

## Supporting Information

### Novel axially symmetric and unsymmetric silicon (IV) phthalocyanines having anti-inflammatory groups-: synthesis, characterization and their biological properties

Gizem Gümüsgöz<sup>1</sup>, Belgin Şahin<sup>1</sup>, Serpil Gonca<sup>2</sup>, Sadin Özdemir<sup>3\*</sup>,

Devrim Atilla<sup>1\*</sup> Ayşe Gül Gürek<sup>1</sup>,

<sup>1</sup>*Gebze Technical University, Department of Chemistry, 41400, Gebze, Kocaeli/TURKEY*

<sup>2</sup>*Department of Pharmaceutical Microbiology, Faculty of Pharmacy, University of Mersin, Turkey, TR-33343 Yenisehir, Mersin, Turkey*

<sup>3</sup>*Food Processing Programme, Technical Science Vocational School, Mersin University, TR-33343 Yenisehir, Mersin, Turkey*

## Contents

Materials and apparatus .....	3
Fig. S1. IR Spectrum of 1 .....	3
Fig. S2. MALDI-TOF MS Spectrum of 1.....	4
Fig. S3. <sup>1</sup> H NMR Spectrum of 1 (in <i>d</i> -CDCl <sub>3</sub> ,*water, and EtOH as residual.....	4
Fig. S4. IR Spectrum of 2. ....	5
Fig. S5. MALDI-TOF MS Spectrum of 2.....	6
Fig. S6. <sup>1</sup> H NMR Spectrum of 2 (in <i>d</i> -CDCl <sub>3</sub> ,*water, and EtOH as residual) .....	6
Synthesis and characterization of 3.....	7
Fig. S7. IR spectra of 3. ....	7
Fig. S8. <sup>1</sup> H-NMR spectra of 3.....	8
Fig. S9. UV-Vis absorption spectra of 2, a) in different solvents (12 μM), b) concentration-dependent (2-12 μM) change at room temperature in DMF, c) concentration-dependent (2-12 μM) change at room temperature in DMSO. ....	8
Fig. S10. a) Normalized emission ( $\lambda_{\text{ex}}$ , 645 nm), excitation and absorbance spectra of 2 at room temperature (concentration 0.5 μM) in DMF, b) Normalized emission ( $\lambda_{\text{ex}}$ , 645 nm), excitation and absorbance spectra of 1 at room temperature (concentration 0.5 μM) in DMSO, c) Fluorescence decay profiles of 2 measured using a 670 nm laser excitation source.....	9
Flouresence quantum yield ( $\Phi_{\text{F}}$ ) calculation.....	9
Fluorescence Lifetime Measurements .....	9
Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) determination.....	10
References .....	10

## Materials and apparatus

Materials and methods IR spectra were recorded between 4000 and 500  $\text{cm}^{-1}$  using a PerkinElmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. UV-Vis spectra of the newly synthesized Pc complexes were determined using Shimadzu 2600 UV/Vis spectrophotometer. MALDI-TOF mass spectrometry analyses were carried out on Bruker microflex LT MALDI-TOF MS spectrometer using dihydroxybenzoic acid as a matrix.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  solutions on a Varian 500 MHz spectrometer. TMS standart was used as internal standart for  $^1\text{H}$ -NMR measurements. Elemental analysis was carried out using Thermo Finnigan Flash 1112 Instrument. Steady-state fluorescence excitation and emission spectra were recorded using a Varian Cary Eclipse spectrofluorometer. Singlet oxygen quantum yield (FD) measurements were done by Horiba Jobin–Yvon Fluorometer with Hamamatsu NIR PMT 5509 by using direct method. All solvents and chemicals were of reagent-grade quality, purchased from Sigma Aldrich Chemical Co. and Merck

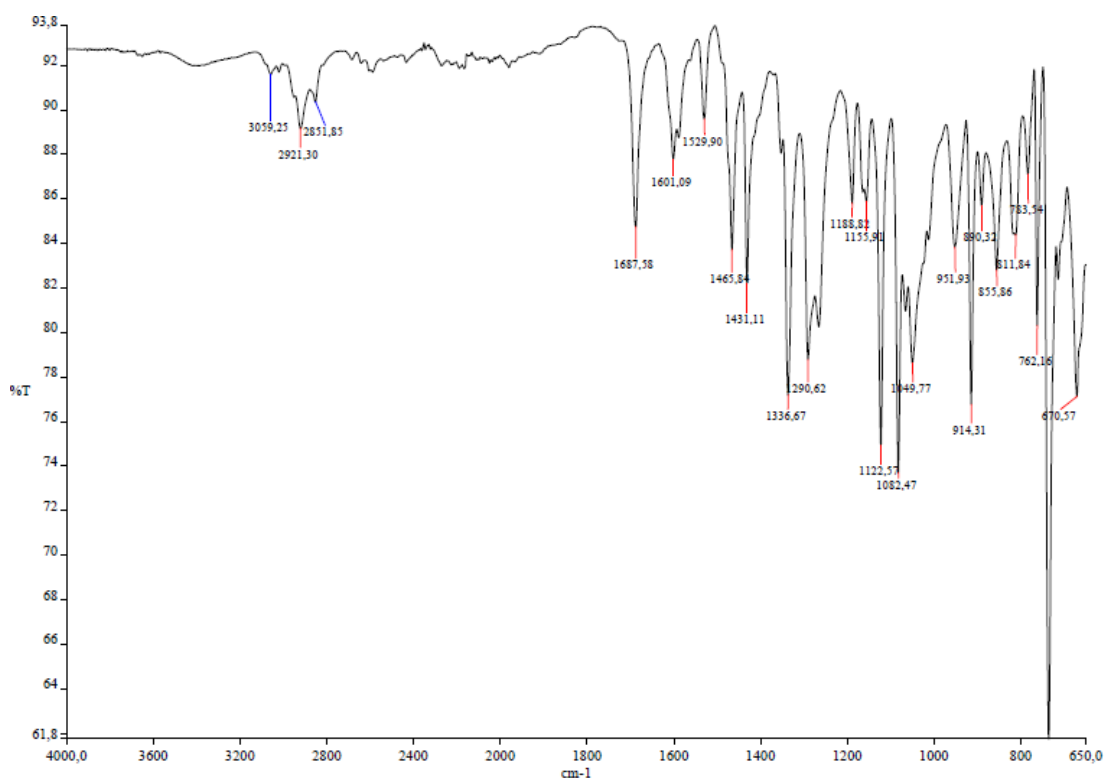


Fig. S1. IR Spectrum of 1.

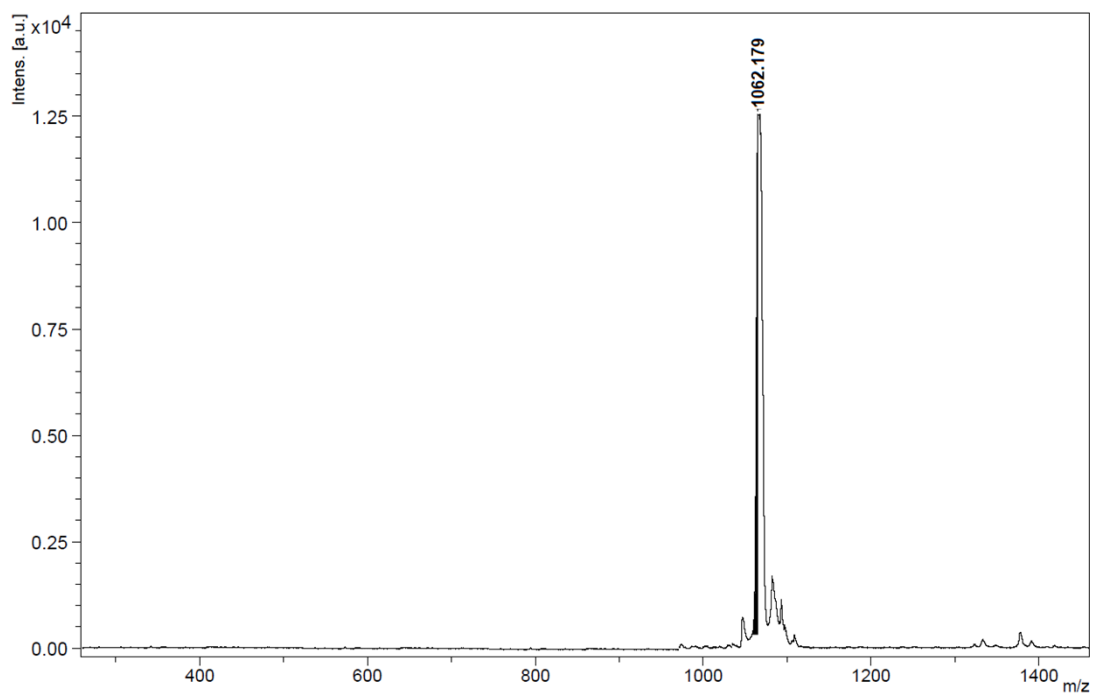


Fig. S2. MALDI-TOF MS Spectrum of 1.

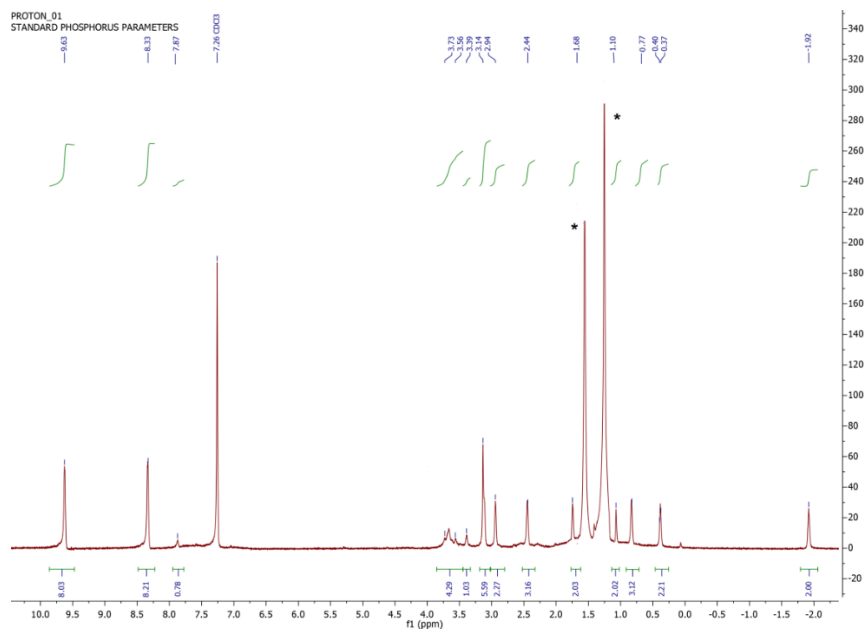


Fig. S3. <sup>1</sup>H NMR Spectrum of 1 (in d-CDCl<sub>3</sub>, \*water, and EtOH as residual).

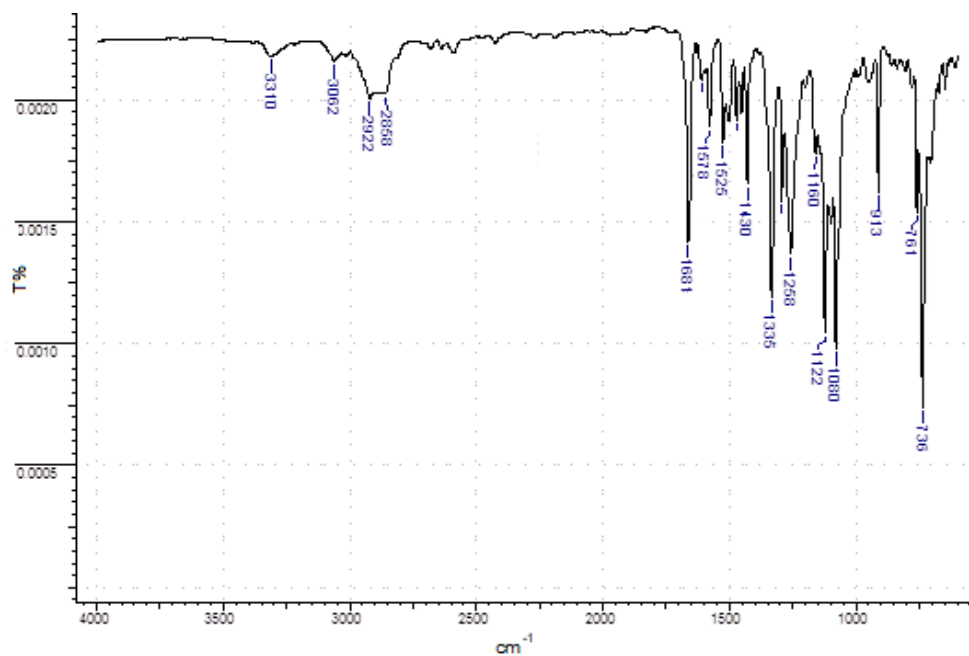
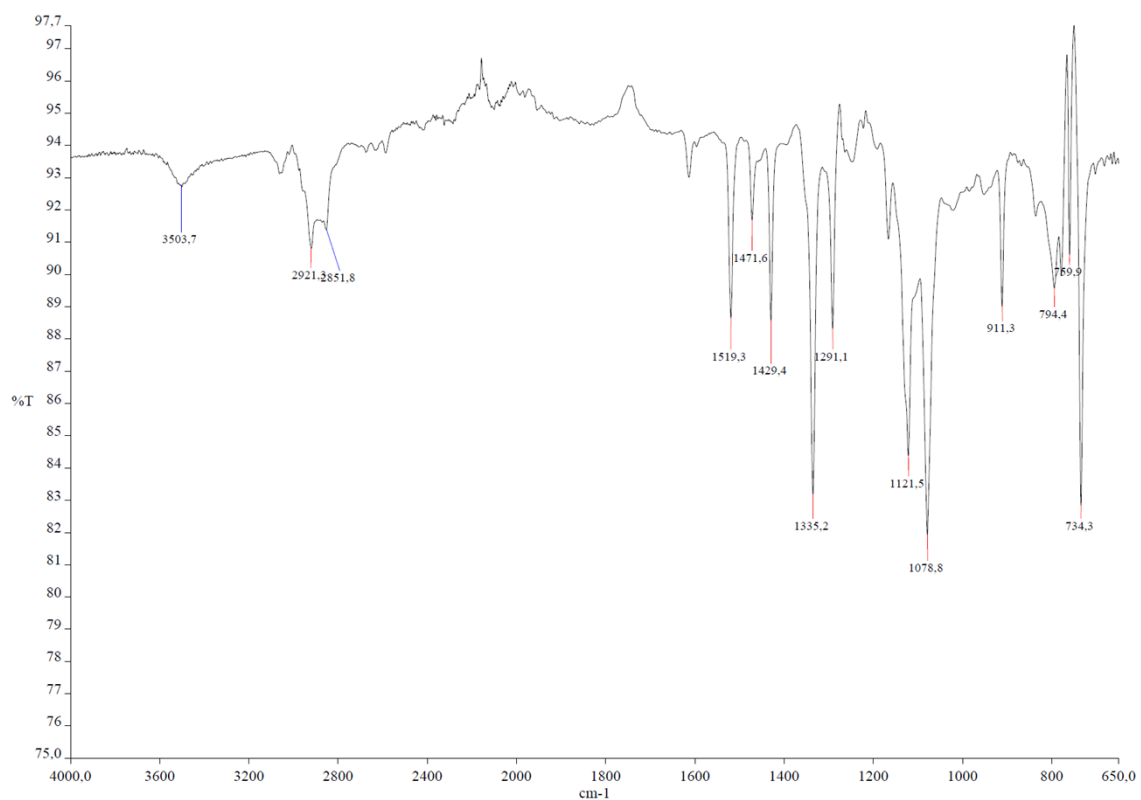


Fig. S4. IR Spectrum of 2.

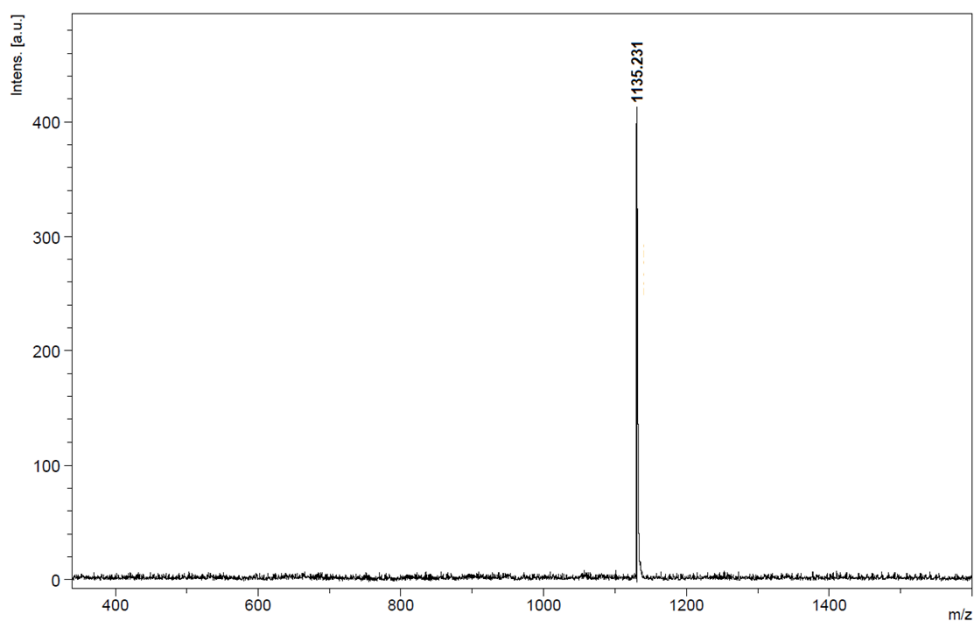


Fig. S5. MALDI-TOF MS Spectrum of 2.

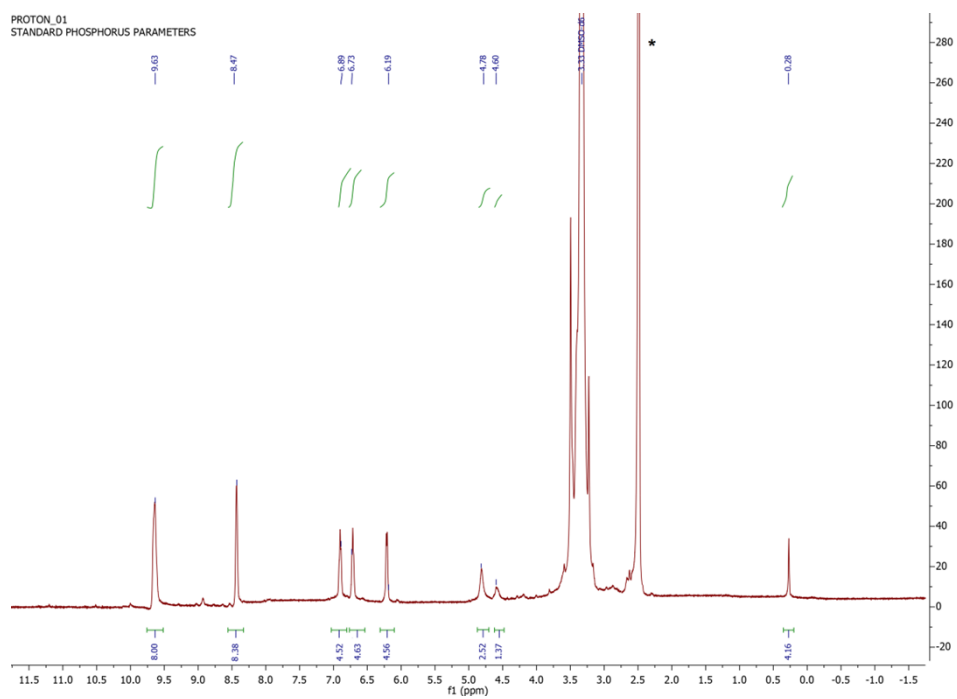


Fig. S6.  $^1\text{H}$  NMR Spectrum of 2 (in  $d\text{-CDCl}_3$ , \*water, and EtOH as residual).

### Synthesis and characterization of 3

A mixture of SiPcCl<sub>2</sub> (0.087 mmol), triethylene glycol monomethyl ether and dry potassium carbonate (0.27 mmol) solved in toluene (20 mL) refluxed with stirring for 18 h under argon atmosphere. After the reaction mixture was cooled at room temperature, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on aluminium oxide with CH<sub>2</sub>Cl<sub>2</sub>:EtOH (50:1) as solvent system. Yield 25%. FT-IR (ATR):  $\nu_{\max}$ , /cm<sup>-1</sup>: 3053 (Ar-H), 2920–2850 (Aliph. C-H), 1522, 1471, 1426, 1332, 1284, 1249, 1201, 1165, 1102, 1074, 945, 905, 872, 839, 791, 730. <sup>1</sup>H NMR (CDCl<sub>3</sub>) ( $\delta$  ppm): 9.6 (s, 8H, Ar-H), 8.3(s, 8H, Ar-H), 3.2 (s, 10H, Aliph-H), 3.0 (s, 4H, Aliph-H), 2,7 (s, 4H, Aliph-H), 1.7 (s, 4H, Aliph-H), 0.4 (s, 4H, Aliph-H), -2.0 (s, 4H, aliph-H).

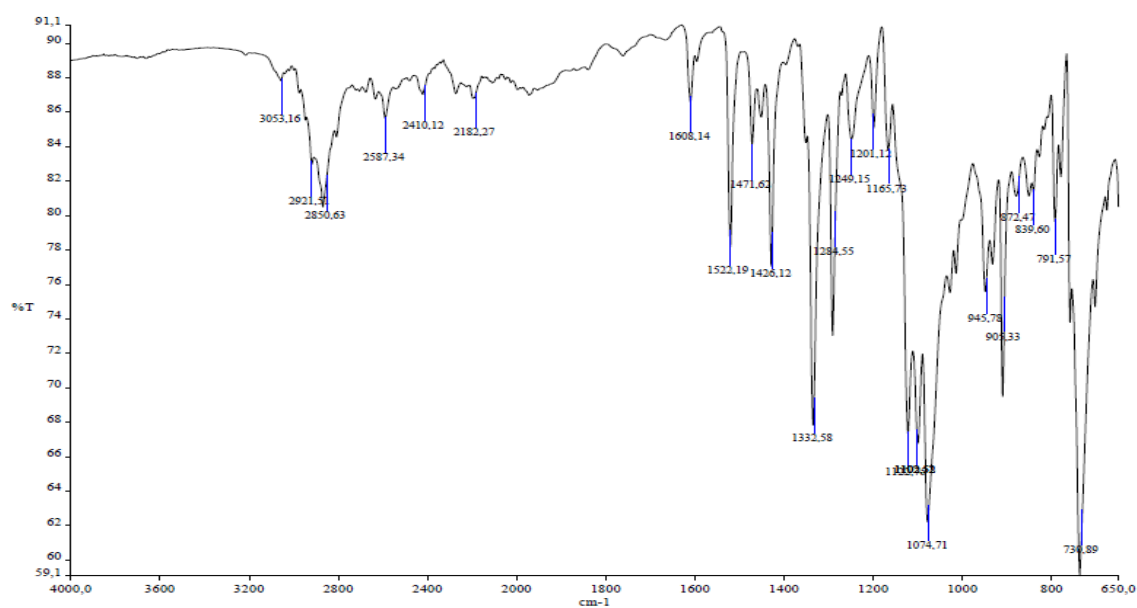


Fig. S7. IR spectra of 3.

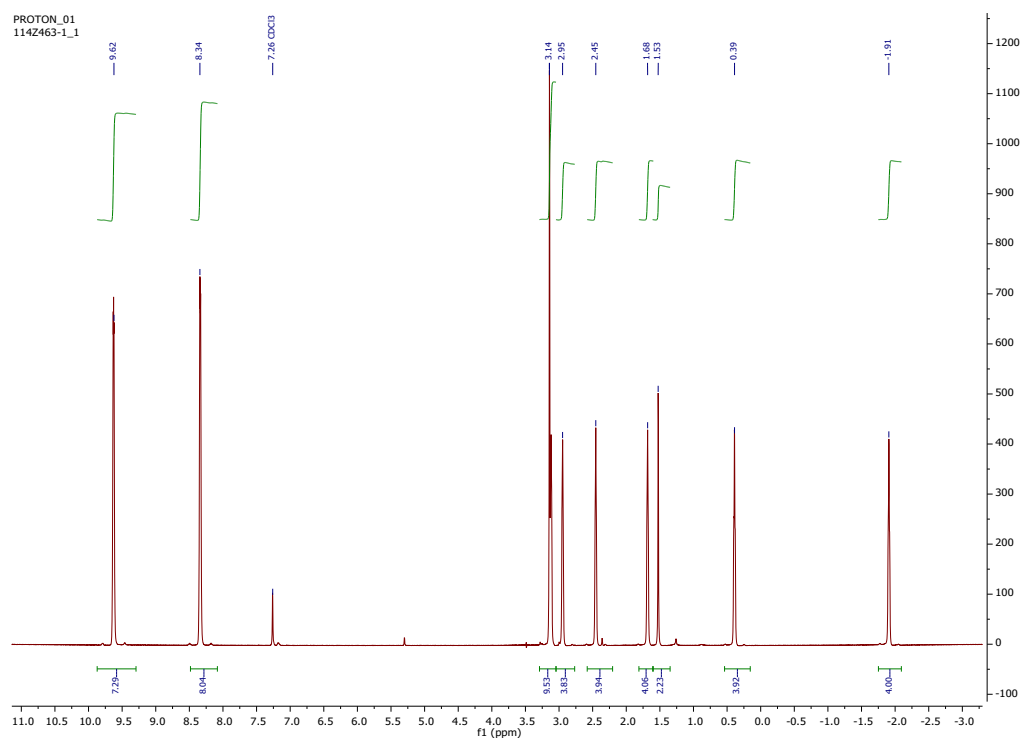


Fig. S8.  $^1\text{H-NMR}$  spectra of 3.

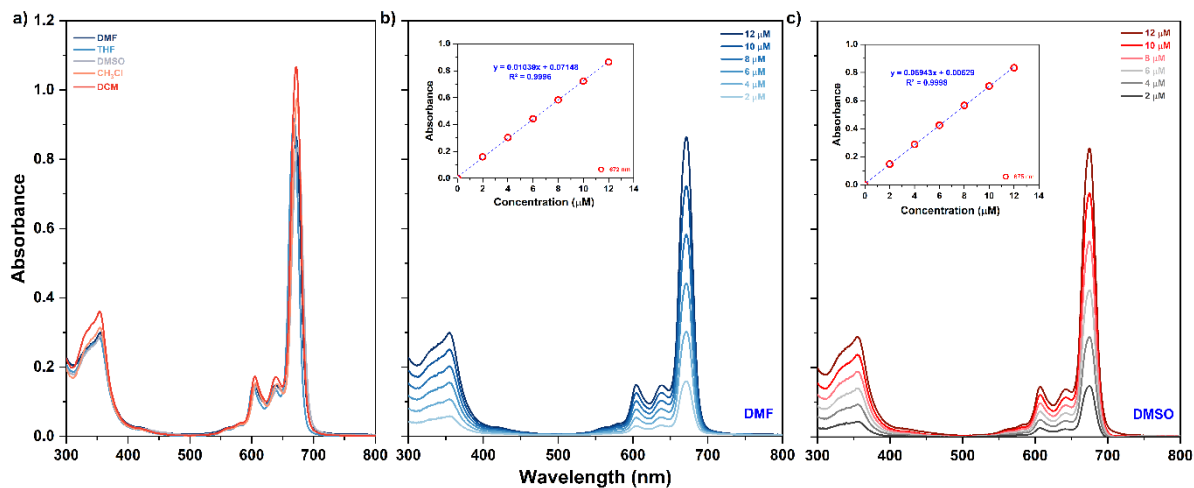


Fig. S9. UV-Vis absorption spectra of 2, a) in different solvents (12  $\mu\text{M}$ ), b) concentration-dependent (2-12  $\mu\text{M}$ ) change at room temperature in DMF, c) concentration-dependent (2-12  $\mu\text{M}$ ) change at room temperature in DMSO.



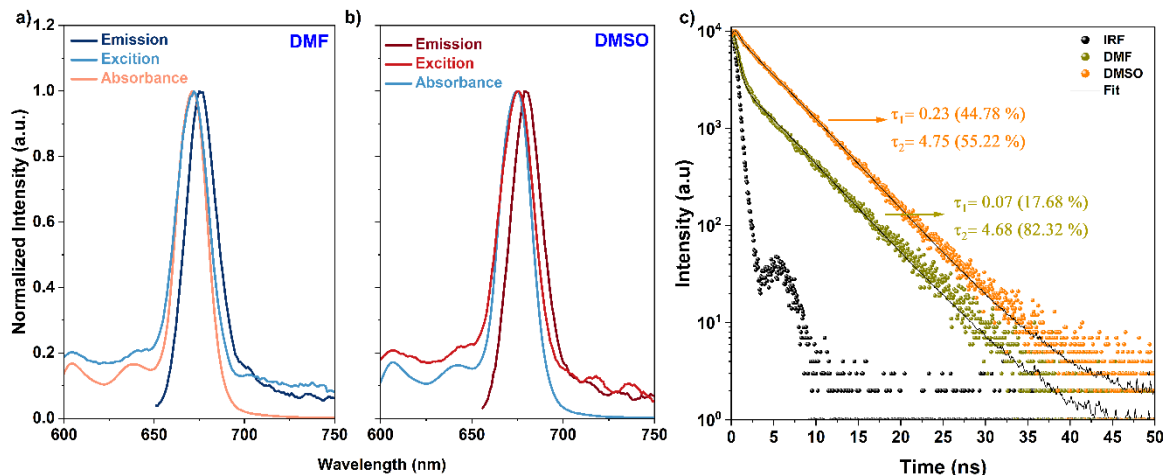


Fig. S10. a) Normalized emission ( $\lambda_{ex}$ , 645 nm), excitation and absorbance spectra of 2 at room temperature (concentration 0.5  $\mu$ M) in DMF, b) Normalized emission ( $\lambda_{ex}$ , 645 nm), excitation and absorbance spectra of 1 at room temperature (concentration 0.5  $\mu$ M) in DMSO, c) Fluorescence decay profiles of 2 measured using a 670 nm laser excitation source

#### Fluorescence quantum yield ( $\Phi_F$ ) calculation

Fluorescence quantum yields ( $\Phi_F$ ) were calculated to compare the photophysical properties of Pcs with a comparative method using unsubstituted ZnPc as a standard in two different solution environments, DMF ( $\Phi_F = 0.25$ ) and DMSO ( $\Phi_F = 0.25$ ). Fluorescence quantum yield was calculated according to the equation (S1).

$$\Phi_F = \Phi_{F_{Std}} \frac{F A_{Std} \eta^2}{F_{Std} A \eta_{Std}^2} \quad (S1)$$

In Eq. S1,  $\Phi_F$  and  $\Phi_{F_{Std}}$  are the quantum yields of the sample and reference and  $\eta_s$  and  $\eta_r$  are refractive indexes of the solvents used for the measurements of the sample and reference.  $F$  and  $F_{std}$  are the integrated areas under the emission spectra of the sample and the reference,  $A$  and  $A_{std}$  are the maximum absorbance value of the sample and the reference

#### Fluorescence Lifetime Measurements

Fluorescence lifetimes were recorded using Horiba FL3-2IHR with a Time Correlated Single Photon Counting (TCSPC) system. The instrument was equipped with a nanoLED 670-LH as the excitation source. During measurements, the Instrument Response Function (IRF) was obtained from a nonfluorescence suspension of a colloidal silica (LUDOX 30%, Sigma

Aldrich) in water, held in 10 mm path length quartz cell and was considered to be wavelength independent

#### Singlet oxygen quantum yield ( $\Phi_{\Delta}$ ) determination

For direct method, the calculation of the  $^1\text{O}_2$  quantum yields was based on the detection of NIR  $^1\text{O}_2$  luminescence by an optical method based on the comparison of single molecular oxygen phosphorescence produced by the Pc sample with that generated by the reference ZnPc in the near infrared region at 1276 nm.  $\Phi_{\Delta}$  values were calculated according to Equation S2.

$$\Phi_{\Delta s} = \Phi_{\Delta r} \frac{\eta_s^2 A_r I_s}{\eta_r^2 A_s I_r} \quad (\text{S2})$$

In Eq. S2,  $\Phi_{\Delta s}$  and  $\Phi_{\Delta r}$  are the singlet oxygen yields of the sample and reference and  $\eta_s$  and  $\eta_r$  are refractive indexes of the solvents used for the measurements of the sample and reference.  $A_s$  and  $A_r$  are the absorbance of the sample and the reference, and  $I_s$  and  $I_r$  are the integrated areas under the singlet oxygen emission spectra of the sample and the reference, respectively.

#### References

1. A. Ogunsipe, D. Maree, T. Nyokong, T., *J Mol Struct.*, 2003, 650 (1-3), 131-140.
2. S. Fery-Forgues, D. Lavabre, *J Chem Educ.*, 1999, 76 (9), 1260-1266.
3. A. Staicu, A. Pascu, M. Boni, M. L. Pascu, M. Enescu, M., *J Mol Struct.*, 2013, 1044, 188-193.
4. F. Wilkinson, W.P. Helman, A. B. Ross, *J Phys Chem Ref Data*, 1993, 22 (1), 113-262.
5. V. Patil, Q. H.Sodji, J. R. Kornacki, M. Mrksich, A. K. Oyelere, *J Med Chem.*, 2013, 56 (9), 3492-506.