was detected using a liquid nitrogen-cooled Ge-detector model (EO-817L, North Coast Scientific Co). Singlet oxygen quantum yields Φ_{Δ} were determined in dichloromethane solutions, using tetraphenylporphyrin (TPP) in dichloromethane as reference solution ($\Phi_{\Delta}[\text{TPP}] = 0.60$) and were estimated from $^1\text{O}_2$ luminescence at 1272 nm.

Two-Photon Absorption Experiments: To span the 790-920 nm range, a Nd:YLF-pumped Ti:sapphire oscillator (Chameleon Ultra, Coherent) was used generating 140 fs pulses at a 80

MHz rate The excitation power is controlled using neutral density filters of varying optical density mounted in a computer-controlled filter wheel. After five-fold expansion through two achromatic doublets, the laser beam is focused by a microscope objective (10x, NA 0.25, Olympus, Japan) into a standard 1 cm absorption cuvette containing the sample. The applied average laser power arriving at the sample is typically between 0.5 and 40 mW, leading to a time-averaged light flux in the focal volume on the order of 0.1–10 mW/mm². The fluorescence from the sample is collected in epifluorescence mode, through the microscope objective, and reflected by a dichroic mirror (Chroma Technology Corporation, USA; “blue” filter set: 675dcxru; “red” filter set: 780dxcr). This makes it possible to avoid the inner filter effects related to the high dye concentrations used (10⁻⁴ M) by focusing the laser near the cuvette window. Residual excitation light is removed using a barrier filter (Chroma Technology; “blue”: e650-2p, “red”: e750sp-2p). The fluorescence is coupled into a 600 μm multimode fiber by an achromatic doublet. The fiber is connected to a compact CCD-based spectrometer (BTC112-E, B&W Tek, USA), which measures the two-photon excited emission spectrum. The emission spectra are corrected for the wavelength-dependence of the detection efficiency using correction factors established through the measurement of reference compounds having known fluorescence emission spectra. Briefly, the set-up allows for the recording of corrected fluorescence emission spectra under multiphoton excitation at variable excitation power and wavelength. 2PA cross sections (σ_2) were determined from the two-photon excited fluorescence (2PEF) cross sections ($\sigma_2 \cdot \Phi_F$) and the fluorescence emission quantum yield (Φ_F). 2PEF cross sections of 10⁻⁴ M dichloromethane solutions were measured relative to fluorescein in 0.01 M aqueous NaOH using the well-established method described by Xu and Webb,¹ and the appropriate solvent-related refractive index corrections.² The quadratic dependence of the fluorescence intensity on the excitation power was checked for each sample and all wavelengths.

¹ C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481-491.

² M. H. V. Werts, N. Nerambourg, D. Pélégry, Y. Le Grand and M. Blanchard-Desce, *Photochem. Photobiol. Sci.*, 2005, **4**, 531-538.

2. Synthesis of the Porphyrins (1-4)

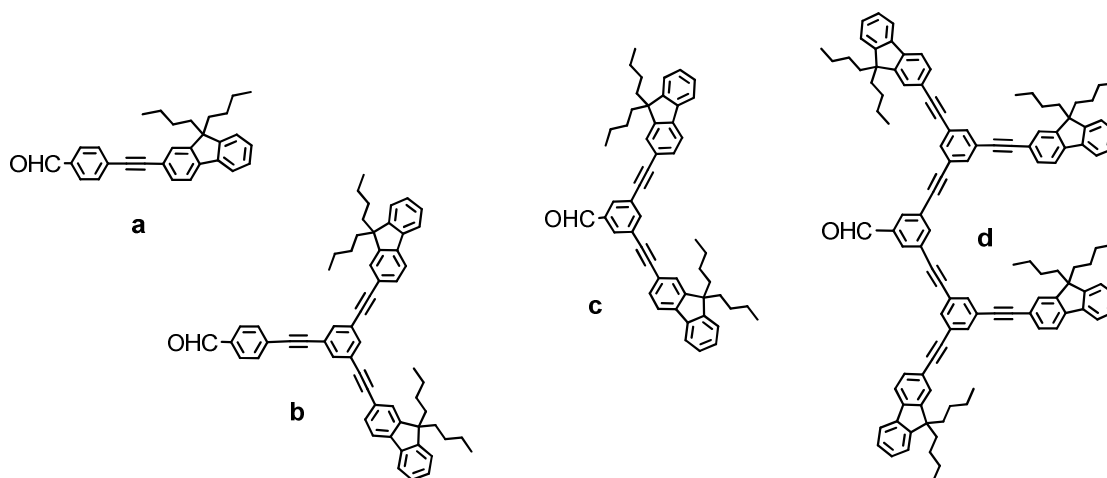


Chart S1. Aldehydes used in the Syntheses of **1-4**.

1. A mixture of aldehyde **a** (700 mg, 1.72 mmol, 1 eq) and propionic acid (6.5 mL) was heated to 120 °C. After dropwise addition of a solution of pyrrole (0.12 mL, 1.72 mmol, 1 eq) in propionic acid (1.0 mL), the reaction medium was further kept refluxing for 1.5 h. After cooling at room temperature, MeOH was added to the reaction mixture and the precipitate was filtered. The residue could be purified by repeated chromatography on silica using petroleum ether/CH₂Cl₂ (1:1) as eluant. The title compound was isolated as a rose-purple powder (220 mg, 28% yield). ¹H NMR (400 MHz, CDCl₃, ppm): 8.92 (s, 8H), 8.24 (d, ³J_{HH} = 7.6 Hz, 8H), 7.99 (d, ³J_{HH} = 7.6 Hz, 8H), 7.78-7.75 (m, 8H), 7.69-7.67 (m, 8H), 7.40-7.35 (m, 12H), 2.05 (t, ³J_{HH} = 8.0 Hz, 16H), 1.19-1.10 (m, 16H), 0.73 (t, ³J_{HH} = 7.2 Hz, 24H), 0.69-0.60 (m, 16H), -2.74 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃, ppm): 151.1 (s), 150.9 (s), 141.9 (s), 141.7 (s), 140.4 (s), 134.6 (s), 130.8 (s), 130.0 (s), 127.6 (s), 126.9 (s), 126.1 (s), 123.1 (s), 122.9 (s), 121.4 (s), 120.1 (s), 119.7 (s), 91.9 (s), 89.3 (s), 55.1 (s), 40.2 (s), 26.0 (s), 23.1 (s), 13.9 (s). UV-vis (CH₂Cl₂): λ_{max}/nm [ε/10³ M⁻¹·cm⁻¹] = 323 [178.4], 427 [670.2], 519 [36.0], 556 [30.1], 592 [17.2], 649 [17.1]. HRMS: *m/z* = 1816.0055 [M+H]⁺ (calcd: 1814.0055). Anal. Calcd: (%) for C₁₃₆H₁₂₆N₄: C, 89.92; H, 6.99; N, 3.08. Found: C, 89.65; H, 6.59; N, 3.12.

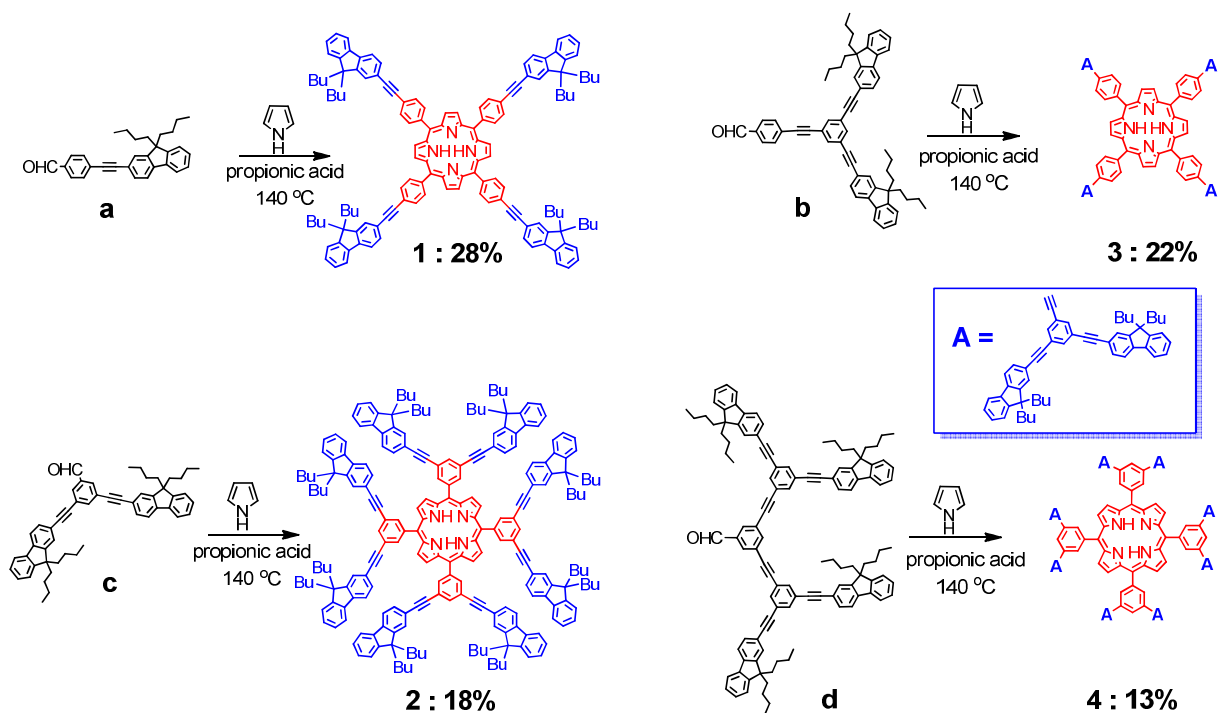
2. A mixture of aldehyde **b** (312 mg, 0.39 mmol, 1 eq) and propionic acid (2 mL) was heated to 120 °C. After dropwise addition of a solution of pyrrole (0.03 mL, 0.39 mmol, 1 eq) in propionic acid (0.5 mL), the reaction medium was further kept refluxing for 5.5 h. After cooling to room temperature, MeOH was added to the reaction mixture and the precipitate was filtered. The residue could be purified by repeated chromatography on silica using petroleum ether/CH₂Cl₂ (5:1) as eluant. The title compound was initially isolated as red powder, and subsequently recrystallized from hot CHCl₃ solutions upon addition of excess MeOH, giving

eventually the title compound as a dark purple powder (72 mg, 22% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): 8.94 (s, 8H), 8.28 (d, $^3J_{\text{HH}} = 8.0$ Hz, 8H), 7.99 (d, $^3J_{\text{HH}} = 8.0$ Hz, 8H), 7.87 (s, 8H), 7.83 (s, 4H), 7.73 (d, $^3J_{\text{HH}} = 8.0$ Hz, 16H), 7.59-7.57 (m, 16H), 7.39-7.32 (m, 24H), 2.02 (t, $^3J_{\text{HH}} = 8.0$ Hz, 32H), 1.17-1.08 (m, 32H), 0.71 (t, $^3J_{\text{HH}} = 7.2$ Hz, 48H), 0.67-0.58 (m, 32H), -2.72 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): 151.1 (s), 150.8 (s), 142.4 (s), 141.8 (s), 140.3 (s), 134.7 (s), 134.2 (s), 134.0 (s), 130.7 (s), 130.2 (s), 127.6 (s), 126.9 (s), 126.1 (s), 124.4 (s), 124.1 (s), 124.0 (s), 122.9 (s), 122.6 (s), 120.9 (s), 120.1 (s), 119.7 (s), 91.9 (s), 90.4 (s), 89.3 (s), 87.9 (s), 55.1 (s), 40.2 (s), 25.9 (s), 23.1 (s), 13.8 (s). UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}$] = 329 [486.6], 347 [484.9], 425 [707.1], 519 [34.5], 555 [27.4], 593 [15.8], 649 [15.4]. HRMS: $m/z = 3416.8821$ [$\text{M}+\text{H}$] $^+$ (calcd: 3416.8819). Anal. Calcd: (%) for $\text{C}_{260}\text{H}_{238}\text{N}_4$: C, 91.34; H, 7.02; N, 1.64. Found: C, 91.05; H, 6.93; N, 1.77.

3. A mixture of aldehyde **c** (860 mg, 1.22 mmol, 1 eq) and propionic acid (6 mL) was heated to 120 °C. After dropwise addition of a solution of pyrrole (0.085 mL, 1.22 mmol, 1 eq) in propionic acid (1.0 mL), the reaction medium was further kept refluxing for 3.0 h. After cooling to room temperature, MeOH was added to the reaction mixture and the precipitate was filtered. The residue could be purified by repeated chromatography on silica using petroleum ether/ CH_2Cl_2 (5:1) as eluant. The title compound was isolated as red powder, and subsequently recrystallized from hot CHCl_3 solutions upon addition of excess MeOH (165 mg, 18% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): 9.02 (s, 8H), 8.43 (s, 8H), 8.26 (s, 4H), 7.67 (d, $^3J_{\text{HH}} = 7.2$ Hz, 16H), 7.59-7.57 (m, 16H), 7.31 (broad, 24H), 1.95 (t, $^3J_{\text{HH}} = 8.0$ Hz, 32H), 1.07-1.02 (m, 32H), 0.65-0.48 (m, 80H), -2.75 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): 151.1 (s), 150.8 (s), 142.5 (s), 141.8 (s), 140.3 (s), 136.7 (s), 134.0 (s), 130.8 (s), 127.6 (s), 126.9 (s), 126.2 (s), 122.9 (s), 122.6 (s), 121.0 (s), 120.0 (s), 119.7 (s), 118.7 (s), 91.6 (s), 88.6 (s), 55.1 (s), 40.1 (s), 25.9 (s), 23.0 (s), 13.8 (s). UV-vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}$] = 327 [393.5], 427 [806.6], 517 [50.8], 551 [30.9], 590 [27.8], 646 [22.4]. HRMS: $m/z = 3016.7647$ [$\text{M}+\text{H}$] $^+$ (calcd: 3016.7567). Anal. Calcd: (%) for $\text{C}_{228}\text{H}_{222}\text{N}_4$: C, 90.73; H, 7.41; N, 1.86. Found: C, 90.39; H, 7.38; N, 1.93.

4. A mixture of aldehyde **d** (500 mg, 0.33 mmol, 1 eq) and propionic acid (3 mL) was heated to 120 °C. After dropwise addition of a solution of pyrrole (0.085 mL, 1.22 mmol, 1 eq) in propionic acid (0.5 mL), the reaction medium was further kept refluxing for 5.5 h. After cooling to room temperature, MeOH was added to the reaction mixture and the precipitate was filtered. The residue could be purified by repeated chromatography on silica using petroleum ether/ CH_2Cl_2 (5:1) as eluant. The title compound was initially isolated as red powder, and subsequently recrystallized from hot CHCl_3 solutions upon addition of excess MeOH, giving eventually the desired compound **1d** as a dark purple powder (66 mg, 13% yield). ^1H NMR (400 MHz, CDCl_3 , ppm): 9.08 (s, 8H), 8.46 (s, 8H), 8.22 (s, 4H), 7.77-7.74 (m, 20H), 7.65-7.61 (m, 32H), 7.52-7.47 (m, 36H), 7.36-7.28 (m, 48H), 1.91 (t, $^3J_{\text{HH}} = 8.0$ Hz, 64H), 1.05-0.99 (m, 64H), 0.63-0.52 (m, 160H), -2.70 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , ppm): 151.0 (s), 150.8 (s), 141.8 (s),

140.3 (s), 134.4 (s), 134.0 (s), 130.7 (s), 127.6 (s), 126.8 (s), 126.1 (s), 124.4 (s), 124.0 (s), 123.6 (s), 122.9 (s), 122.2 (s), 120.8 (s), 120.0 (s), 119.6 (s), 91.9 (s), 89.4 (s), 89.1 (s), 87.8 (s), 55.0 (s), 40.1 (s), 25.8 (s), 23.0 (s), 13.8 (s). UV-vis (CH₂Cl₂): $\lambda_{\text{max}}/\text{nm}$ [$\epsilon/10^3 \text{ M}^{-1}\cdot\text{cm}^{-1}$] = 327 [916.6], 348 [821.6], 426 [566.1], 517 [27.8], 551 [14.9], 590 [12.9], 645 [9.3]. HRMS: $m/z = 3109.7570$ [$\text{M}+2\text{H}$]²⁺ (calcd: 3109.7584). Anal. Calcd: (%) for C₄₇₆H₄₄₆N₄: C, 91.88; H, 7.22; N, 0.90. Found: C, 91.67; H, 7.17; N, 0.72.



Scheme S1. Syntheses of **1-4**.

3. ^1H NMR Spectra of the Porphyrins (1-4)

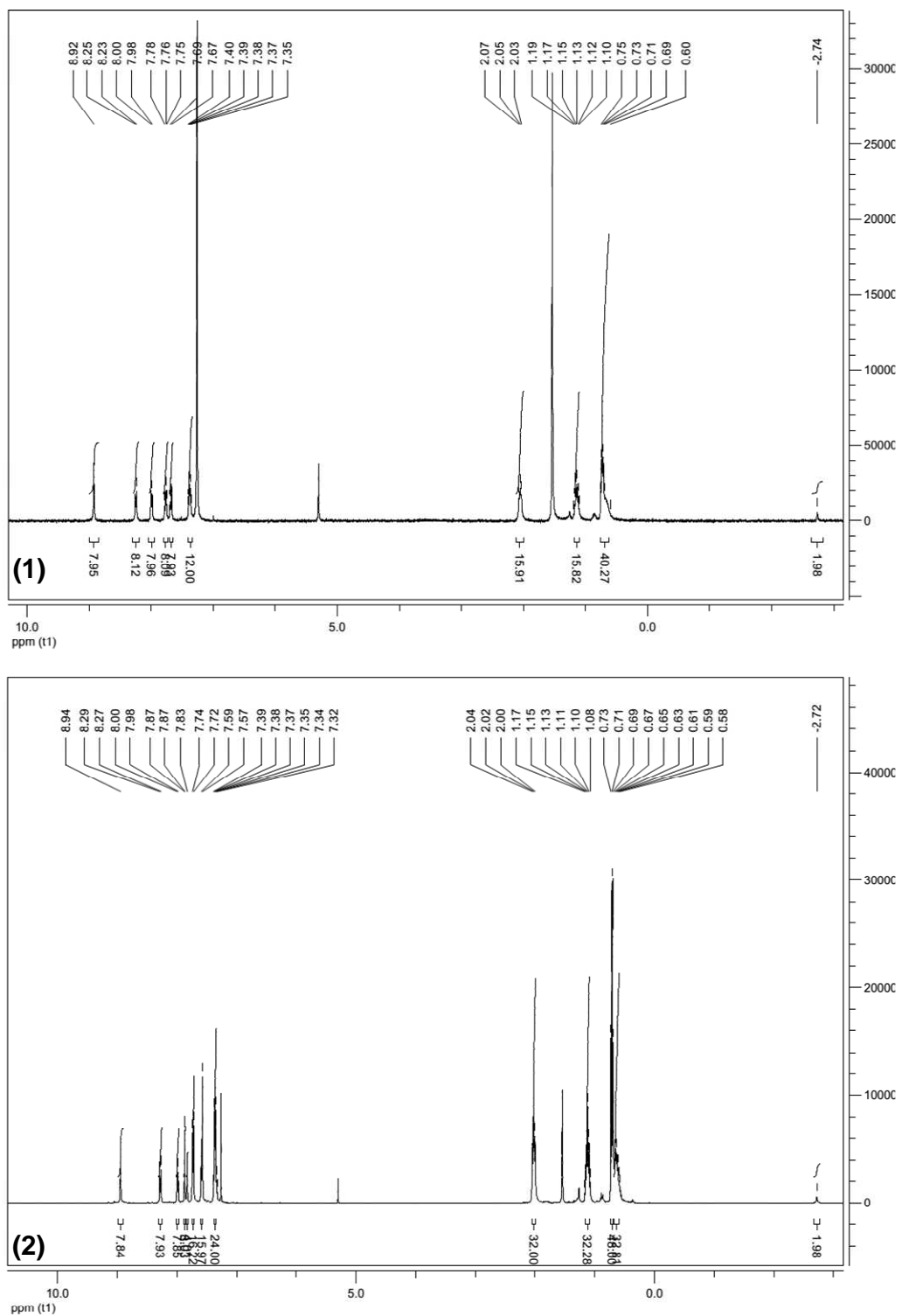


Figure S1. ^1H NMR Spectra at 400 MHz for **1** and **2** in CDCl_3 .

4. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of the Porphyrins (1-4)

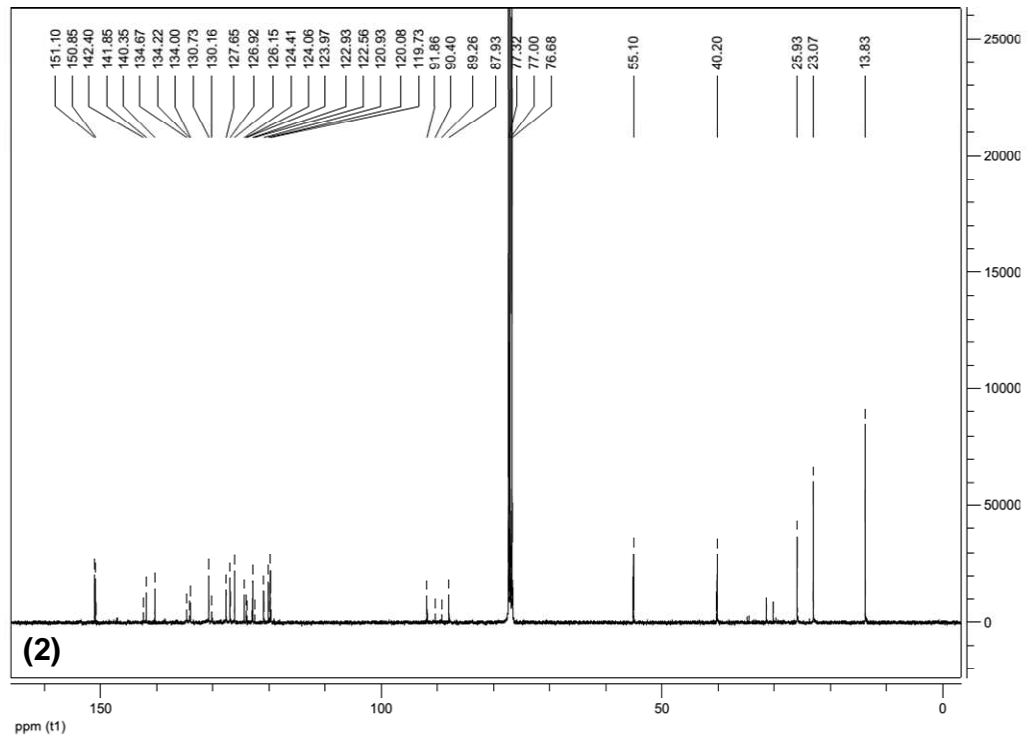
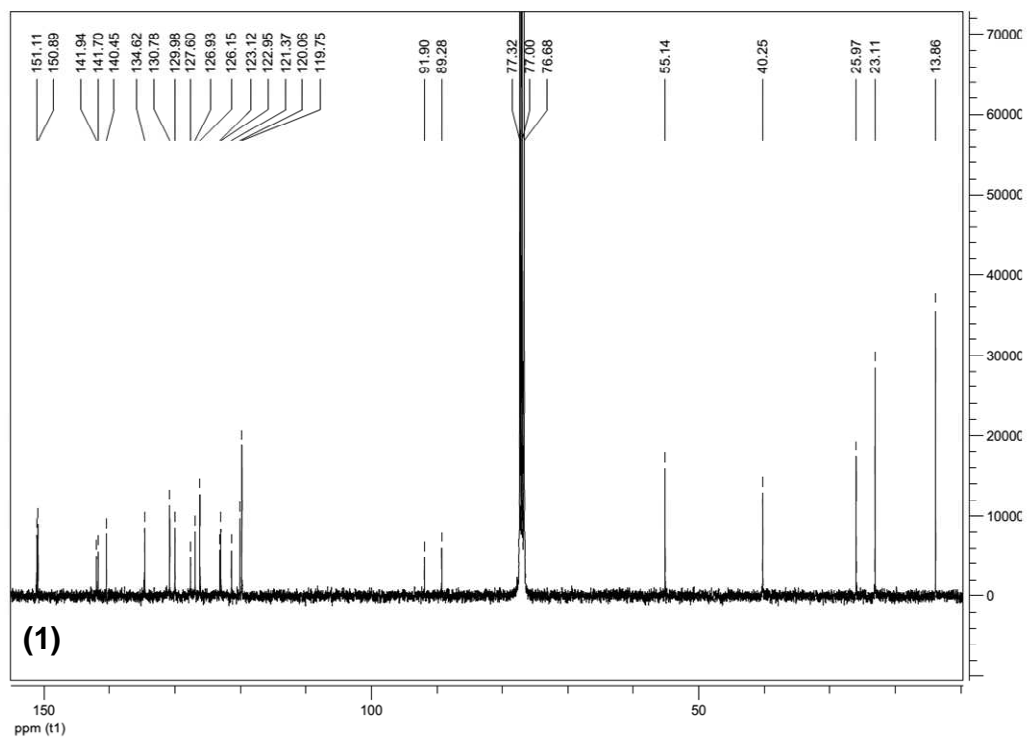


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra at 100 MHz for **1** and **2** in CDCl_3 .

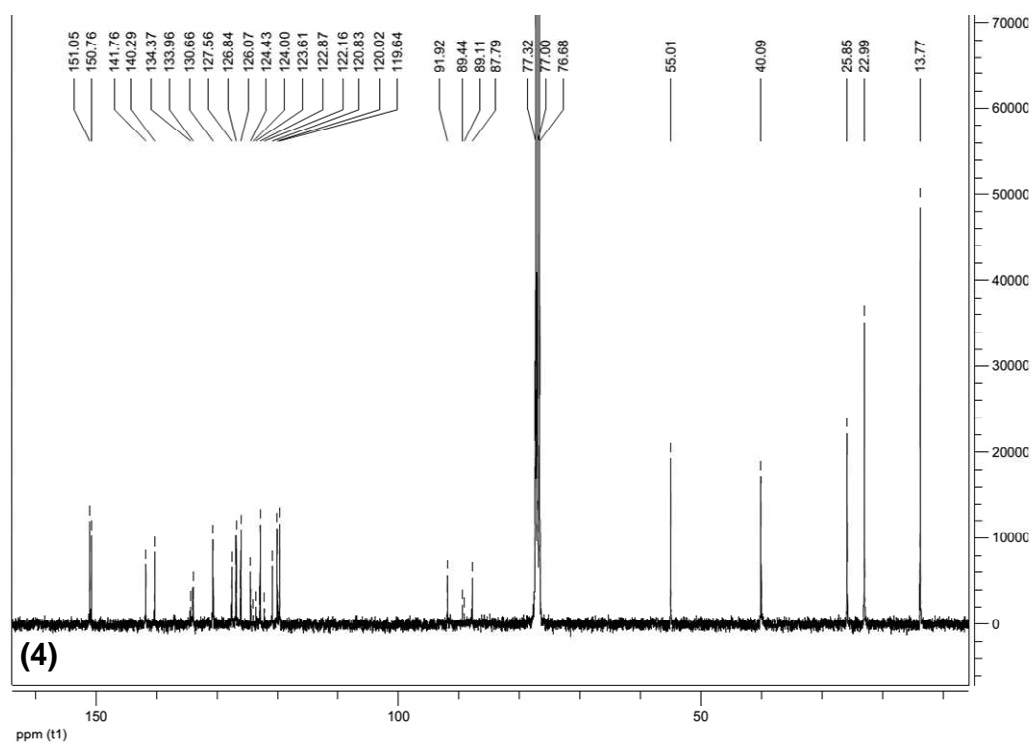
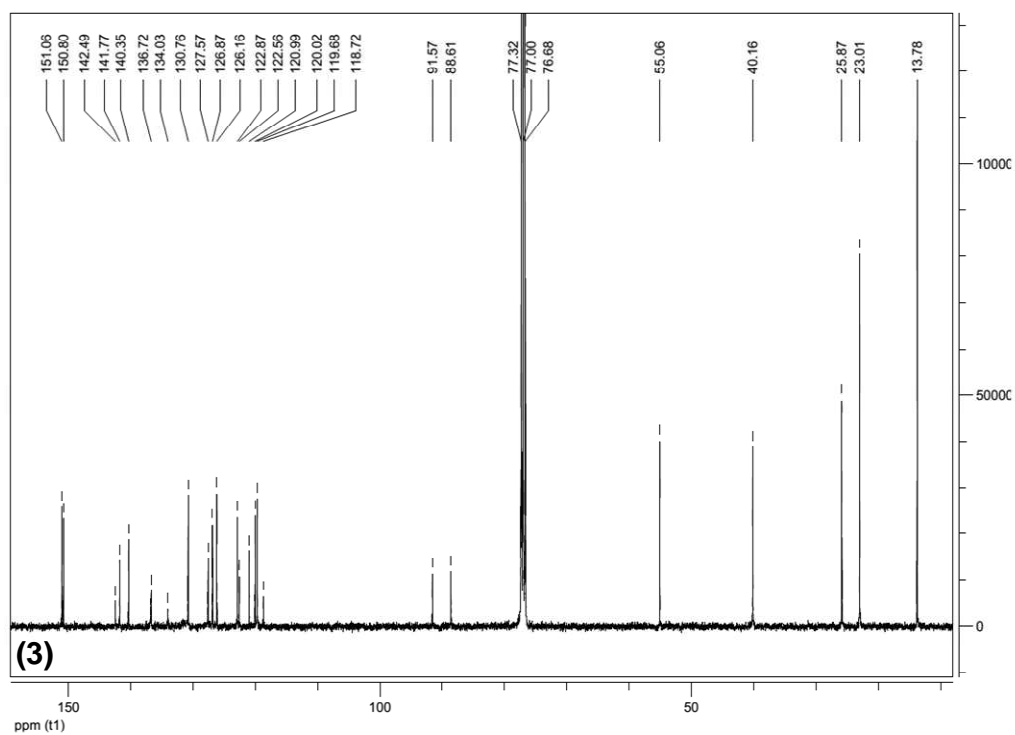


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra at 100 MHz for **3** and **4** in CDCl_3 .

5. Two-Photon Absorption Spectra of the Porphyrins (1-4) and Corresponding Dependence of Intensity vs. Fluence

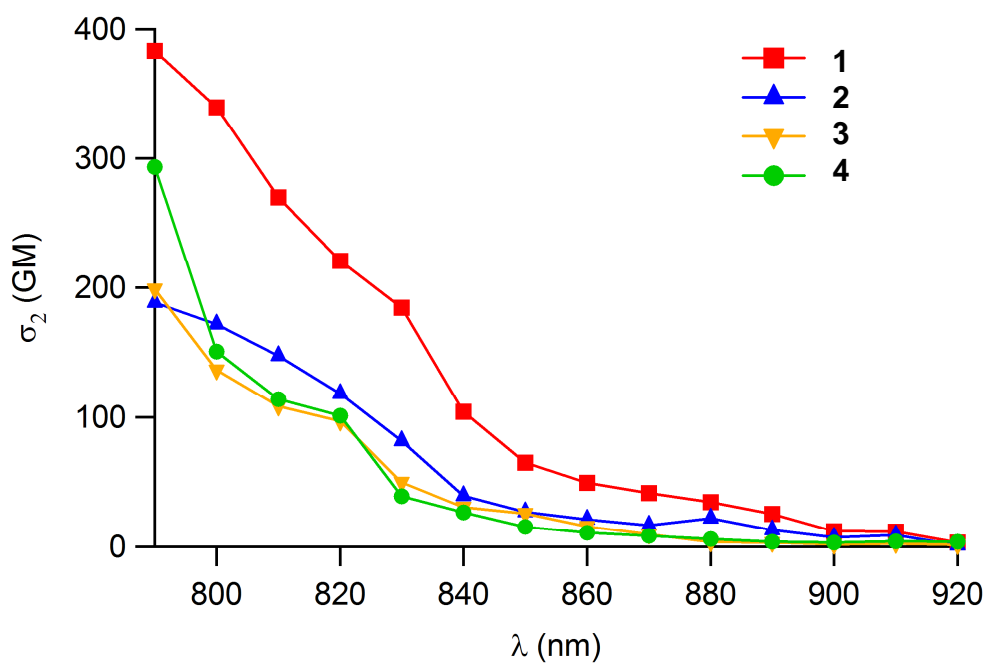


Figure S5. Two-photon absorption spectra of **1-4** in dichloromethane (obtained two-photon excited fluorescence measurements in the femtosecond regime).

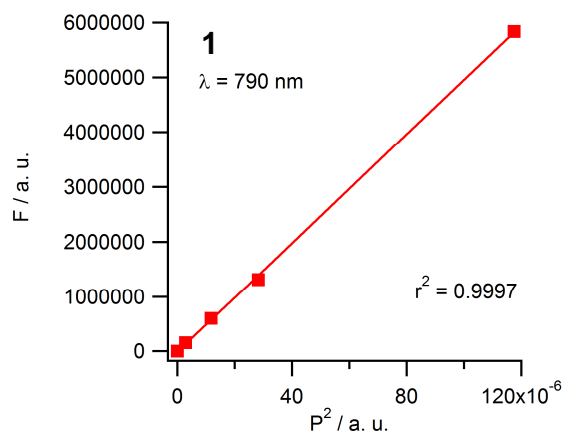
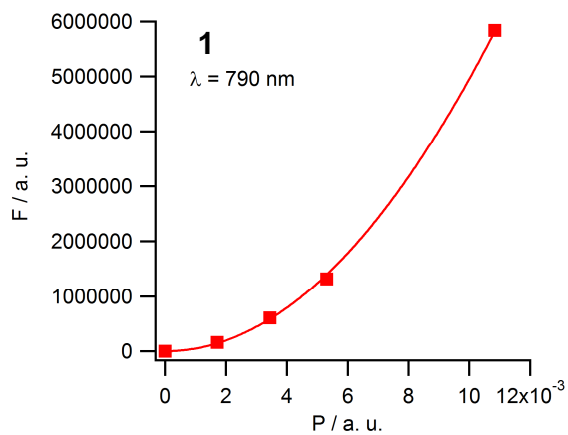


Figure S6. Left: quadratic dependence of the emission intensity (F) on laser excitation power (P) for compound **1** at 790 nm. Right: dependence of F on P².

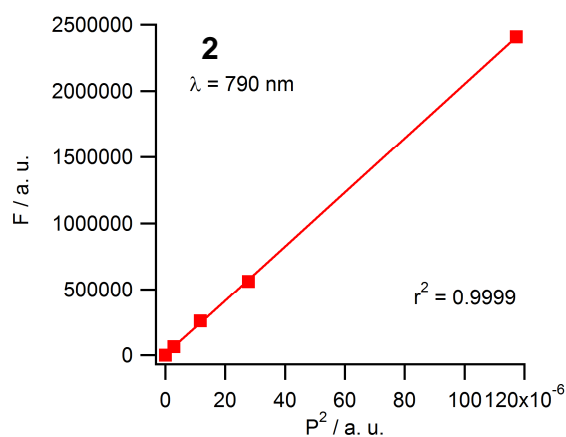
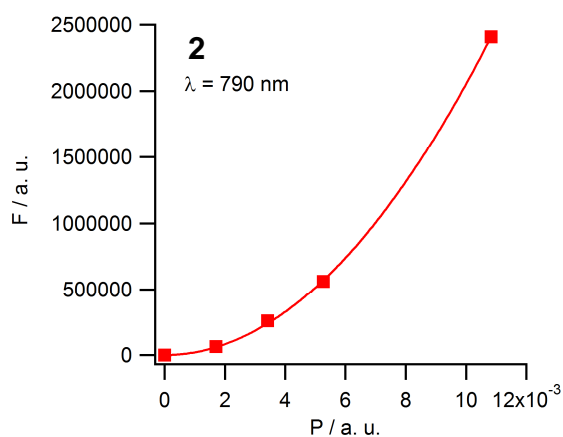


Figure S7. Left: quadratic dependence of the emission intensity (F) on laser excitation power (P) for compound **2** at 790 nm. Right: dependence of F on P².

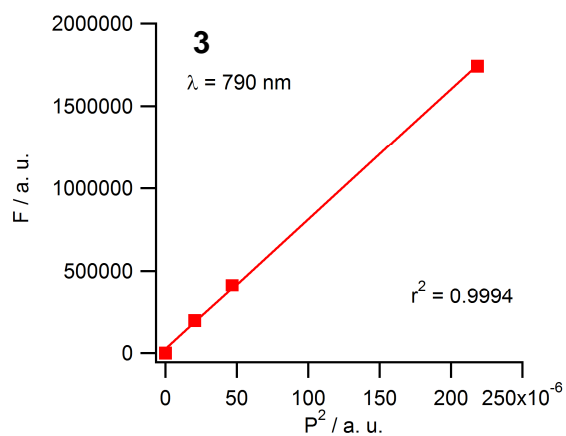
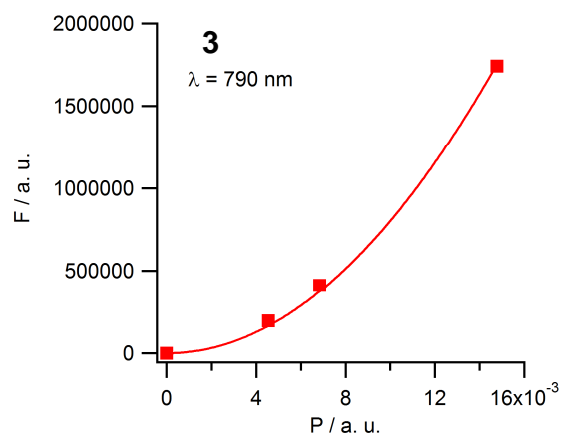


Figure S8. Left: quadratic dependence of the emission intensity (F) on laser excitation power (P) for compound **3** at 790 nm. Right: dependence of F on P^2 .

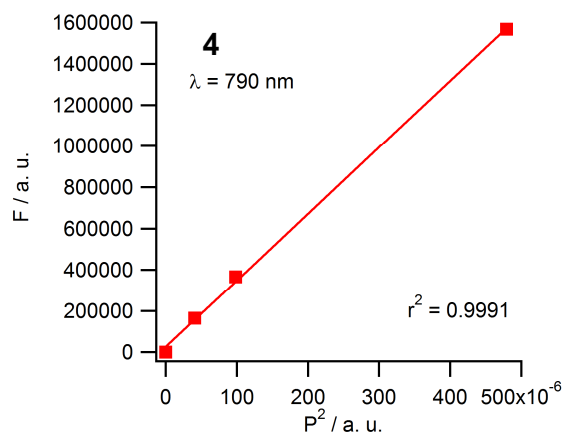
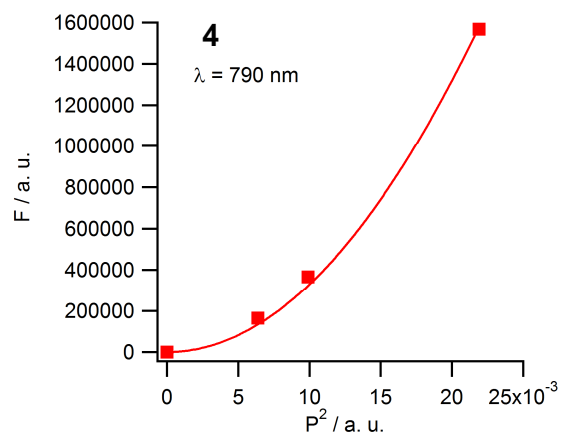


Figure S9. Left: quadratic dependence of the emission intensity (F) on laser excitation power (P) for compound **4** at 790 nm. Right: dependence of F on P^2 .