

Synthesis, Photo-physicochemical and Biological Properties Novel Tetrahydropyrimidone Substituted Metallo Phthalocyanines

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Materials and methods: IR spectra were recorded between 4000 and 500 cm⁻¹ using a PerkinElmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. MALDI- TOF mass spectrometry analyses were carried out on Bruker microflex LT MALDI-TOF MS spectrometer using dihydroxybenzoic acid as a matrix. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ and DMSO solutions on a Varian 500 MHz spectrometer. Electronic absorption spectra in the UV–visible region were recorded with a Thermo scientific Evolution 220 UV-Visible spectrophotometer using a 1 cm path length cuvette at room temperature. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Fluorescence lifetimes were measured by a time correlated single photon counting (TCSPC) method using FLUOROLOG-3 spectrofluorometer (Horiba JobinYvon, Edison, NJ) equipped with a NanoLED and a standard air cooled R928 PMT detector. Photo-irradiations were done by using a General Electric quartz line lamp (300W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Mol electron detector

incorporated) power meter. All solvents and chemicals were of reagent-grade quality, purchased from Sigma Aldrich Chemical Co. and Merck.

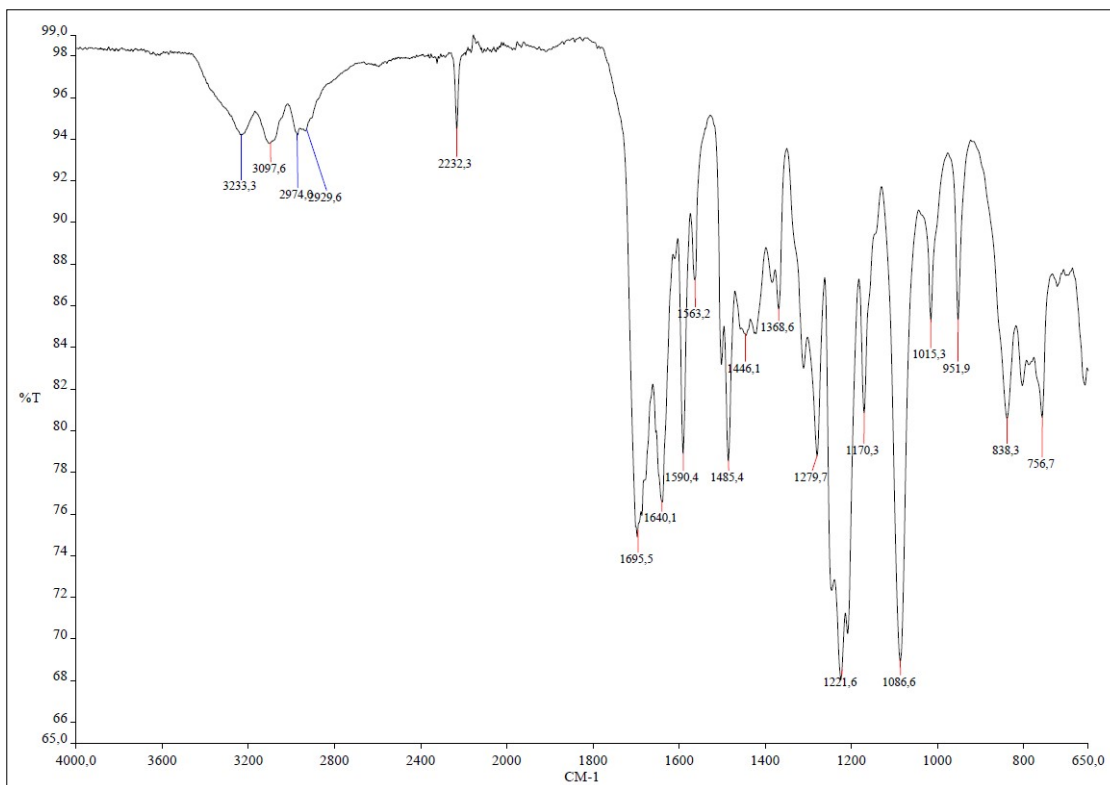


Fig. S1. FT-IR spectrum of compound 3.

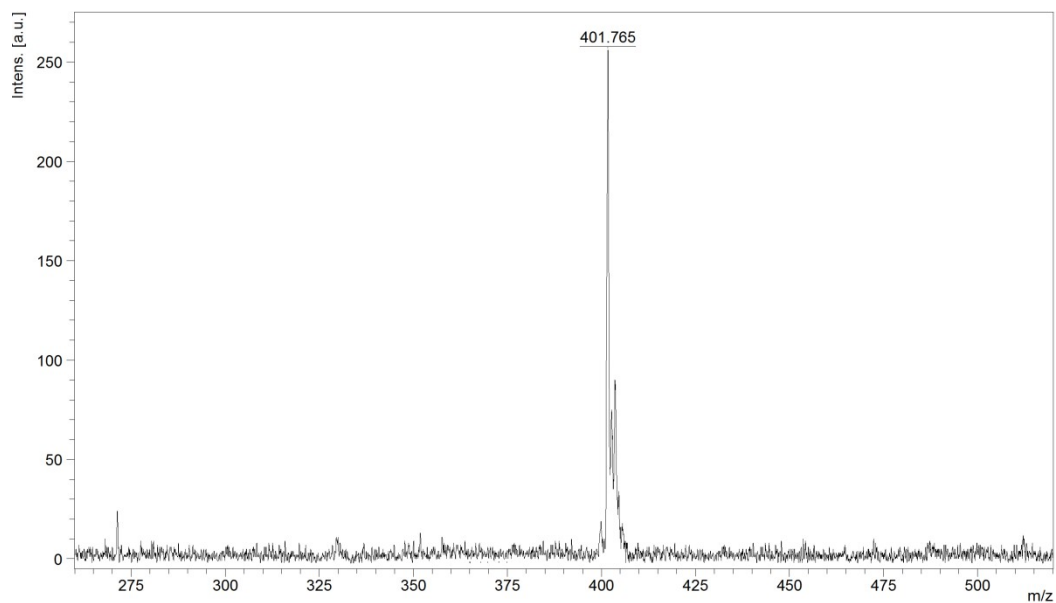


Fig. S2. MALDI-TOF mass spectrum of compound 2 (DHB).

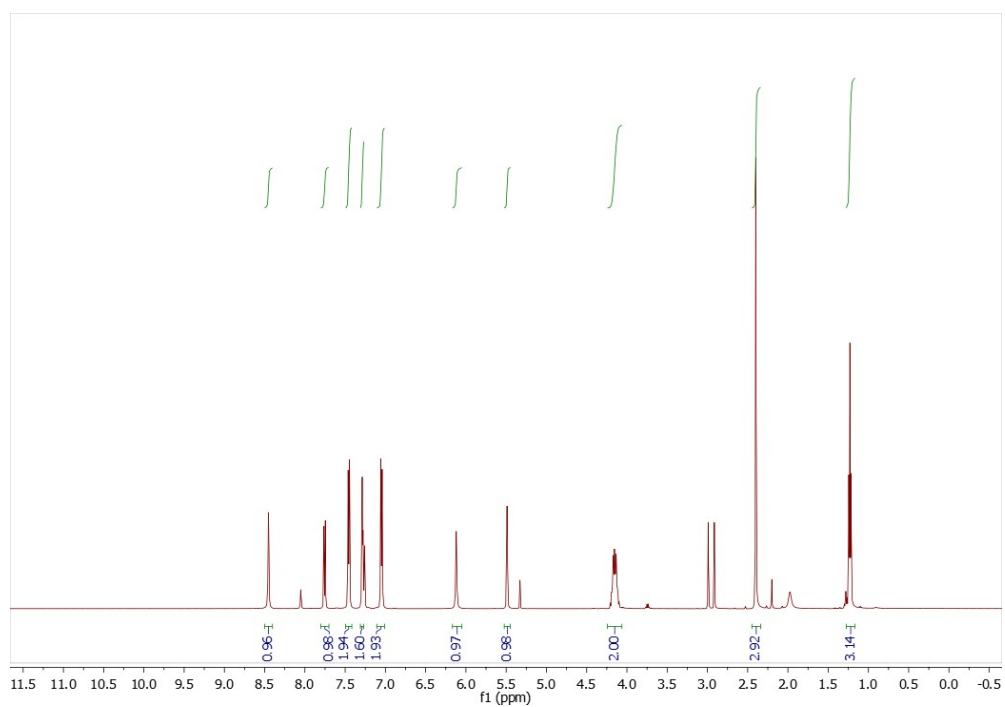


Fig. S3. ^1H NMR spectrum of compound **3** (500 MHz, in CDCl_3).

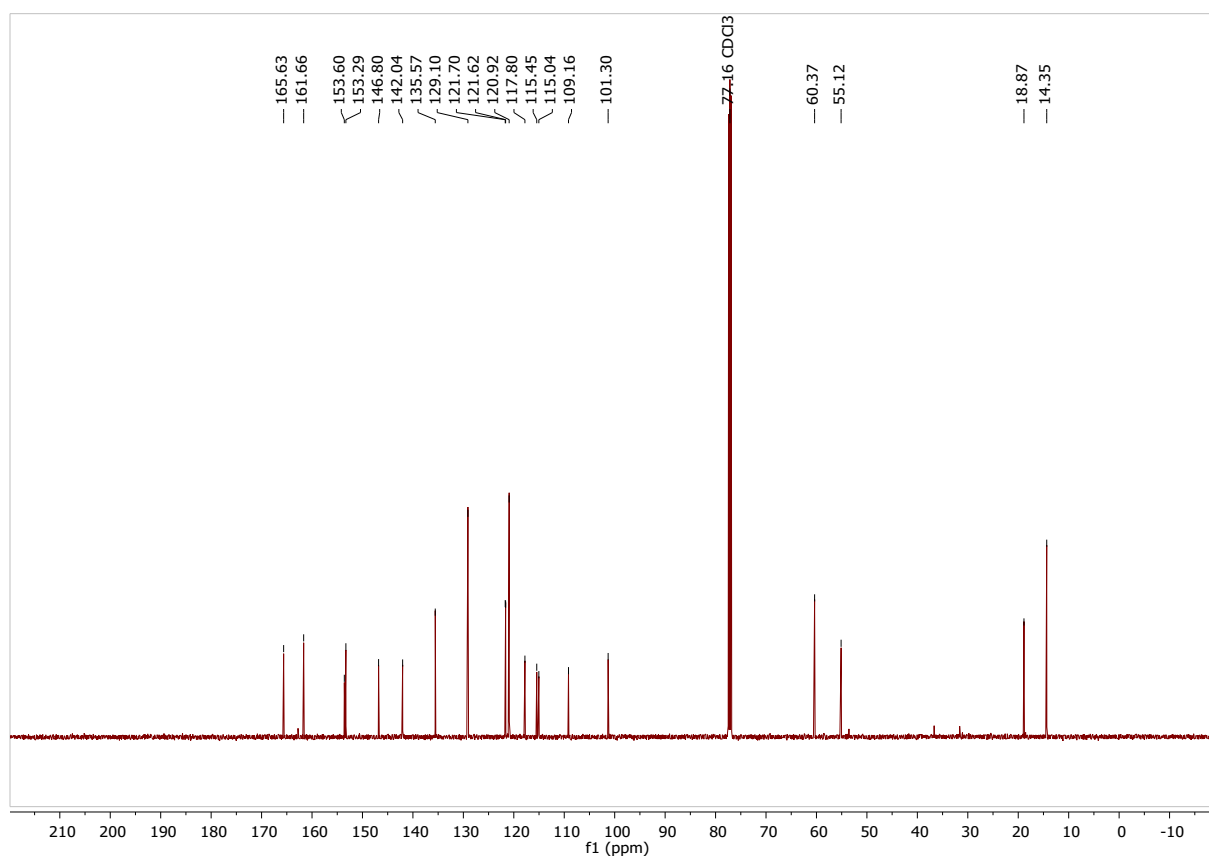


Fig. S4. ^{13}C NMR spectrum of compound **3** (125 MHz, in CDCl_3).

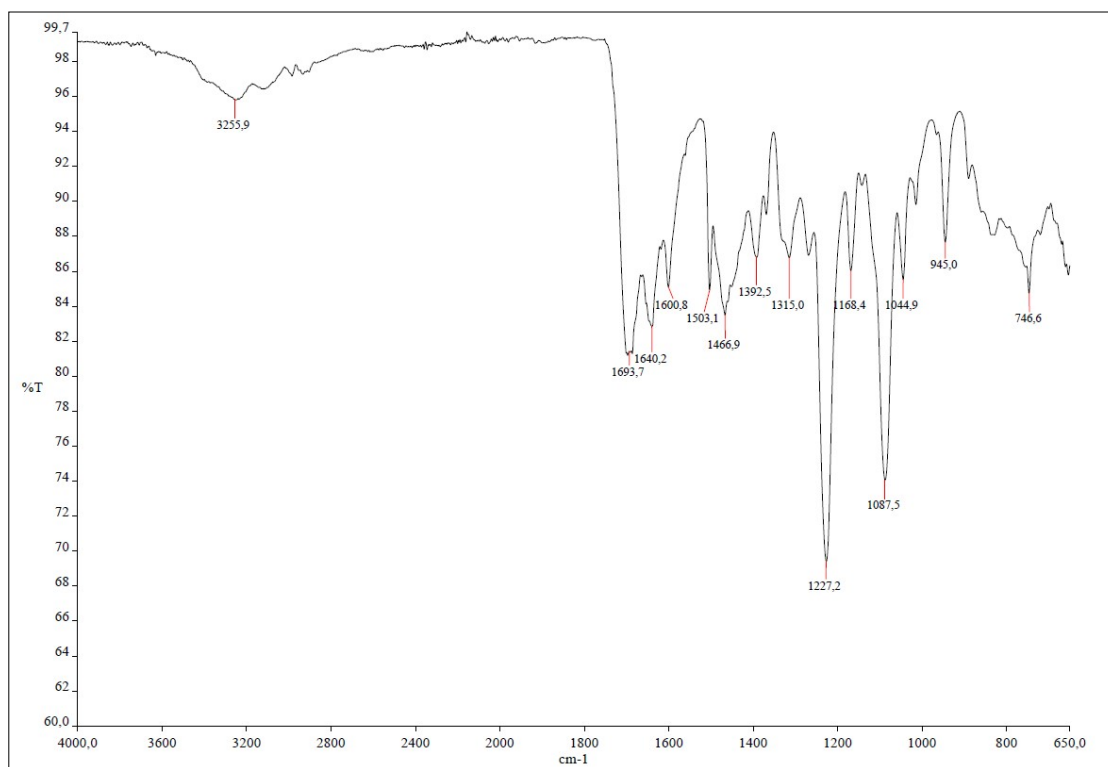


Fig. S5. FT-IR spectrum of compound 4.

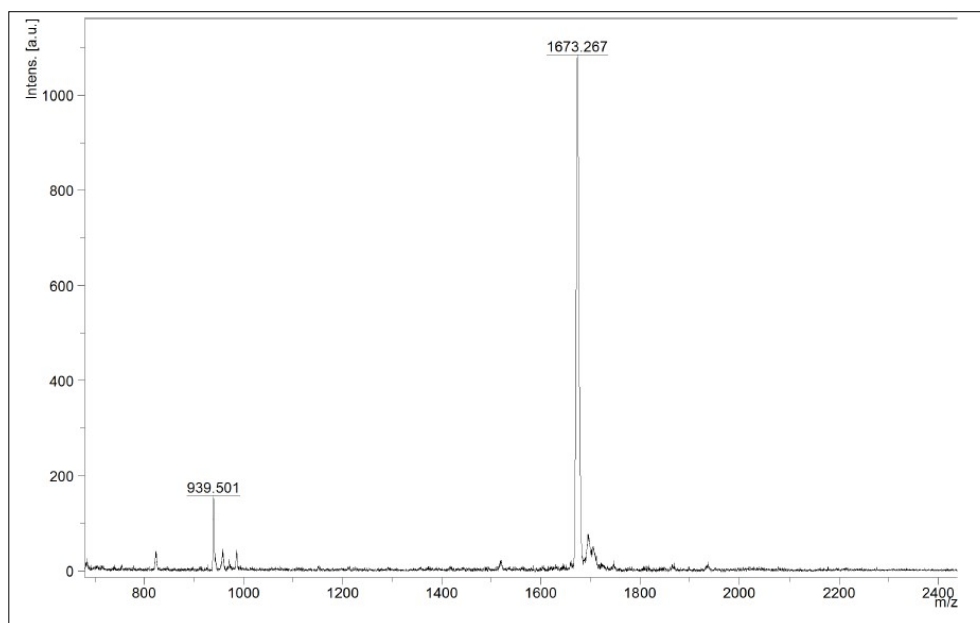


Fig. S6. MALDI-TOF mass spectrum of compound 4 (DIT).

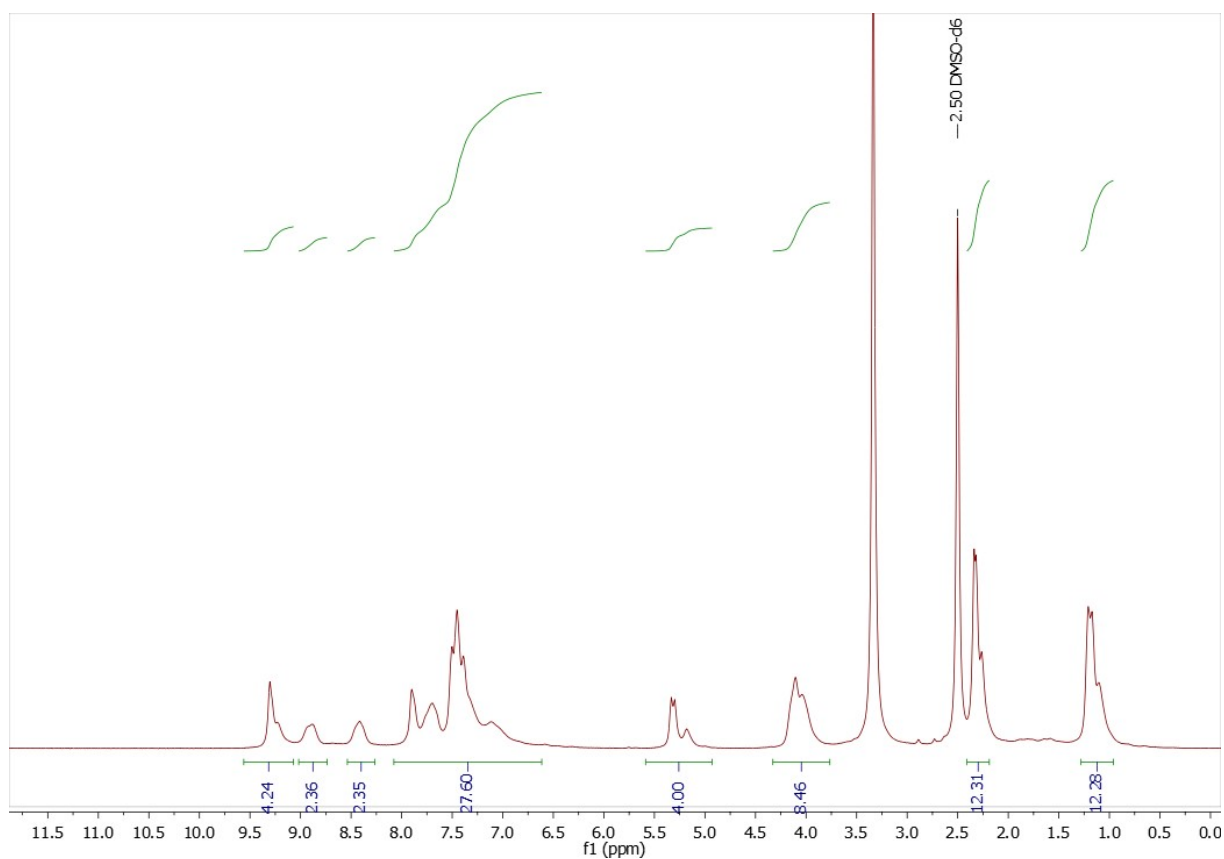


Fig. S7. ¹H NMR spectrum of compound **4** (500 MHz, in DMSO-d₆).

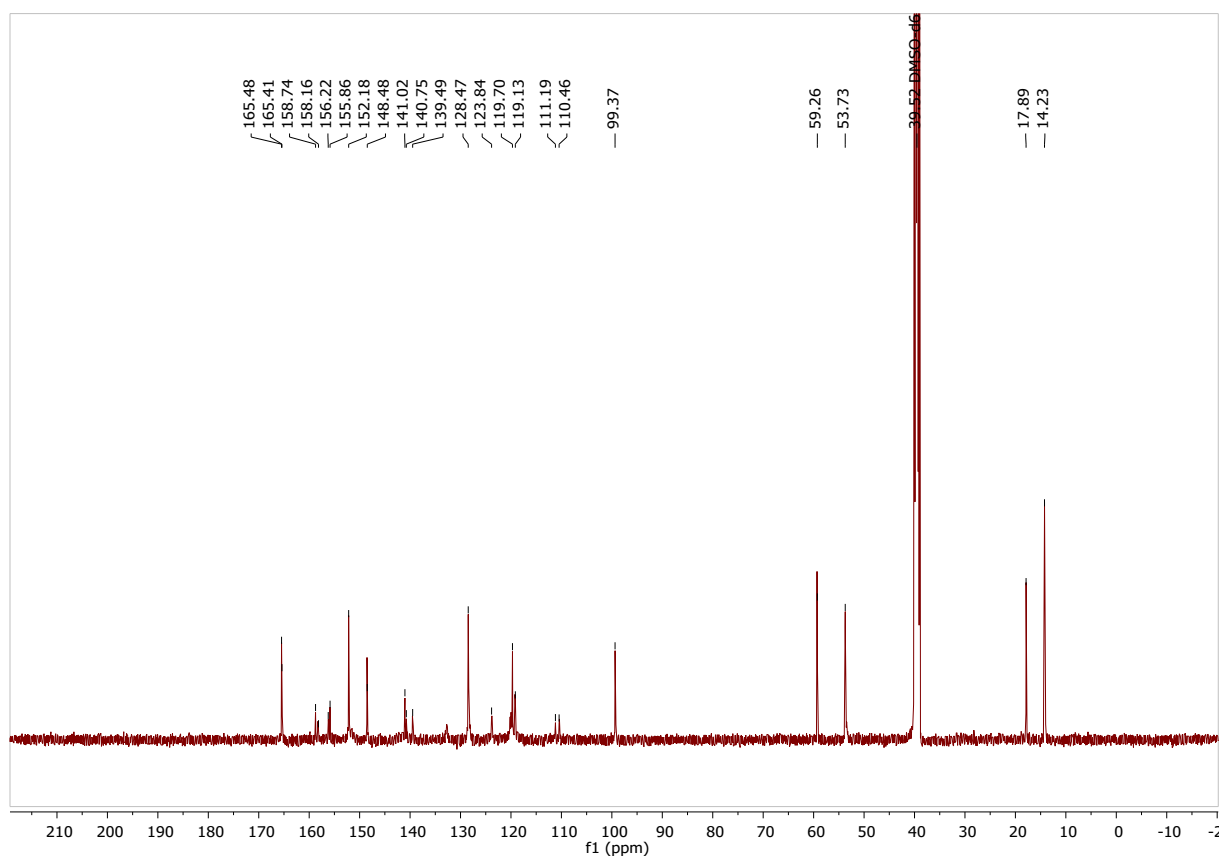


Fig. S8. ¹³C NMR spectrum of compound **4** (125 MHz, in DMSO-d₆).

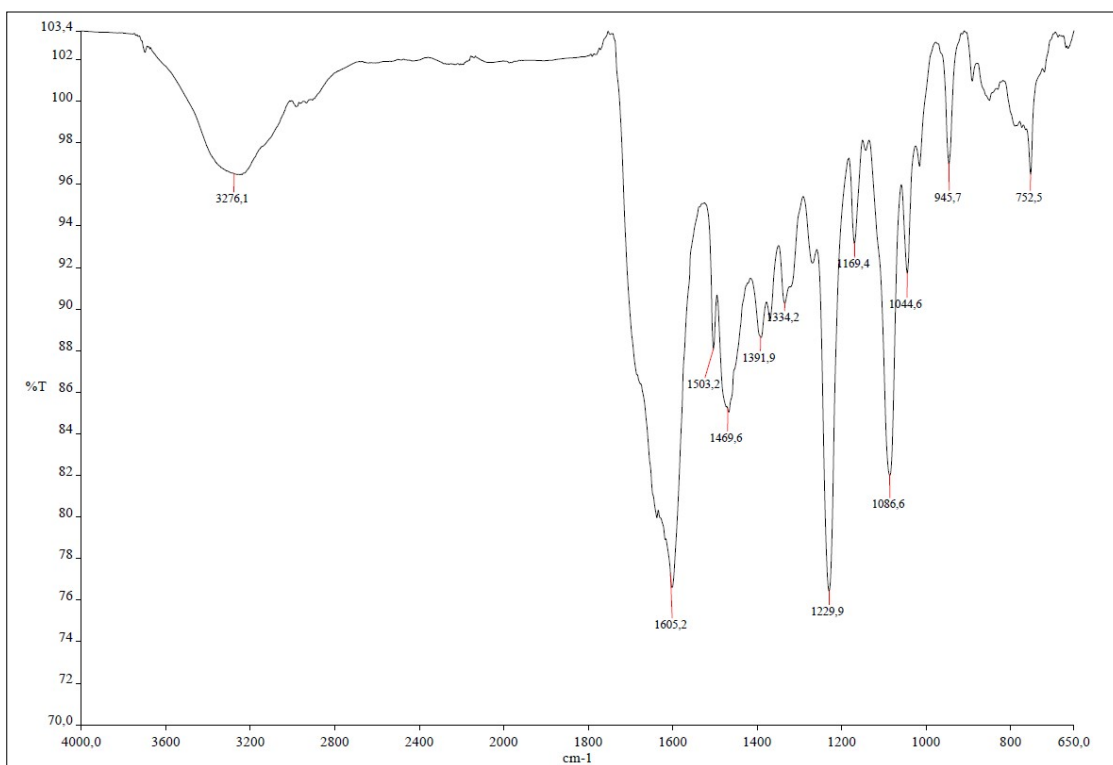


Fig. S9. FT-IR spectrum of compound 5.

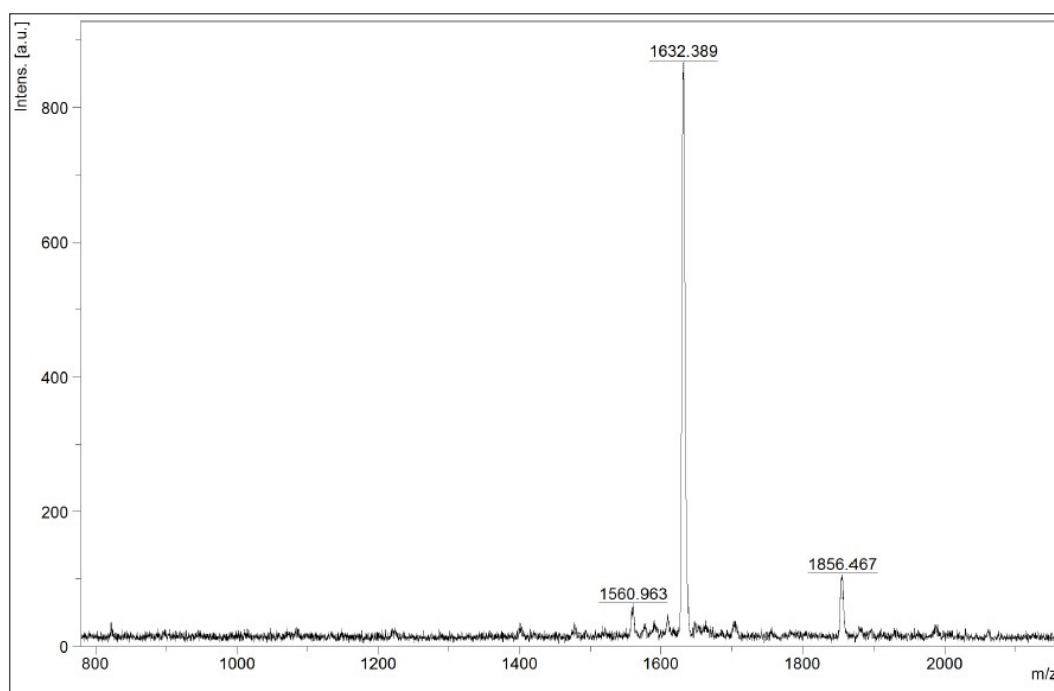


Fig. S10. MALDI-TOF mass spectrum of compound 5 (DIT).

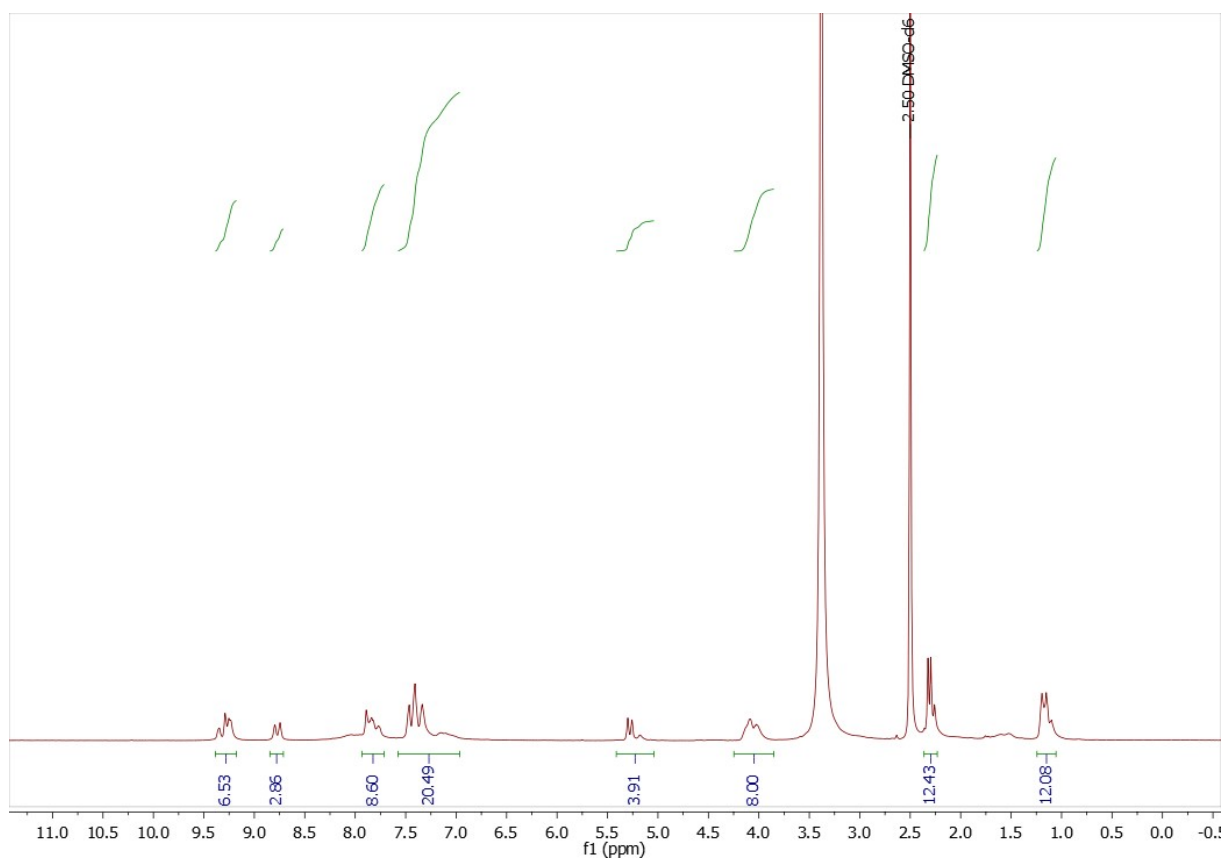


Fig. S11. ¹H NMR spectrum of compound **5** (500 MHz, in DMSO-d₆).

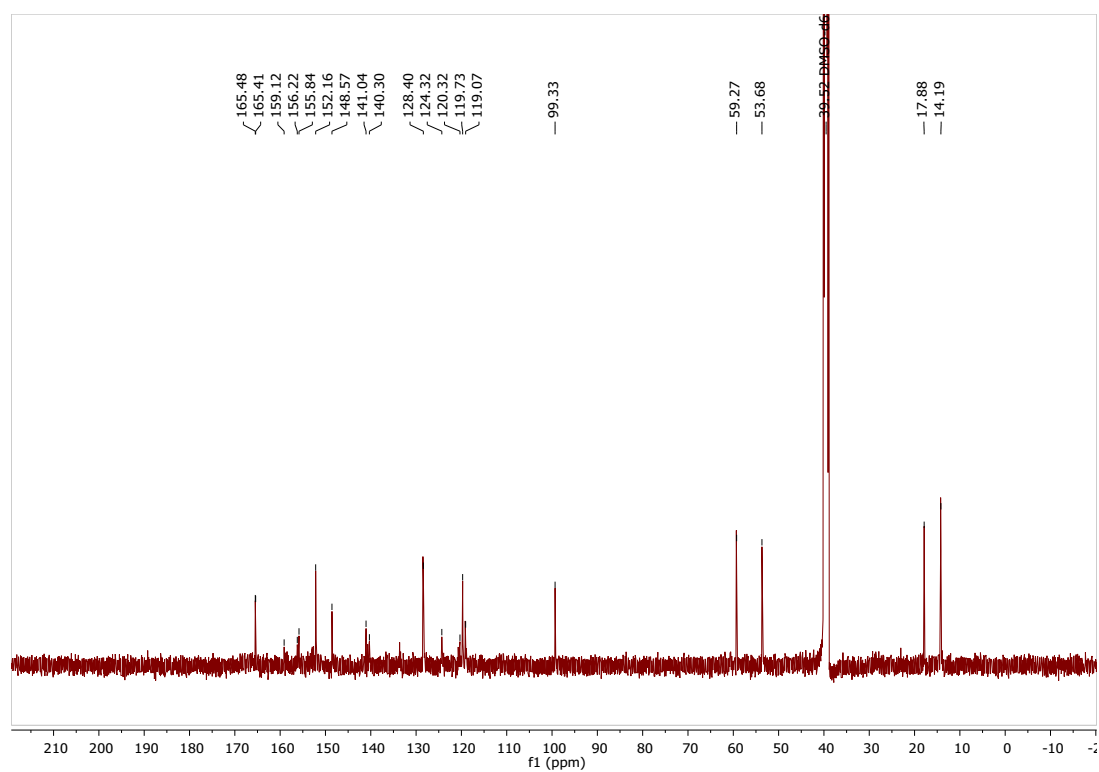


Fig. S12. ¹³C NMR spectrum of compound **5** (125 MHz, in DMSO-d₆).

Photophysical parameters

Fluorescence quantum yields and lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using (Equation 1)^{1,2}

$$\Phi_F = \Phi_F(\text{Std}) \frac{F \cdot A_{\text{Std}}}{F_{\text{Std}} \cdot A} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**4** and **5**) and the standard, respectively. A and A_{Std} are the relative absorbance of the samples (**4** and **5**) and standard at the excitation wavelength, respectively. Unsubstituted **ZnPc** was employed as the standard ($\Phi_F = 0.20$ in DMSO).³

Fluorescence lifetime measurements were performed with FLUOROLOG-3 spectrofluorometer instrument using TCSPC technique. A NanoLED was used as a light source, and standard air cooled R928 PMT as a detector. The instrumental response function was measured with Ludox® (Sigma-Aldrich) colloidal solution at excitation wavelengths of samples. Signals were acquired using a Datastation FluoroHub-B single photon counting controller and data analysis was performed using the commercially available DAS 6 decay analysis software package from Horiba JobinYvon. Goodness of fit was assessed by minimizing the reduced chi squared function, each trace contained 10000 points and the reported lifetime values are the result from at least three independent measurements.

Photochemical parameters

Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in literature.⁴ Typically, a 3 mL portion of the respective substituted zinc(II) phthalocyanine solutions (concentration = 1×10^{-5} M) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described in the reference.⁴ The Φ_Δ values were determined in air using the relative method with unsubstituted ZnPc (in DMSO) as a standard. 1,3-diphenylisobenzofuran (DPBF) was used as chemical quencher for singlet oxygen in DMSO. The Φ_Δ values of the studied zinc(II) phthalocyanines were calculated using equation 2:

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}}$$

(2)

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard unsubstituted ZnPc ($\Phi_{\Delta}^{\text{Std}} = 0.67$ in DMSO).³ R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (4 and 5) and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples and standard, respectively. I_{abs} was determined by using equation 3.

$$I_{\text{abs}} = \frac{\alpha \cdot S \cdot I}{N_A} \quad (3)$$

To avoid chain reactions induced by DPBF in the presence of singlet oxygen⁵ the concentration of quenchers (DPBF) was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizers (concentration = 1×10^{-5} M) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described in literature.⁴ DPBF degradation at 417 nm was monitored. The light intensity used for Φ_{Δ} determinations was found to be 6.51×10^{15} photons $\text{s}^{-1} \text{cm}^{-2}$.

Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in literature.⁴ Photodegradation quantum yields were determined using equation 4,

$$\Phi_d = \frac{(C_0 - C_t) \cdot V \cdot N_A}{I_{\text{abs}} \cdot S \cdot t} \quad (4)$$

where C_0 and C_t are the samples (4 and 5) concentrations before and after irradiation respectively, V is the reaction volume, N_A is the Avogadro's constant, S is the irradiated cell area, t is the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (4 and 5). A light intensity of 2.17×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$ was employed for Φ_d determinations.

References

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