

Electronic Supplementary Information

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## Near-infrared dual luminescence from an extended zinc porphyrin

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## Experimental methods: Spectroscopy and Photophysics

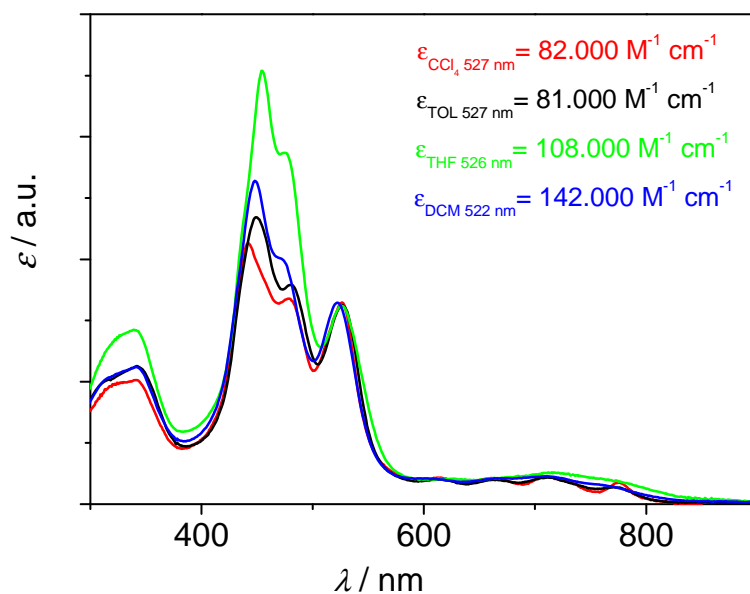
Solvents used for photophysical determinations were spectroscopic grade (C. Erba). Absorption spectra were recorded in diluted solutions by using a Perkin–Elmer Lambda 950 UV/vis/NIR spectrophotometer in 1 cm square optical quartz cuvettes. The determination of molar absorption coefficients in the different solvents has been performed by different methods and at various concentrations, due to the low solubility of **1** in some solvents, TOL in particular (solubility limit of  $5 \times 10^{-6}$  M). A comparative method produced the most reliable results. In this method  $5 \times 10^{-7}$  M solutions in DCM, well below the solubility limit for all solvents, have been evacuated and re-dissolved by the same volume of the other solvents. Use of cuvettes with different optical paths (0.2–4 cm) allowed the exploration of a wide range of concentrations for **1** in TOL (see main text).

Emission spectra were measured on sample solutions with  $A \leq 0.1$  at the excitation wavelength in right-angle mode by using a FLS920 spectrofluorimeter (Edinburgh) equipped with an Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM300 emission monochromator with a grating blazed at 1000 nm. The latter spectrofluorimeter was also used to measure the singlet oxygen luminescence quantum yield of **1** in  $\text{CCl}_4$  using 5,10,15,20-tetraphenylporphyrin (TPP) in the same solvent as reference ( $\phi_{\Delta} = 0.62$ )<sup>1</sup>. A Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube, was also used in some cases, limiting the detected region in the UV-Vis range. Corrected spectra were employed throughout this work, unless specified, by applying a correction curve of the wavelength dependent phototube response to the raw data. Luminescence quantum yields in solution were evaluated by comparing the wavelength integrated intensities ( $I$ ) with reference to  $[\text{Os}(\text{ttpy})_2]^{2+}$  ( $\phi_r = 0.021$ ,  $\text{O}_2$ -free butyronitrile, ttpy is tolylterpyridine)<sup>2</sup>, by using the following equation:<sup>3</sup>

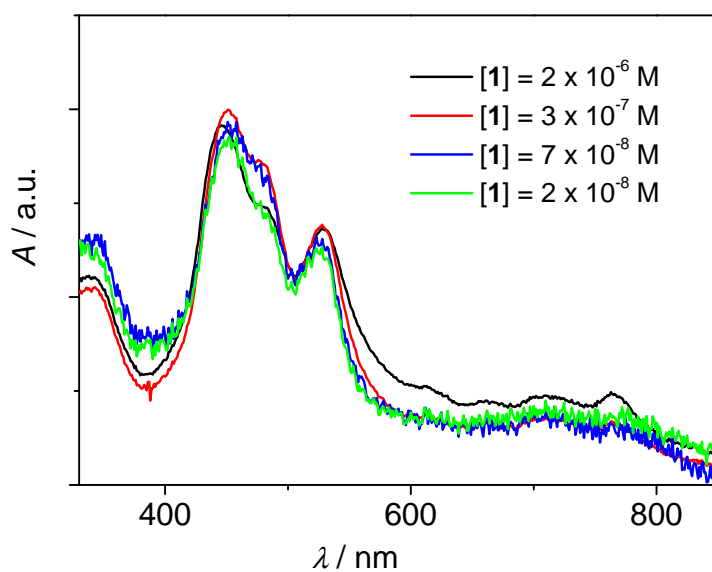
$$\phi_{em} = \frac{A_r n^2 I}{n_r^2 I_r A} \phi_r$$

in which  $A$  and  $n$  are the absorbance values at the employed excitation wavelength and refractive index of the solvent, respectively ( $r$  is for reference). 1 cm square optical quartz cuvettes were used for measurements at room temperature and quartz capillary tubes immersed in liquid nitrogen in a cold finger quartz dewar were used for measurements of frozen glasses at 77K. Estimated errors are: 2 nm on band maxima and 20% on quantum yields. Luminescence lifetimes were determined by an apparatus based on a Nd:YAG laser (Continuum PY62-10) with excitation at 532 nm, 35 ps pulse duration, 1.7 mJ/pulse, and a Streak Camera (Hamamatsu C1587 equipped with M1952). The luminescence signals from 10000 laser shots were averaged and the time profiles of the various emission bands were measured from the streak image in a wavelength range of ca. 20 nm around the selected wavelength. The overall time resolution of the system after deconvolution procedure is 5 ps.<sup>4</sup> Luminescence lifetimes in the nanosecond range were also measured with higher accuracy by using an IBH 5000F time-correlated single-photon counting device, by using a pulsed NanoLED excitation source at  $\lambda = 465$  nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer. Experimental

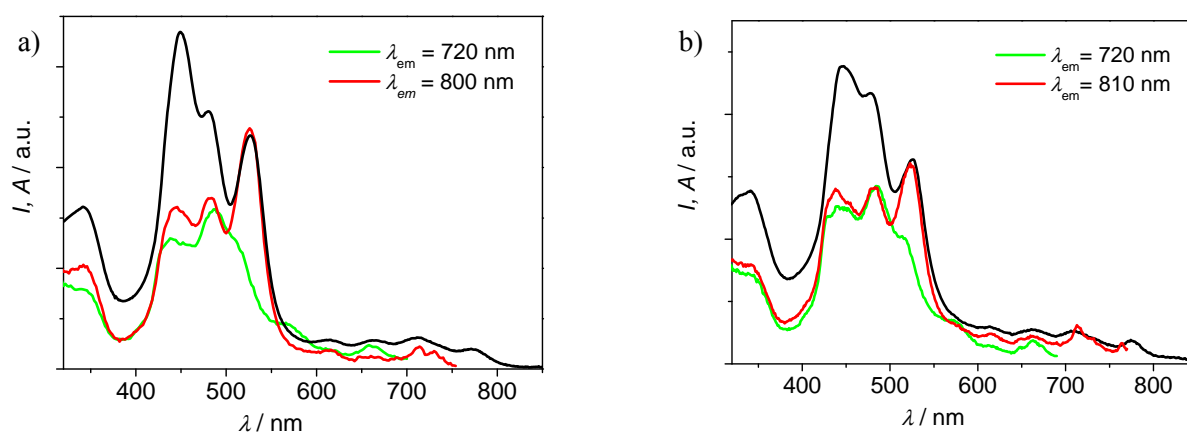
uncertainties in the lifetime determinations are estimated to be 10%. Laser flash photolysis in the nanosecond range was performed by a Nd:YAG (JK) laser (18 ns pulse duration, 532 nm, 3.0 mJ/pulse). More details on the transient absorption apparatuses can be found elsewhere.<sup>5</sup>



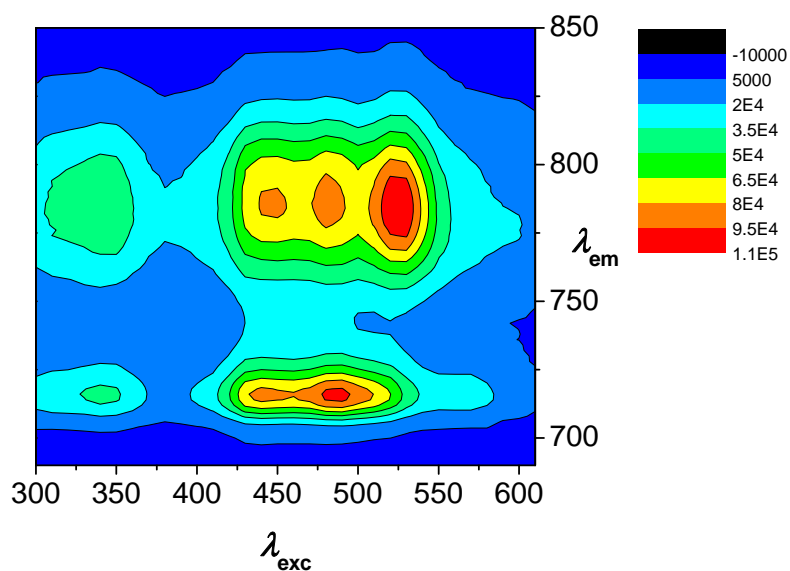
**Figure S1.** Normalized molar absorption coefficients of **1** at 527 nm in  $\text{CCl}_4$  (red), TOL (black), THF (green) and DCM (blue).



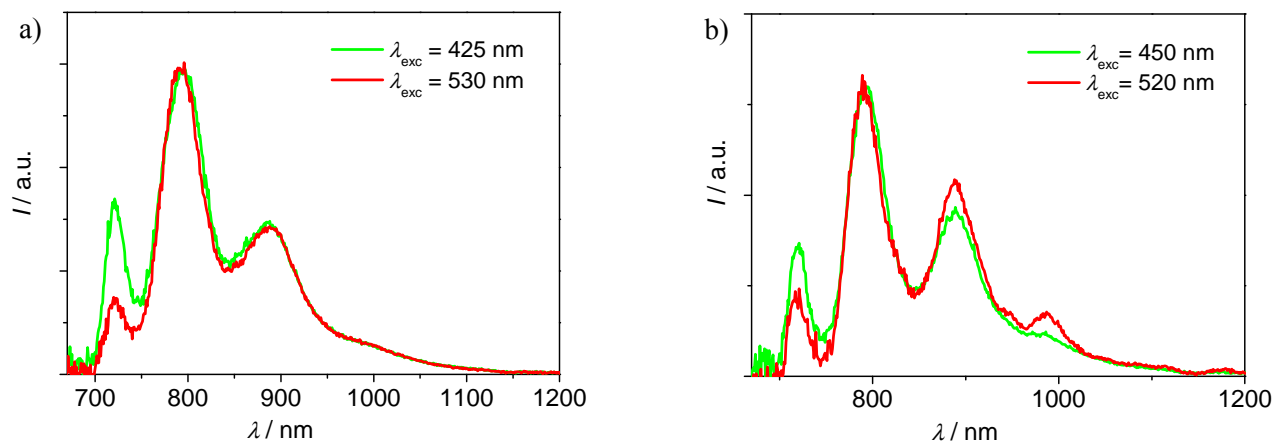
**Figure S2.** Normalized absorption spectra of **1** in TOL at the indicated concentrations.



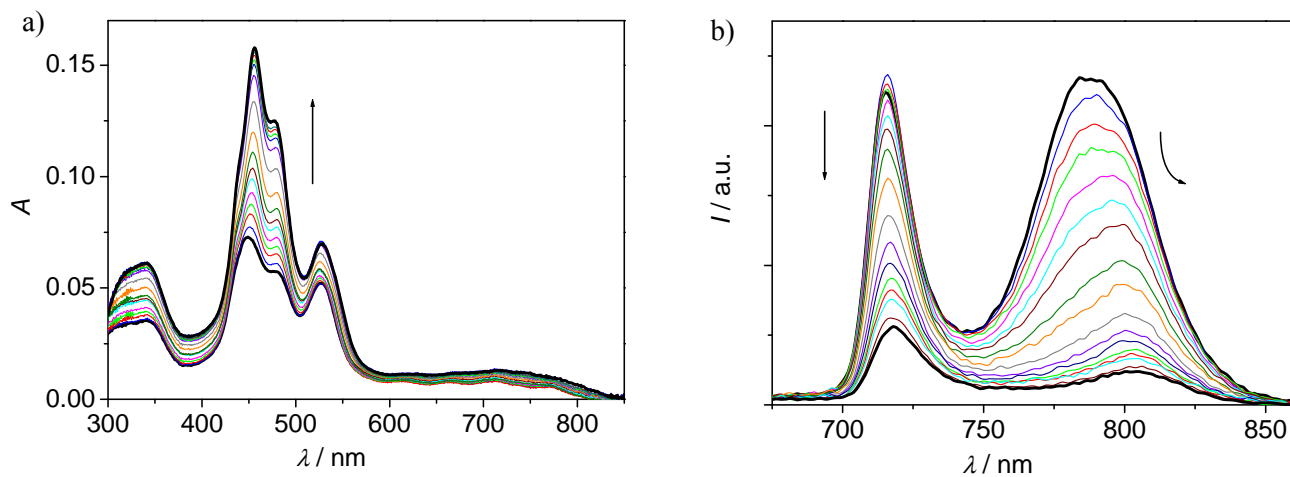
**Figure S3.** Arbitrarily scaled corrected excitation spectra of **1** collected at 720 nm and 800 nm in a) TOL and b)  $CCl_4$ . The arbitrarily scaled absorption spectra are also reported (black).



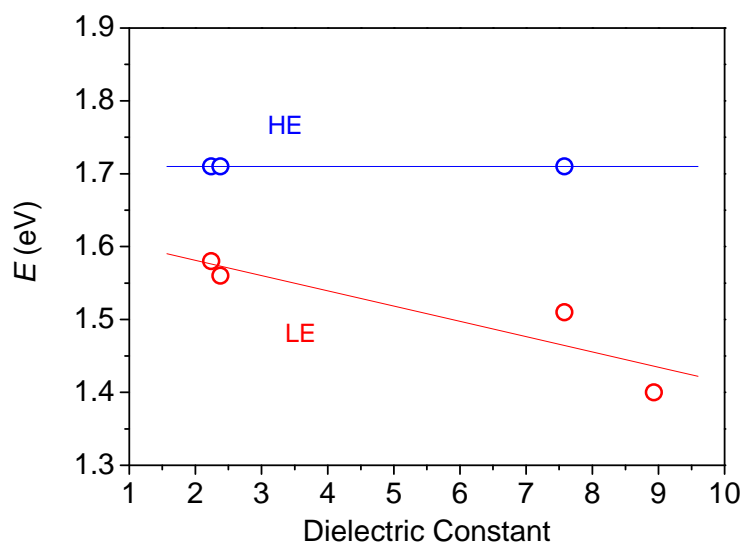
**Figure S4.** Contour plot of excitation/emission of **1** in TOL. The spectra are non-corrected.



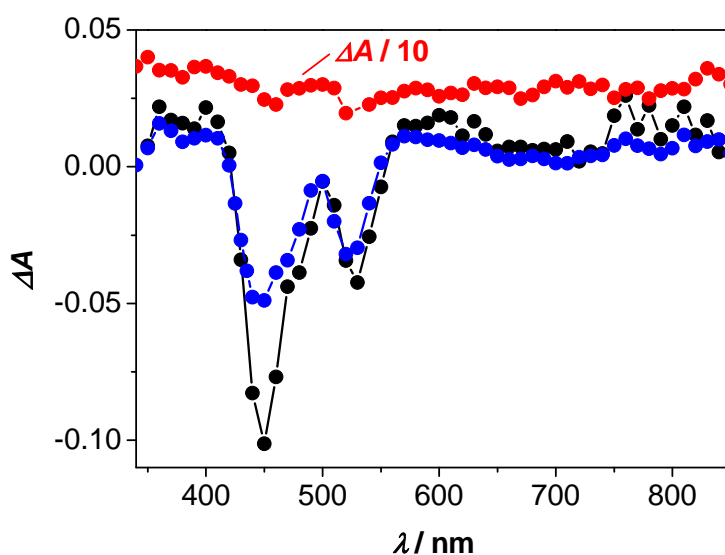
**Figure S5.** Corrected emission spectra of **1** in TOL upon excitation at two different wavelengths a) at room temperature and b) at 77 K in frozen glass. The spectra are normalized at 790 nm.



**Figure S6.** Absorption a) and emission b) spectra of **1** in TOL upon addition of MeOH (from  $4.1 \times 10^{-3}$  M to  $9.5 \times 10^{-1}$  M). In b) the excitation is at 430 nm, the spectra are corrected for the absorbance values. The spectra were obtained with a UV-Vis spectrofluorimeter with no sensitivity above 850 nm.



**Figure S7.** Plot of the energy level of HE ( $\pi$ - $\pi^*$ ) and LE (CT) states (from Table 1, main text) as a function of the dielectric constant of the solvent. Linear fittings are also reported.



**Figure S8.** Transient absorption spectra of **1** in DCM (blue) and in TOL (black) detected 40  $\mu$ s after the laser pulse. In red is reported the spectrum measured in TOL 60 ns after the pulse ( $\Delta A$  is divided by 10).  $\lambda_{exc}$  = 532 nm,  $A$  = 0.79, 3.0 mJ/pulse.

## References

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