Electronic Supplementary Information (ESI)

Synthesis, characterization and photophysicochemical properties of zinc(II) phthalocyanine with new benzenesulfonamide derivative substituents

Authors: Gülen Atiye Öncül[1] · Ömer Faruk Öztürk[1*] · Mehmet Pişkin[2]

✉ Ömer Faruk Öztürk

ofozturk@comu.edu.tr

[1] Çanakkale Onsekiz Mart University, Faculty of Arts and Sciences, Department of Chemistry, Çanakkale, Turkey.

[2] Çanakkale Onsekiz Mart University, Technical Sciences School, Food Processing, Çanakkale, Turkey.

Materials

All the chemicals used in this study were of reagent grade quality. Sulphapyridine, 5-Bromo-3-methoxysalicylaldehyde, p-Toluenesulfonic acid monohydrate, 4-Nitrophthalonitrile, Potassium carbonate, Zinc acetate dihydrate and 1,3-diphenylisobenzofuran (DPBF) were purchased from Sigma-Aldrich and used in experimental studies as purchased. Before starting to work, the solvents were purified, dried, and stored over molecular sieves (4Å) as described by Perrin and Armarego [S1]. All reactions were carried out under dry nitrogen atmosphere unless otherwise noted. The novel 2.9(10),16(17),23(24)-tetra-[(E)-4-((5-bromo-3-methoxy-2-(λ^1-oxidanyl)benzylidene)amino-N-(pyridin-2-yl)benzenesulfonamide)]zinc(II) phthalocyanine (the **ZnPc 3**) synthesized in this study was purified by washing in Soxhlet apparatus with hot water, ethanol methanol, acetonitrile, acetone and diethyl ether, respectively. In this study, column chromatography on silica gel 60 was performed as an advanced purification technique to obtain the pure new type benzenesulfonamide-containing phthalonitrile derivative (**2**) and its pure **ZnPc 3**. The purity of the products was tested in each step by thin layer chromatography (Silica gel F-254 coated TLC plate).

Equipment

Melting points of each synthesized compounds (**1** and **2**) and the **ZnPc 3** in this study was measured by an electro thermal apparatus. IR spectra were recorded on a Perkin Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer. ^{1}H-NMR and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of the TUBITAK, Marmara Research Centre. The mass spectrum was acquired on Microflex MALDI-TOF mass spectrometer (Bruker Daltonics MS Germany) equipped with a nitrogen UV-Laser operating at 337 nm and spectra were recorded in reflectron mode with an average of 50 shots using 2,5-dihydroxy benzoic acid (DHB) as a matrix. The sample for matrix-assisted laser desorption/ionization

(MALDI) was prepared by mixing sample solutions (1 mg/mL in $CHCl_3$) with the matrix solution (1:10 v/v) in a 0.5 mL eppendorf® micro tube. Finally, 0.5 μL of this mixture was deposited on the sample plate, dried at room temperature, and then analyzed. Optical spectra in the UV-*vis* region were recorded with a Perkin Elmer Lambda 25 spectrophotometer and a Shimadzu 2101 UV/Vis spectrophotometer. Fluorescence lifetime was measured by 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. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvette at room temperature. The instrumental response function was measured with the use of Ludox® (Sigma-Aldrich) colloidal solution at excitation wavelengths of samples. Signals were received 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 were obtained from at least three independent measurements [S2, S3].

Photophysical parameters

●Fluorescence quantum yield and lifetime

Fluorescence quantum yield (Φ_F) was determined by the comparative method using Equation 1 [S4, S5].

$$\Phi_F = \Phi_F(Std)\frac{F.A_{Std}.n^2}{F_{Std}.A.n_{Std}^2} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the **ZnPc 3** and the standard, respectively. A and A_{Std} are the relative absorbance of the **ZnPc 3** and standard at the

excitation wavelength, respectively. n^2 and n_{Std}^2 are the refractive indices of solvents for the **ZnPc 3** as a sample and standard, respectively. Unsubstituted zinc(II) phthalocyanine (**Std-ZnPc**) (in DMSO) (Φ_F = 0.20) [S6] was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions was ranged between 0.04 and 0.05 at the excitation wavelength. Natural radiative lifetime (τ_0) was evaluated using Equation 2 [S4, S5].

$$\Phi_F = \frac{\tau_F}{\tau_0} \qquad (2)$$

The rate constant for fluorescence (k_F) was evaluated using Equation 3.

$$k_F = \Phi_F / \tau_F \qquad (3)$$

The non-radiative rate constant (k_{nr}) was evaluated using Equation 4 [S7].

$$k_{nr} = 1 - \Phi_F / \tau_F \qquad (4)$$

The observed fluorescence-decay rate constant (k_{obs}) was evaluated using

Equation 5[S8].

$$k_{obs} = k_F + k_{nr} \qquad (5)$$

The natural radiative lifetime (τ_0) was evaluated using Equation 6.

$$\tau_0 = \tau_F / \Phi_F \qquad (6)$$

The non-radiative lifetime (τ_{nr}) was evaluated using Equation 7 [S8].

$$\tau_{nr} = 1 / k_{nr} \qquad (7)$$

Photochemical parameters

Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations are carried out using the experimental set-up described in literature in DMSO solution [S9, S10]. Typically, a 3 mL portion of the respective standard ZnPc and the **ZnPc 3** solutions (C = 1×10^{-5} M) containing the singlet oxygen quencher was irradiated in the Q band region with the photoirradiation set-up described in the references [S8, S9]. Φ_Δ value was determined in air using the relative method with ZnPc as standard in DMSO. 1,3-Diphenylisobenzofuran (DPBF) was used as the chemical quencher for singlet oxygen [S11]. Equation 8 was employed for the determination of Φ_Δ values:

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R \cdot I_{abs}^{Std}}{R^{Std} \cdot I_{abs}} \qquad (8)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yields for the standard ZnPc (Φ_Δ^{Std} = 0.67 in DMSO) [S12] and R and R_{Std} are the DPBF photobleaching rates in the presence of the respective the **ZnPc 3** and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the samples and standard, respectively. To avoid chain reactions induced by quencher (DPBF) in the presence of singlet oxygen, the concentration of quencher (DPBF) was lowered to ~3×10^{-5} M [S13].

Solutions of sensitizer (C = 1×10^{-5} M) containing quencher (DPBF) were prepared in the dark and irradiated in the Q band region. DPBF degradation at 417 nm was monitored. The light intensity 6.21×10^{15} photons s^{-1} cm^{-2} was used for Φ_Δ determinations.

Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations are carried out using the experimental set-up described in the literature [S9, S10]. Photodegradation quantum yield were determined using equation 9 in DMSO,

$$\Phi_d = \frac{(C_0 - C_t) \,.\, V \,.\, N_A}{I_{abs} . S \,.\, t} \qquad (9)$$

where C_0 and C_t are the samples concentrations before and after irradiation, respectively. V is the reaction volume, N_A the Avogadro's constant, S the irradiated cell area and t the irradiation time, I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the sample. A light intensity of 2.23×10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

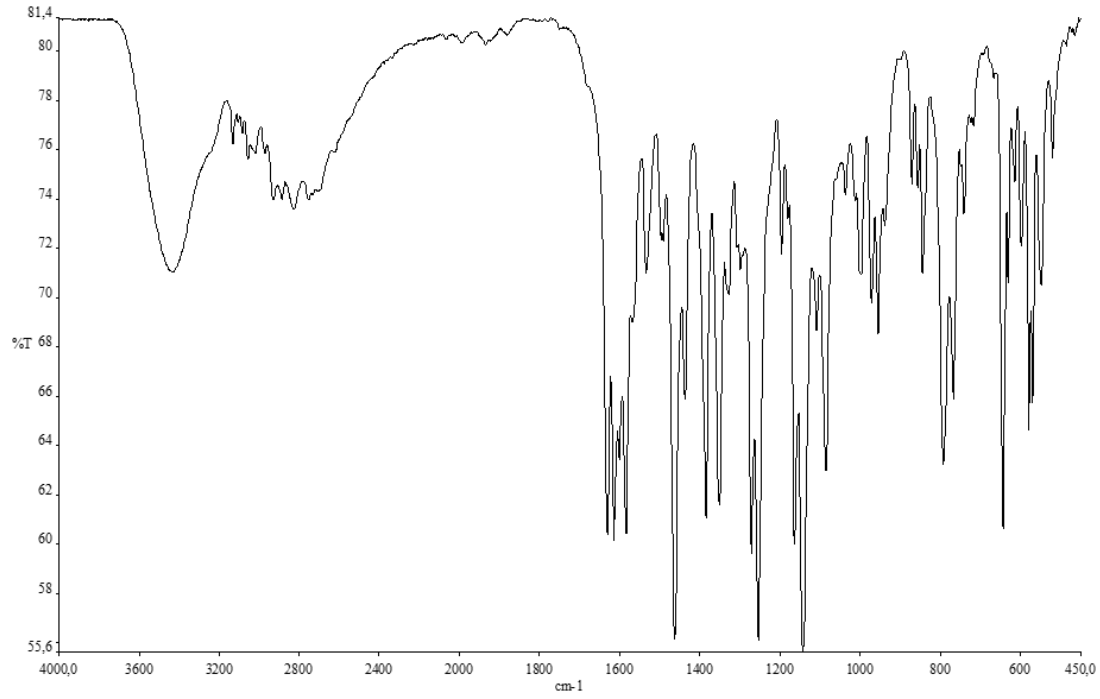

Figure S1. FTIR spectrum of the compound **1**.

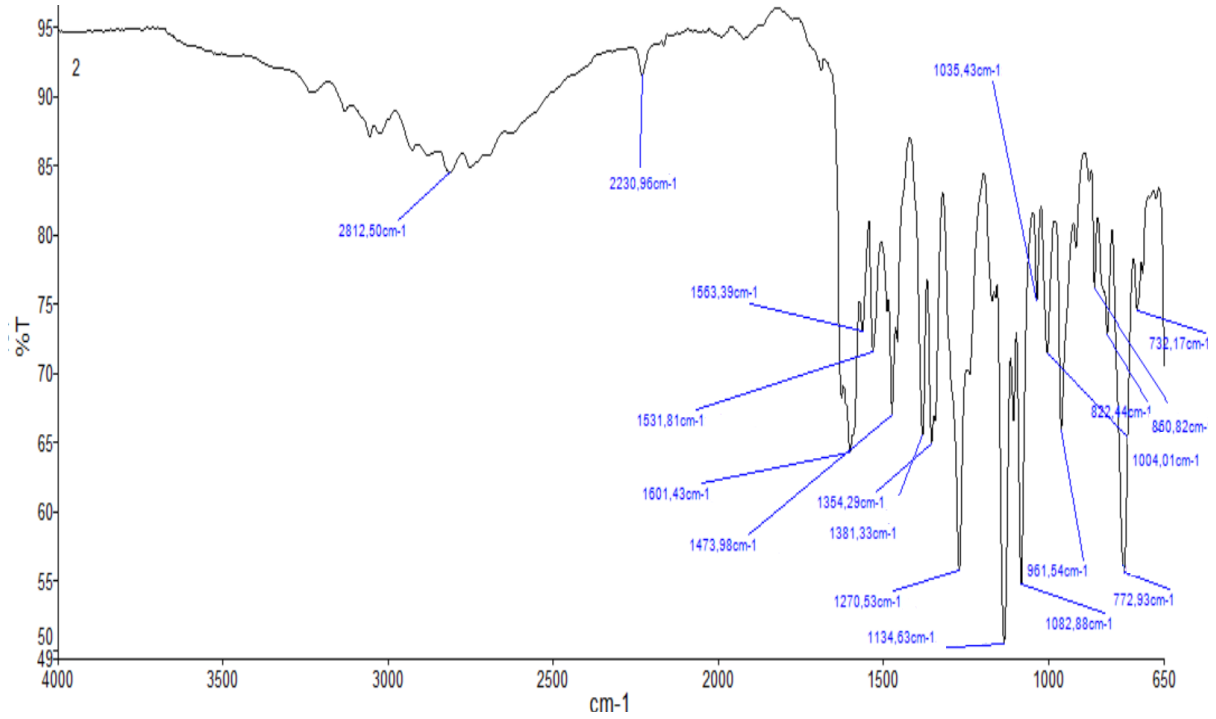

Figure S2. FTIR spectrum of the compound **2.**

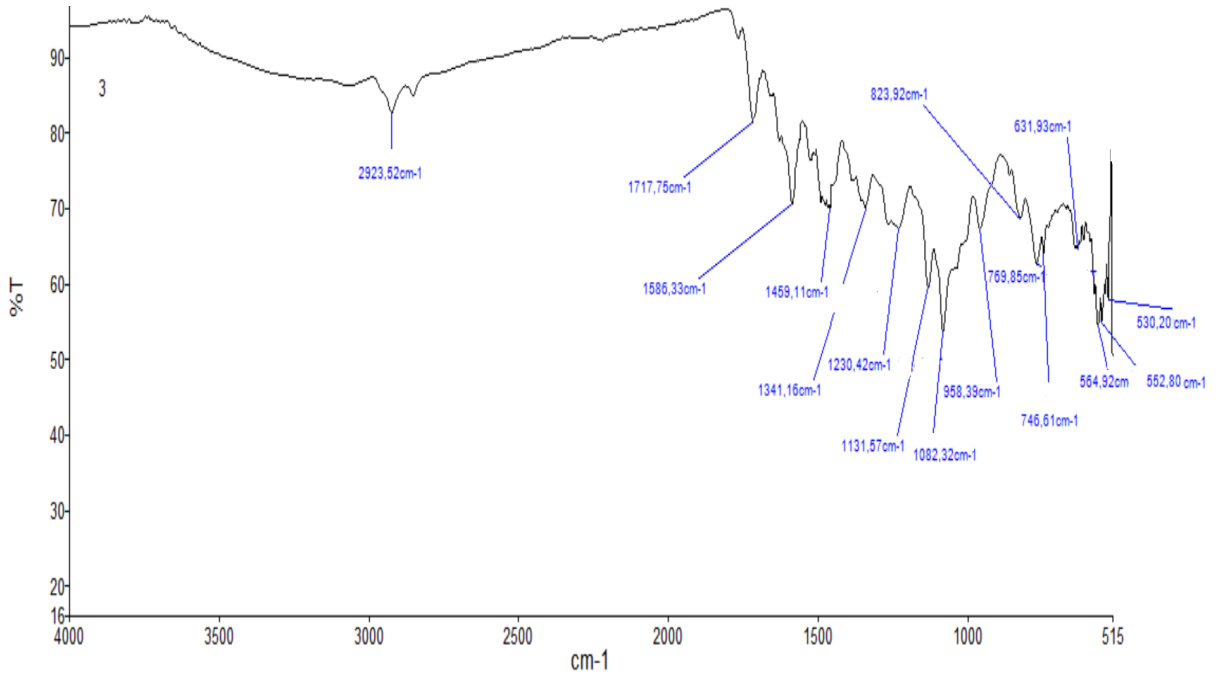

Figure S3. FTIR spectrum of the **ZnPc 3**.

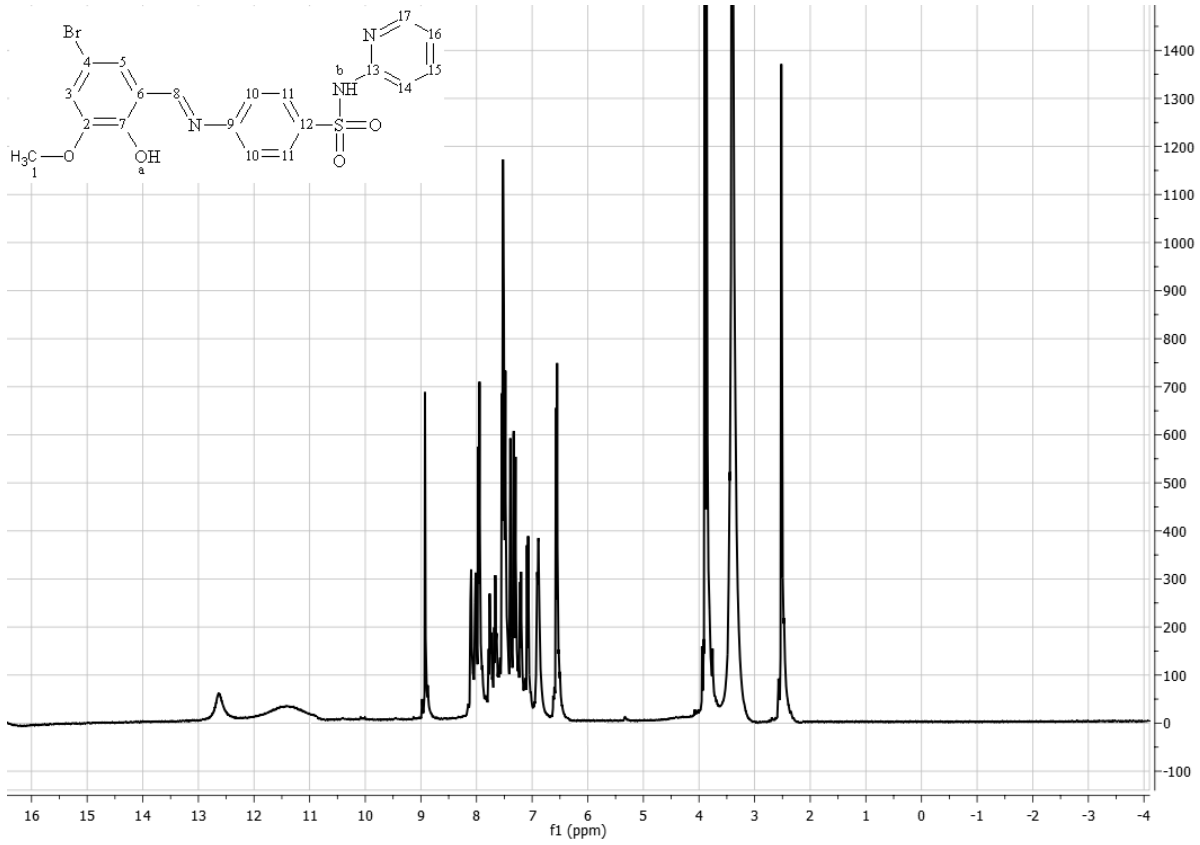

Figure S4. ^{1}H NMR spectrum of the compound **1** in DMSO-d_6.

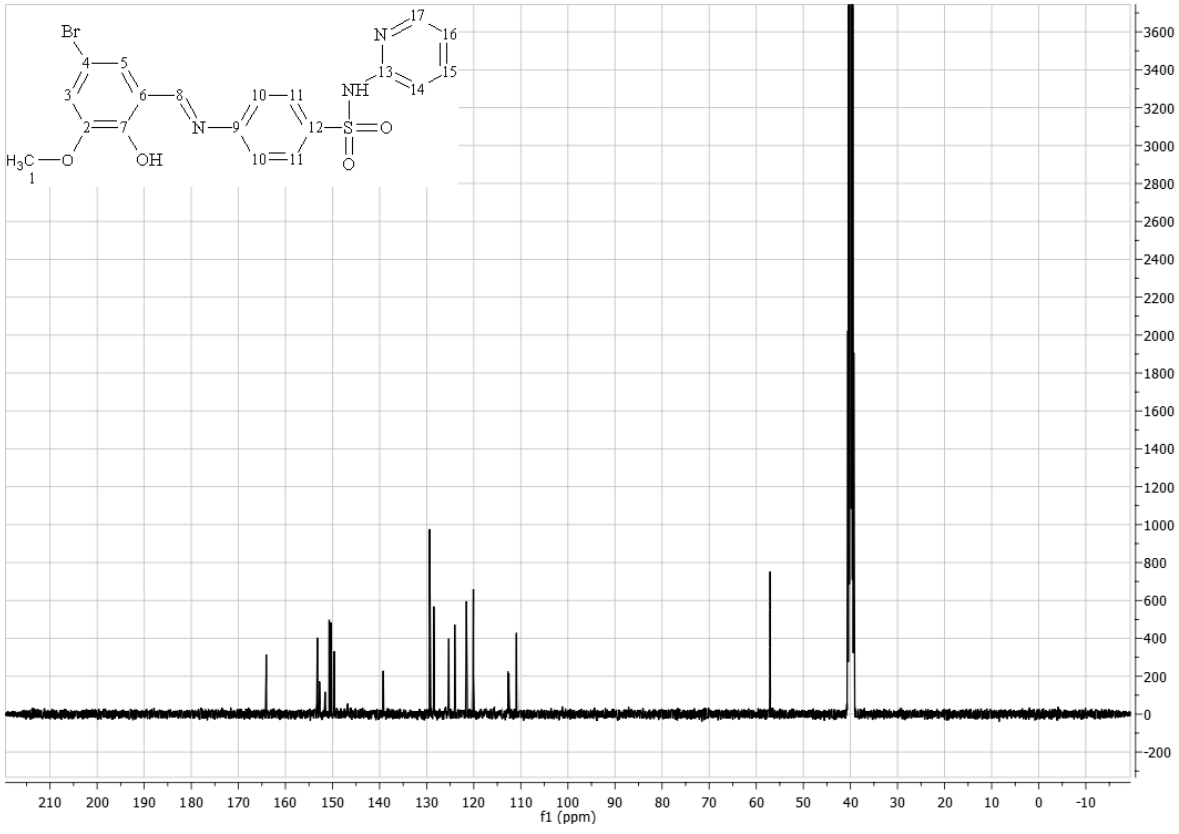

Figure S5. ^{13}C NMR spectrum of the compound **1** in DMSO-d_6.

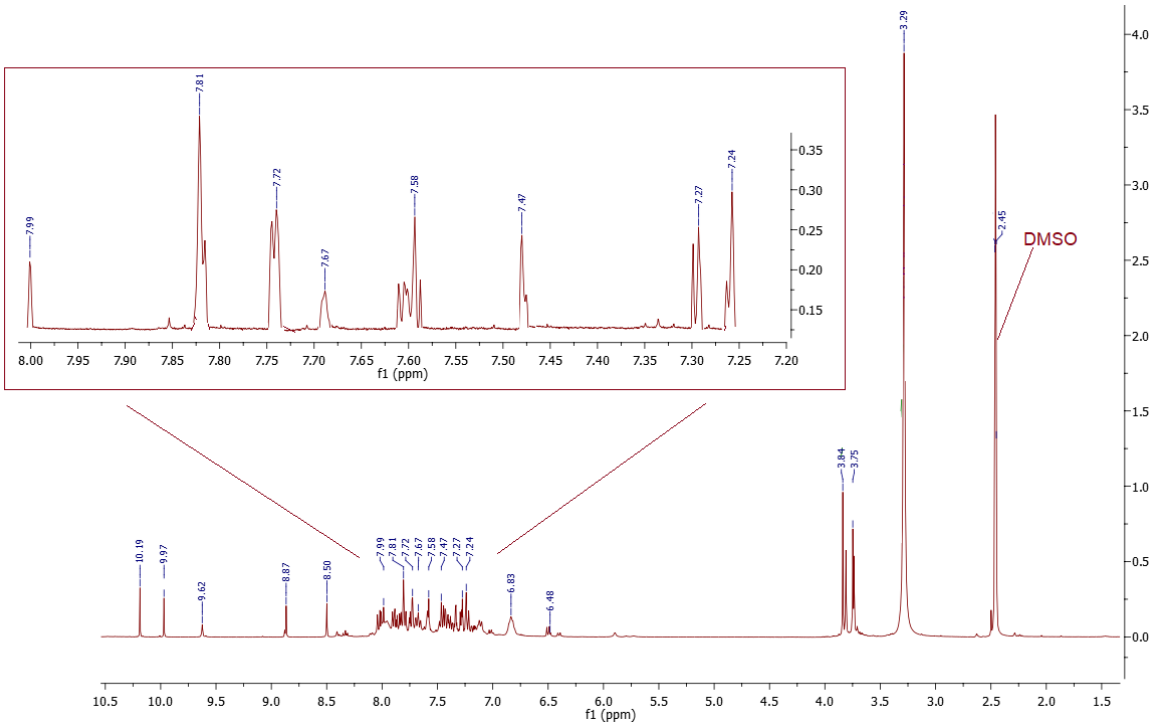

Figure S6. ^{1}H NMR spectrum of the compound **2** in DMSO-d$_6$.

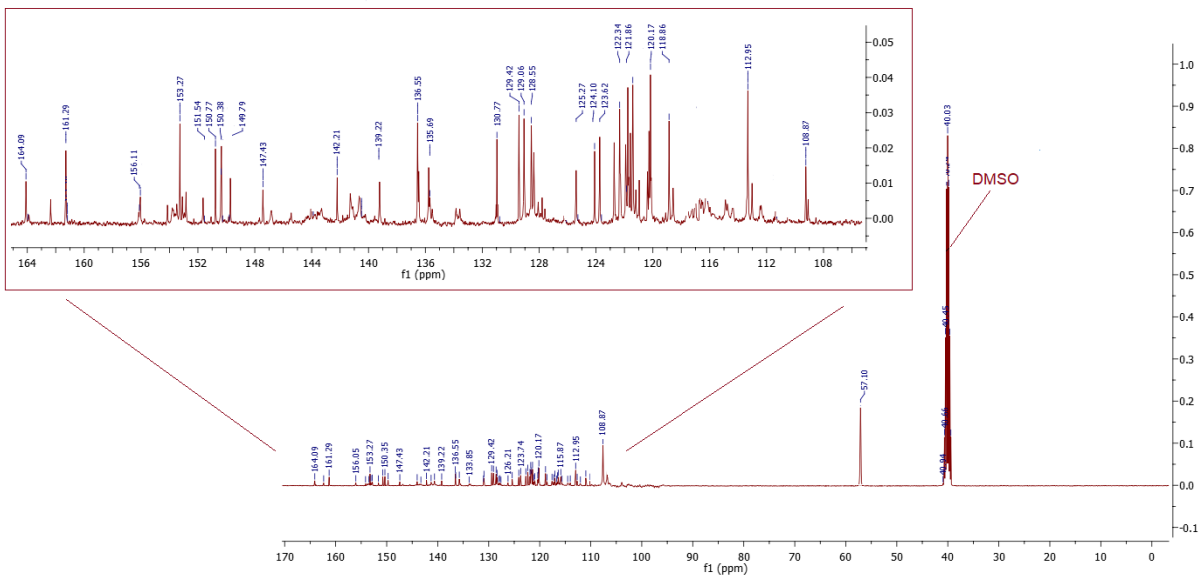

Figure S7. ^{13}C NMR spectrum of the compound **2** in DMSO-d$_6$.

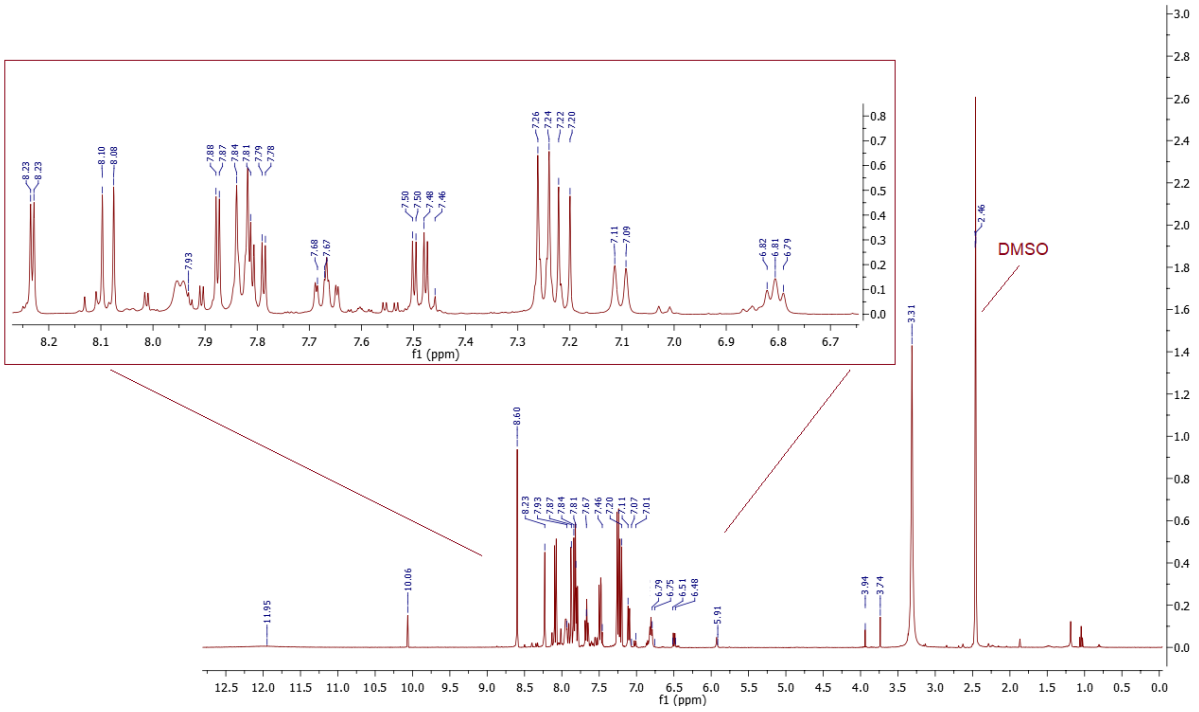

Figure S8. ^{1}H NMR spectrum of the **ZnPc 3** in DMSO-d$_6$.

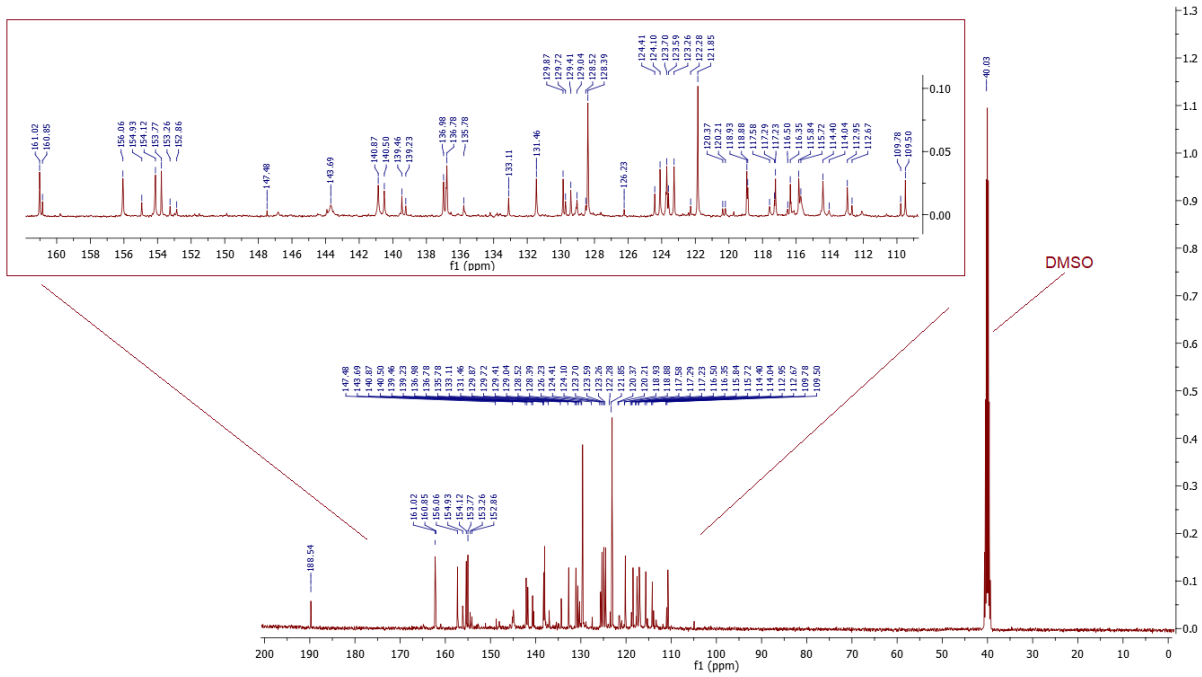

Figure S9. ^{13}C NMR spectrum of the **ZnPc 3** in DMSO-d$_6$.

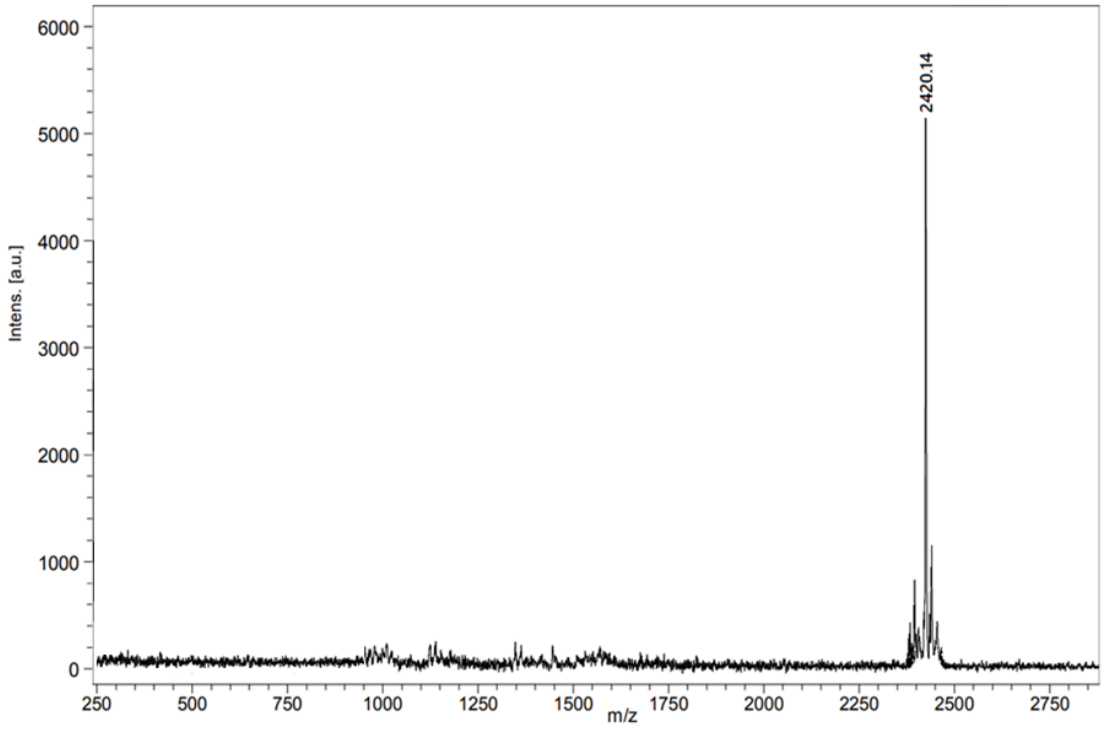

Figure S10. MALDI-TOF mass spectrum of the **ZnPc 3**

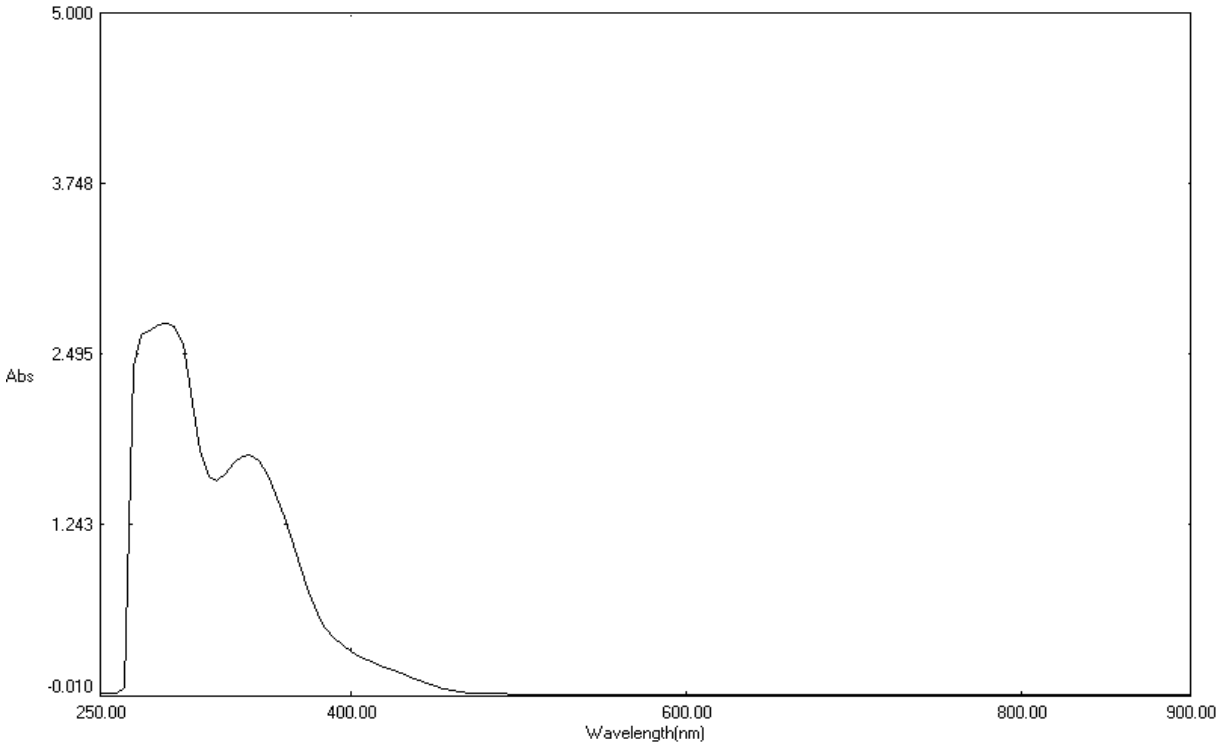

Figure S11. Electronic absorption spectrum of the compound **1** in DMSO at 1.20×10^{-5} M

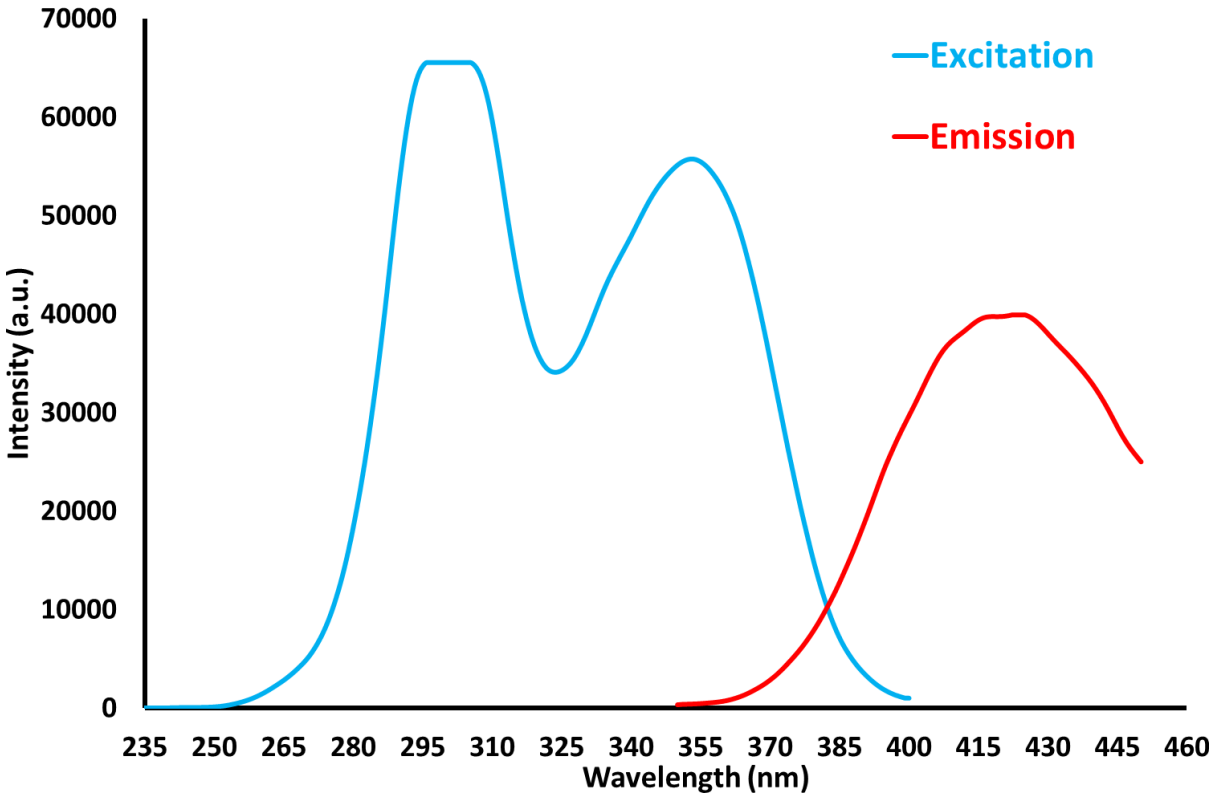

Figure S12. Fluorescence absorption, emission, and excitation spectra of the compound **2** in DMSO. Excitation wavelength: 345 nm.

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