Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information for

Exocyclically Metallated Tetrapyridinoporphyrazine as a Potential Photosensitizer for Photodynamic Therapy

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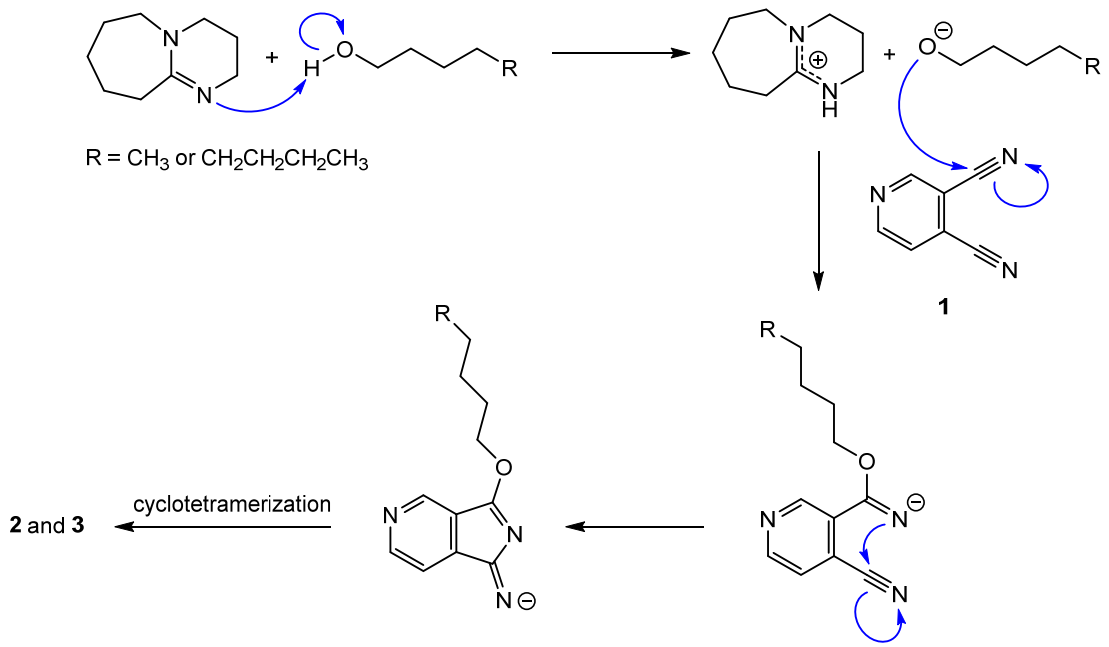


Scheme S1. A reaction mechanism for the formation of **2** and **3** analogous to the one proposed by Tomoda *et al.*[1]

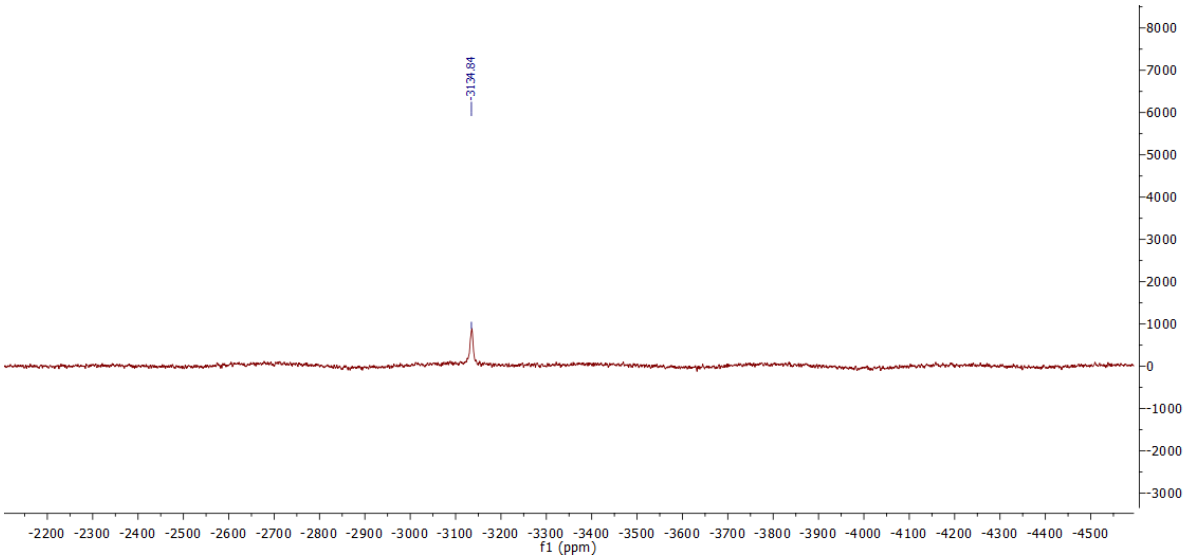


Figure S1: ^{195}Pt-NMR spectrum of **4** measured in DMSO-d_6:Methanol-d_4 = 9:1.

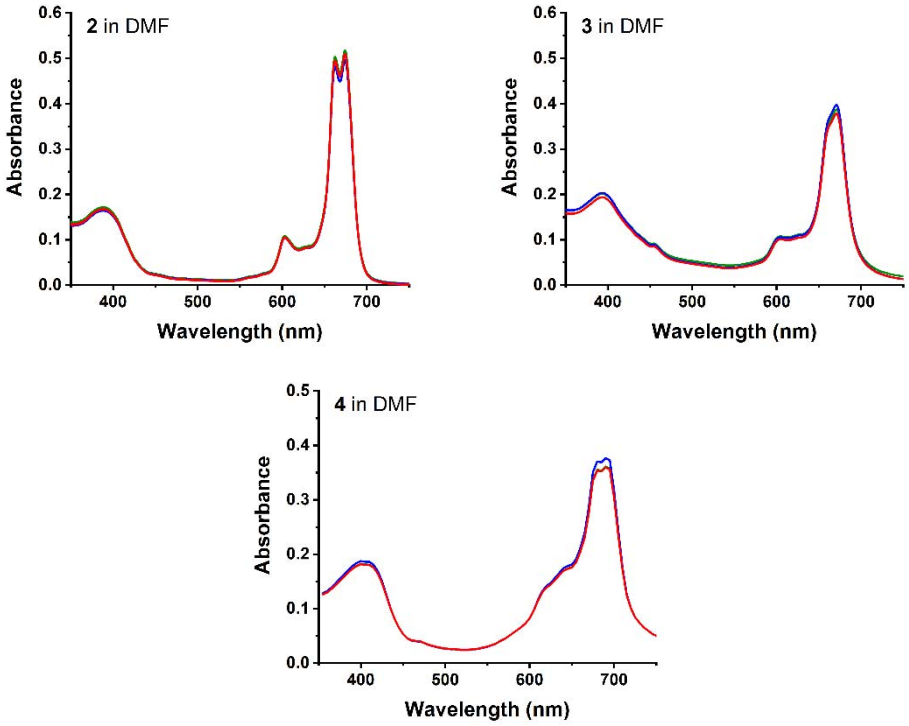


Figure S2. UV-Vis absorbance spectra of **2**, **3** and **4** in DMF: Instantly measured (green), after one week under light exclusion (blue) and after one additional week in daylight (red).

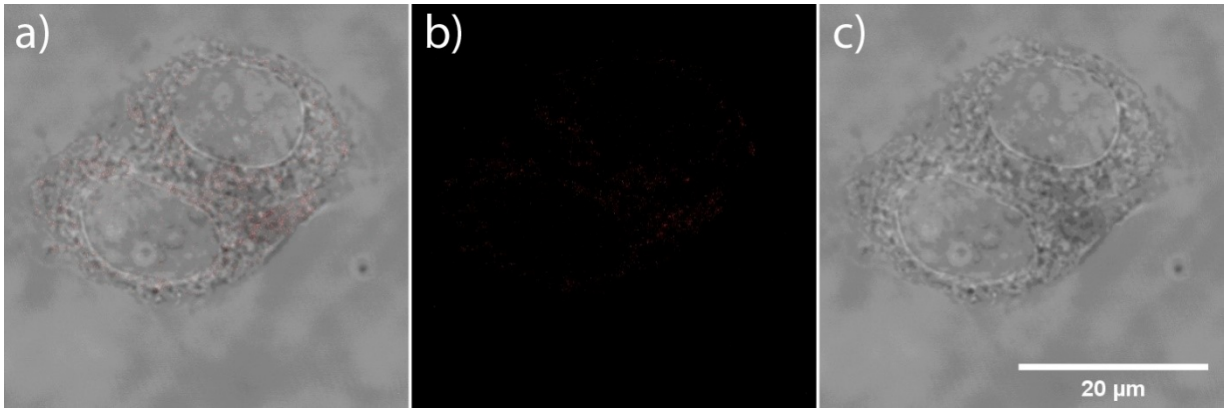
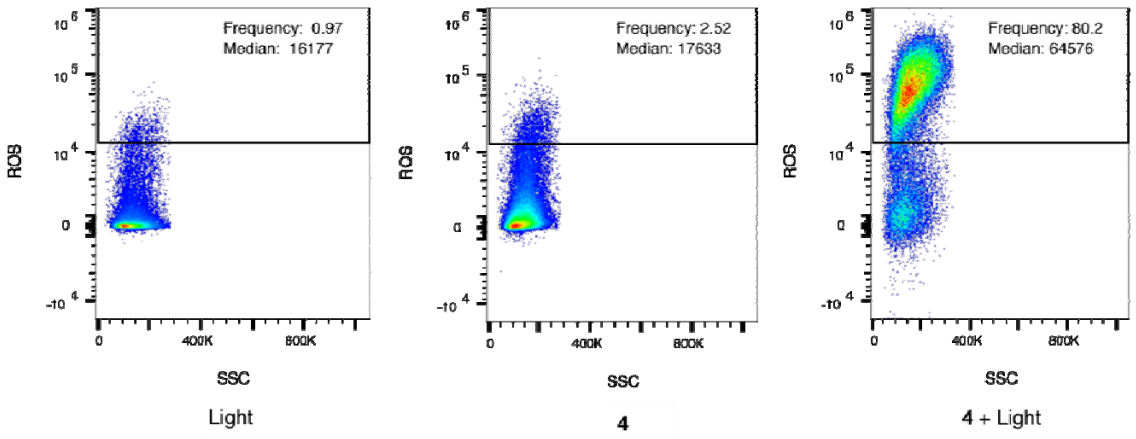


Figure S3. Control experiment for the intracellular localization of compound **4** in HeLa cells. Confocal images of cells without Hoechst 33258 staining and without compound **4** are shown: a) merge, b) red channel, c) wide-field.



In the table below, the average ROS levels for 3 independent experiments are given.

Treatment	Frequency	S.D
Light	0.64	0.34
4	2.53	0.49
4 + Light	71.5	8.46

Figure S4. A typical experiment showing the intracellular ROS levels in HeLa cells irradiated with red light for 20 min (left), treated with 12 µM compound **4** for 4 h (middle) or treated with 12 µM compound **4** for 4 h and irradiated with red light for 20 min (right). ROS signal is indicated as DCF fluorescence, measured using the BL1 channel (excitation 488 nm, emission 530 nm) on an Attune NxT Cytometer and is plotted against side scatter (SSC). The median fluorescence intensity and the frequency of cells displaying ROS signal are shown. S.D designates the standard deviation.

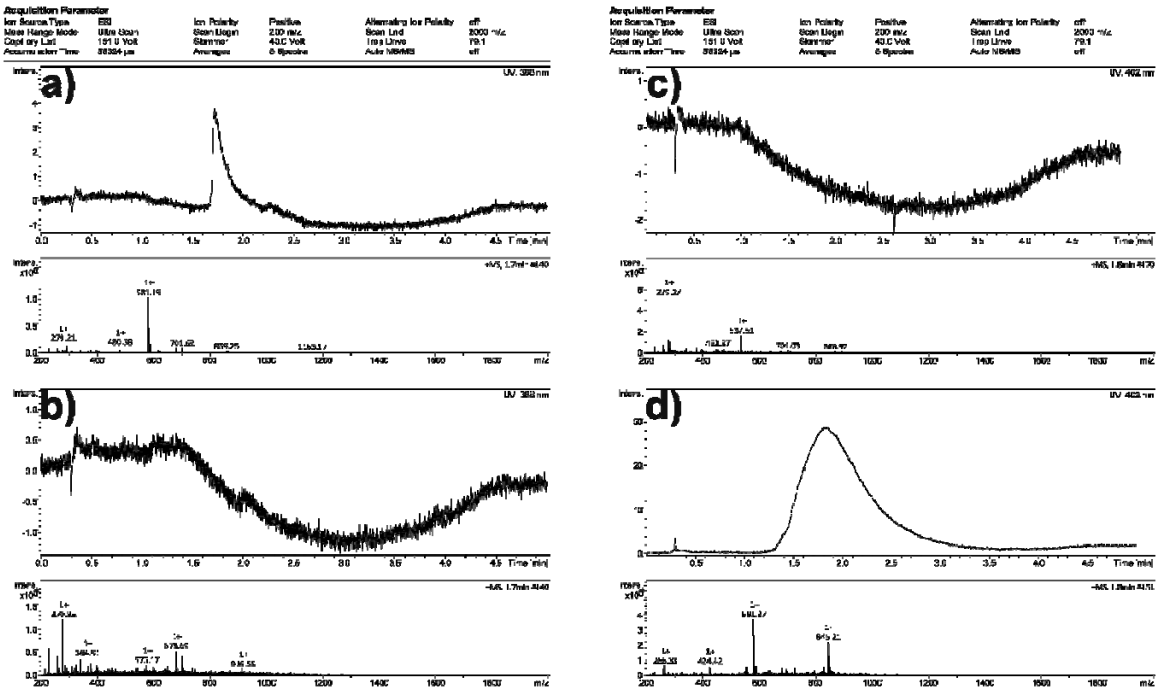


Figure S5. RP-UPLC-ESI-MS spectra of a) *n*-octanol phase (**2**), b) PBS phase (**2**), c) *n*-octanol phase (**4**), d) PBS phase (**4**), showing that **2** only accumulates in the *n*-octanol phase and **4** only in the PBS phase.

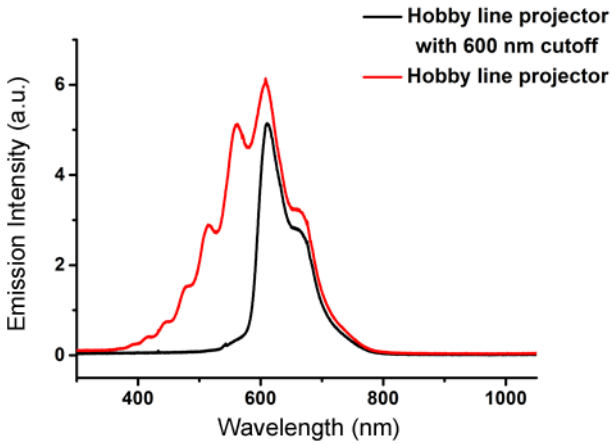


Figure S6. Emission of the white light projector with and without an applied filter at 600 nm.

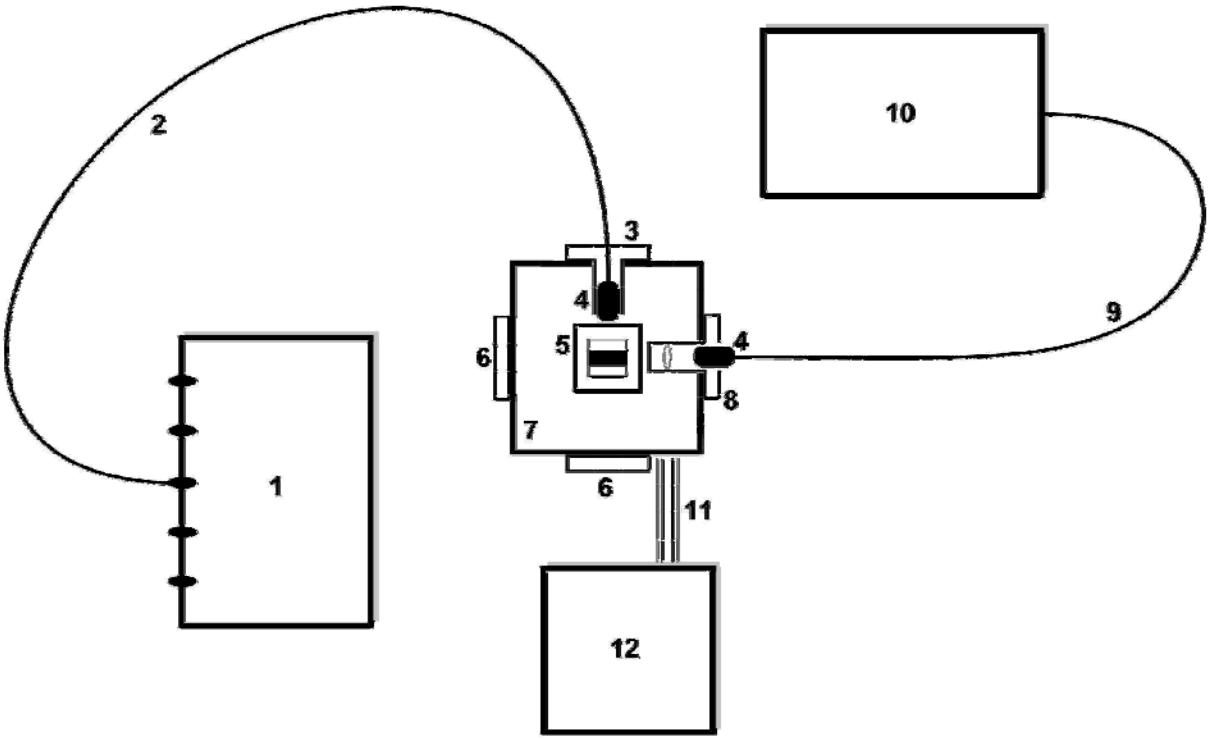


Figure S7. Setup used for NIR emission spectroscopy. **1)** LED light source, **2)** Optical fibre (1000 µm), **3)** Custom-built connection piece, **4)** SMA 905 fibre optic connector, **5)** Cuvette in cuvette holder, **6)** Blank, **7)** Temperature-controlled Qpod cuvette holder, **8)** Connection piece with QIL-UV AR-coated fused-silica imaging lens, **9)** Optical fibre (600 µm), **10)** NIR detector, **11)** Plastic hose, **12)** Cooling bath.

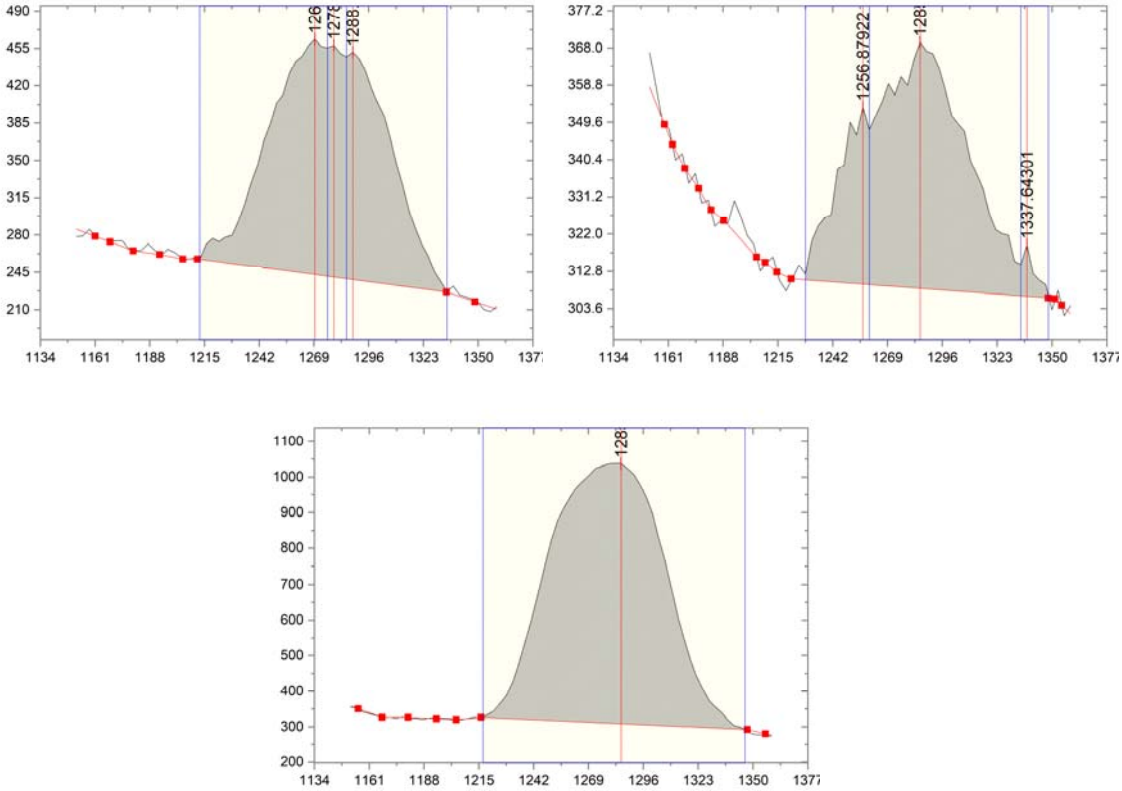


Figure S8. Singlet oxygen phosphorescence emission intensity (a.u.) vs. wavelength (nm) plots of the measured solutions of substances **2** (top left), **3** (top right), and zinc phthalocyanine (**ZnPc**, bottom left).

References

1. H. Tomoda, S. Saito, S. Ogawa and S. Shiraishi, Synthesis of Phthalocyanines from Phthalonitrile with Organic Strong Bases, *Chem. Lett.*, 1980, **9**, 1277-1280.