

SUPPLEMENTARY INFORMATION

Synthesis, characterization, photophysics, and photochemistry of peripherally tetrakis(quinolinylethylenephenoxy)-substituted zinc(II) phthalocyanines

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EXPERIMENTAL

Materials and methods

The phthalonitrile compound **1** was prepared *via* the nucleophilic aromatic substitution between 2-chloro-6-methoxyquinoline-3-carbaldehyde and [4-(3,4-dicyanophenoxy)phenyl]acetic acid. The phthalocyanine compound **2** was prepared *via* cyclotetramerization of the phthalonitrile **1** according to the procedure giving in literature [1–4]. N,N-dimethylformamide (DMF), N,N-dimethylaminoethanol (DMAE), n-butane-1-thiol, n-hexane-1-thiol, 3-sulfanylpropanoic acid, 7-sulfanyl-2H-1-benzopyran-2-one, zinc(II) acetate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, potassium carbonate (K_2CO_3), tetrahydrofuran (THF), chloroform (CHCl_3), methanol (CH_3OH), ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$), acetone (CH_3COCH_3), and diethyl ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$) were purchased from Aldrich. The used solvents were dried according to the procedure given in the literature [5]. The progress of the reactions and the purity of the products were checked by thin-layer chromatography (TLC) technique.

FT-IR spectra were recorded on Perkin Elmer Spectrum 100 FT-IR Spectrometer with an attenuated total reflectance (ATR) unit. ^1H -NMR spectra were recorded on Bruker Avance III 500 spectrometer in deuterated dimethyl sulfoxide (DMSO-d_6). Electronic absorption spectra (UV–vis) were recorded on Shimadzu UV-2450 UV–Visible Spectrophotometer. Mass spectra were recorded on Bruker Micro flex LT MALDI-TOF MS spectrometer using 2,5-dihydroxybenzoic acid (DHB) and dithranol (DIT) as matrixes for MALDI. Elemental analyses were obtained from Thermo Finnigan Flash 1112 Instrument. Fluorescence excitation and emission spectra were recorded on Hitachi F-7000 spectrofluorometer using a 1-cm path length cuvette at room temperature. Fluorescence lifetimes were measured using a time-correlated single-photon counting setup (TCSPC) (Horiba Fluorolog 3 equipment). Photo-irradiations were done using an Osram optic halogen lamp (300W-120V). A 600 nm glass cut off filter (Schott), and a water filter was used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a bandwidth of 40 nm) was

additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX PM5100 laser (Molelectron detector incorporated) power meter.

Photophysical and Photochemical Parameters

Fluorescence Quantum Yields and Lifetimes

Fluorescence quantum yields (Φ_F) were determined by the comparative method using equation 1 [6,7].

$$\Phi_F = \frac{F \times A_{std} \times \eta^2}{F_{std} \times A \times \eta_{std}^2} \quad (1)$$

where F and F_{std} are the areas under the fluorescence emission curves of the samples (**2-6**) and the standard (unsubstituted ZnPc), respectively. A and A_{std} are the relative absorbance of the samples (**2-6**) and standard at the excitation wavelength, respectively. η^2 and η_{std}^2 are the refractive indices of solvents for the samples (**2-6**) and standard, respectively.

Unsubstituted ZnPc ($\Phi_F= 0.20$ in DMSO) [8] was employed as the standard. Both the sample and standard were excited at the same wavelength. The absorbance of the solutions was ranged between 0.10 and 0.12 at the excitation wavelength.

Fluorescence lifetime (τ_F) values were measured using a time-correlated single photon counting setup (TCSPC). The natural radiative lifetime (τ_0) values were evaluated using Equation 2 [9].

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

Singlet oxygen quantum yields

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental set-up described in the literature [10-12]. Typically, a 3 mL portion of the respective unsubstituted ZnPc and the peripherally tetra-substituted zinc(II) phthalocyanine (**2-6**) solutions (concentration = 1×10^{-5} M) containing the singlet oxygen quencher was irradiated in the Q band region by the photo-irradiation set-up described in the reference [10-12]. The Φ_Δ values were determined in

air using the relative method with unsubstituted ZnPc in DMSO as standard. 1,3-Diphenylisobenzofuran (DPBF) was used as a chemical quencher for singlet oxygen in DMSO. The Φ_{Δ} values of the studied Pc complexes were calculated using Equation 3:

$$\Phi_{\Delta} = \Phi_{\Delta}^{std} \frac{R \times I_{abs}^{std}}{R^{std} \times I_{abs}} \quad (3)$$

where Φ_{Δ}^{std} is the singlet oxygen quantum yield of the standard. Unsubstituted ZnPc ($\Phi_{\Delta}^{std} = 0.67$ in DMSO [13]) was used as standard. R and R_{std} are the DPBF photobleaching rates in the presence of the respective samples (**2-6**) and standard zinc phthalocyanine (**ZnPc**), respectively. I_{abs} and I_{abs}^{std} are the rates of light absorption by the samples (**2-6**) and standard zinc(II) phthalocyanine (**ZnPc**), respectively I_{abs} was determined by using Equation 4.

$$I_{abs} = \frac{\alpha \times S \times I}{N_A} \quad (4)$$

N_A is the Avogadro's constant, S is the irradiated cell area, α is the irradiation time and I_{abs} is the overlap integral of the radiation source light intensity and the absorption of the samples (**2-6**) or standard zinc(II) phthalocyanine (**ZnPc**).

To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of quenchers (DPBF) was lowered to $\sim 3 \times 10^{-5}$ M. Solutions of sensitizer (concentration = 1×10^{-5}) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described in the literature [10-12]. DPBF degradation at 417 nm was monitored. The light intensity used for Φ_{Δ} determinations was found to be 6.60×10^{15} photons $s^{-1} cm^{-2}$.

Photodegradation quantum yields

Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental set-up described in the literature [10-12]. Photodegradation quantum yields were determined using Equation 5 given below.

$$\Phi_d = \frac{(C_0 - C_t) \times V \times N_A}{I_{abs} \times S \times t} \quad (5)$$

where C_0 and C_t are the samples (2-6) 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 (2-6). A light intensity of 2.15×10^{16} photons $s^{-1} cm^{-2}$ was employed for Φ_d determinations.

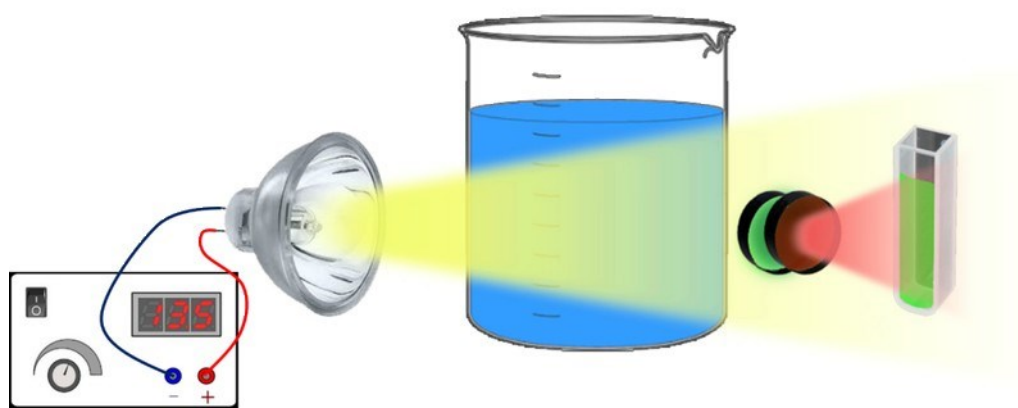


Figure S1. Photophysical and photochemical measurement set-up.

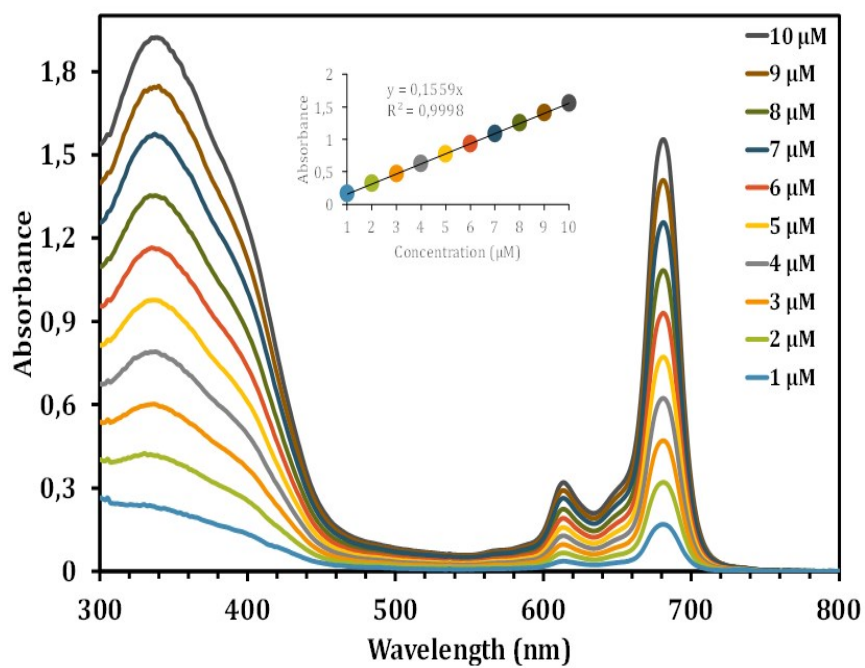


Figure S2. UV-Vis electronic absorption spectra of compound **2** at different concentrations ranging from 1 to 10 μM in DMSO.

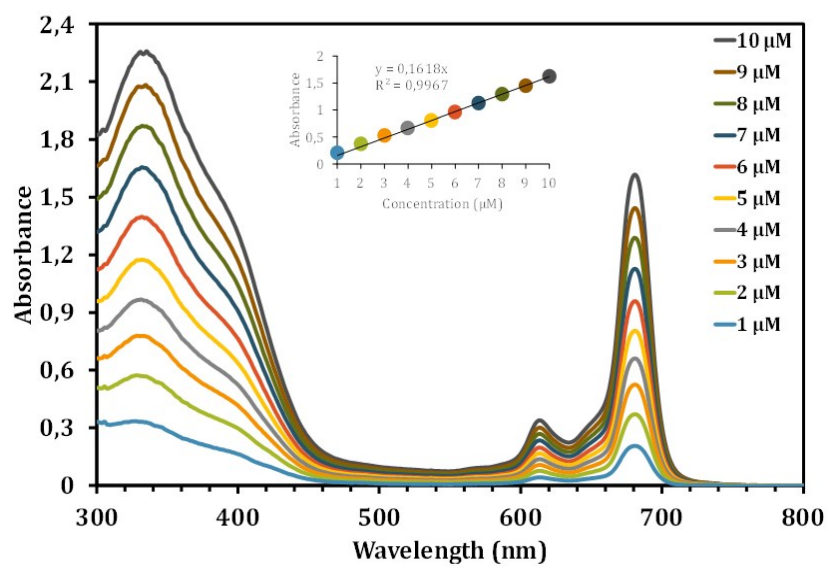


Figure S3. UV-Vis electronic absorption spectra of compound **3** at different concentrations ranging from 1 to 10 μM in DMSO.

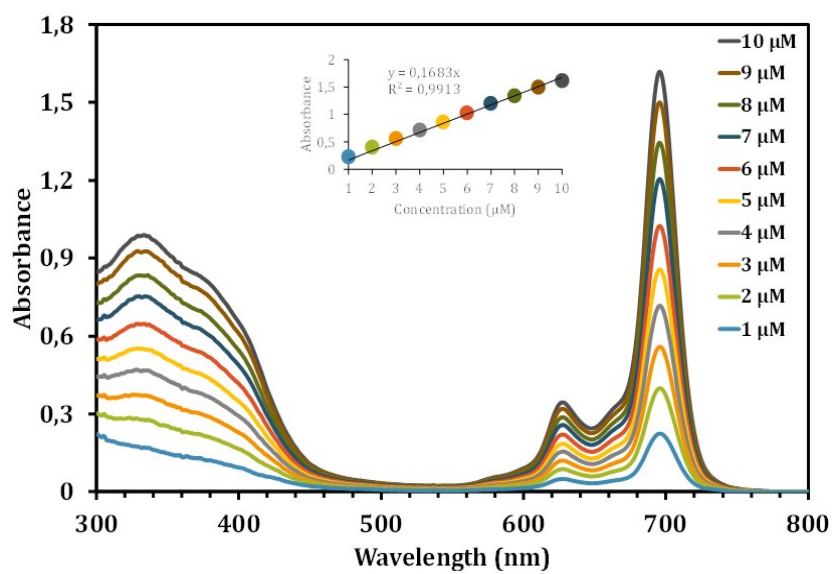


Figure S4. UV-Vis electronic absorption spectra of compound 4 at different concentrations ranging from 1 to 10 μM in DMSO.

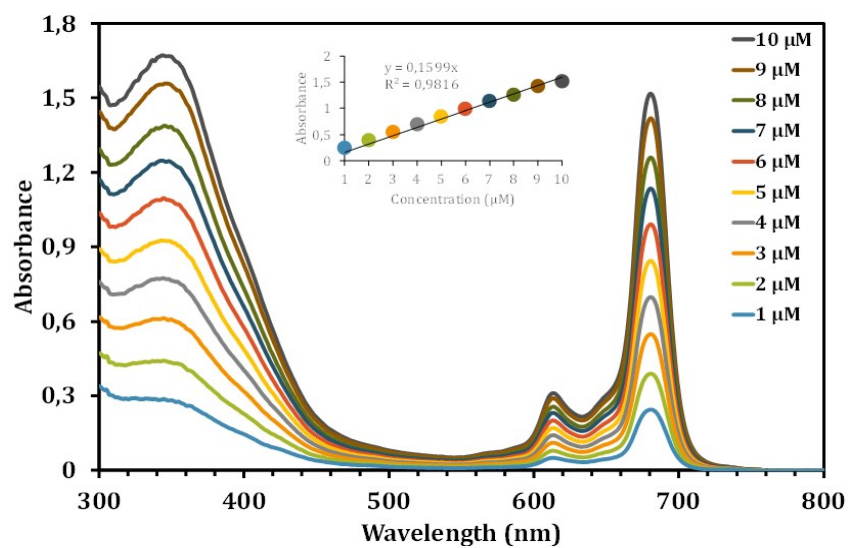


Figure S5. UV-Vis electronic absorption spectra of compound **5** at different concentrations ranging from 1 to 10 μM in DMSO.

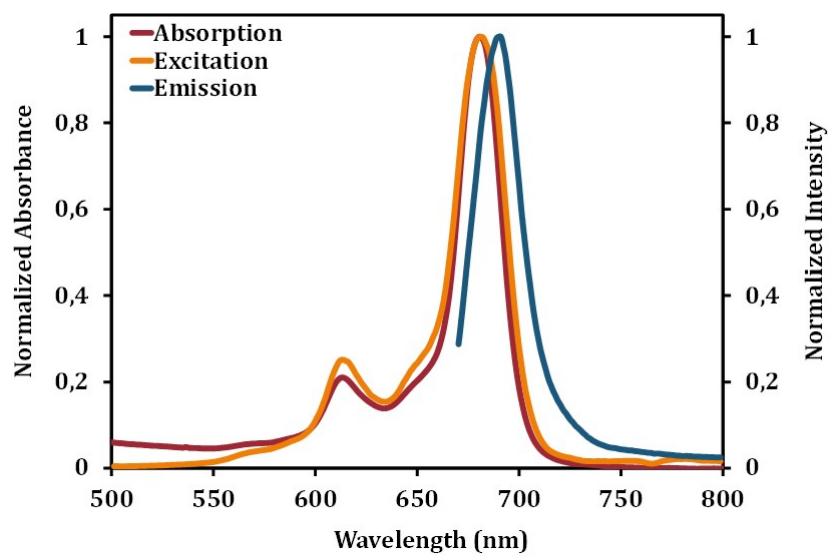


Figure S6. Fluorescence emission, excitation, and absorption spectra of compound **2** in DMSO (concentration 5×10^{-5} M).

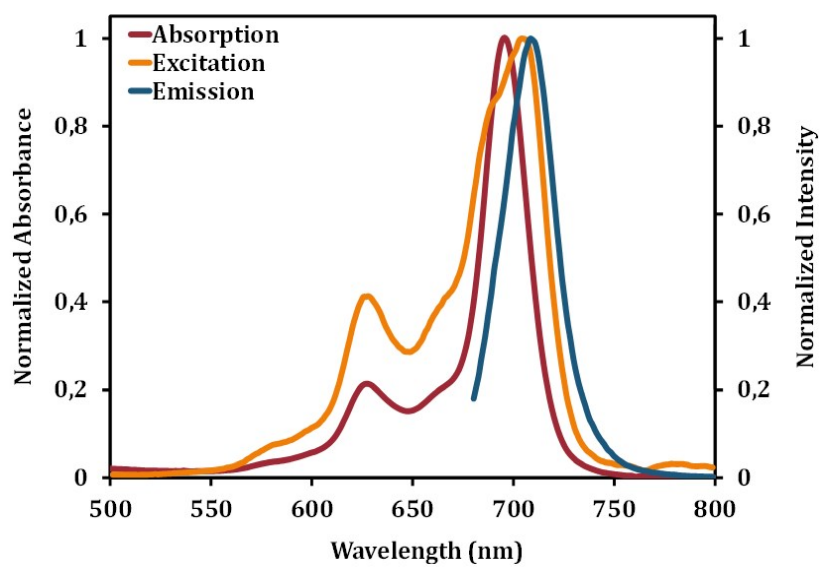


Figure S7. Fluorescence emission, excitation, and absorption spectra of compound **4** in DMSO (concentration 5×10^{-5} M).

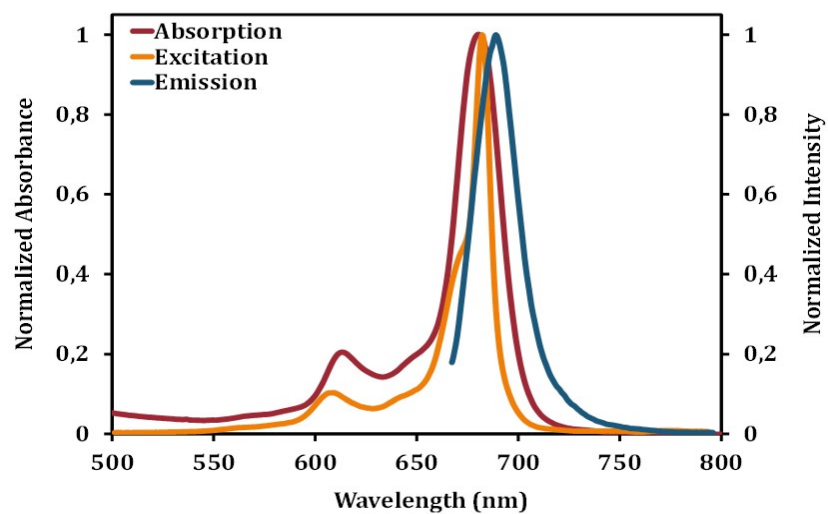


Figure S8. Fluorescence emission, excitation, and absorption spectra of compound **5** in DMSO (concentration 5×10^{-5} M).

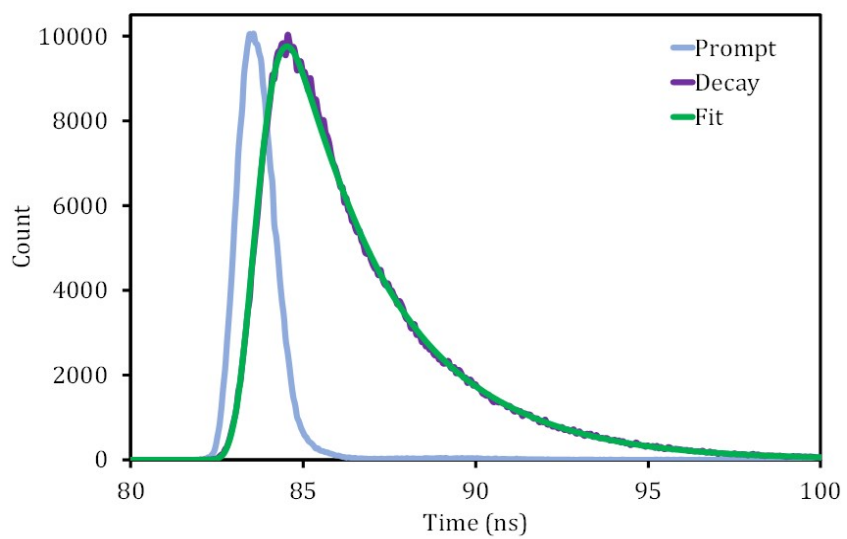


Figure S9. Time-correlated single-photon counting (TCSPC) trace for compound **4** in DMSO.

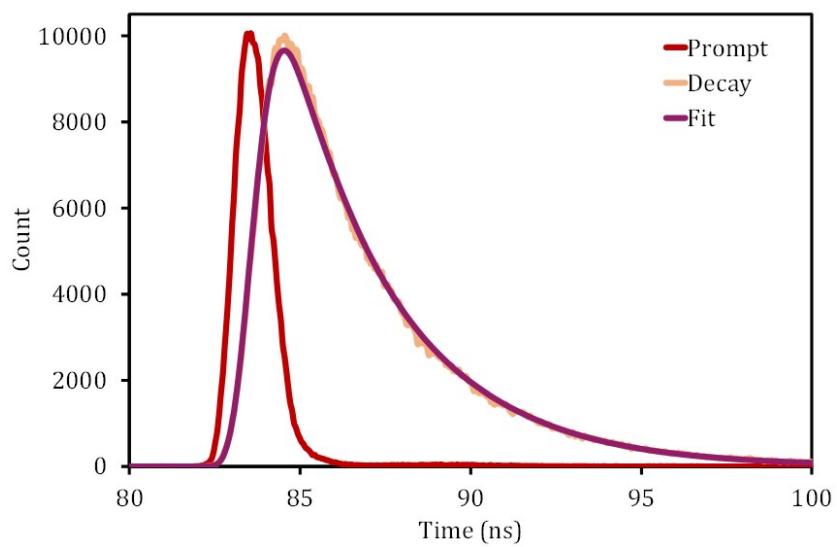


Figure S10. Time-correlated single-photon counting (TCSPC) trace for compound **5** in DMSO.

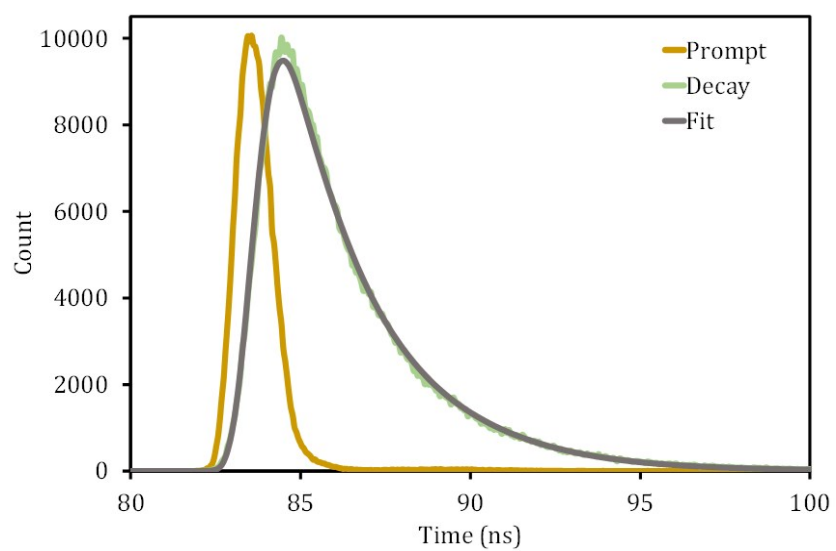


Figure S11. Time-correlated single-photon counting (TCSPC) trace for compound **6** in DMSO.

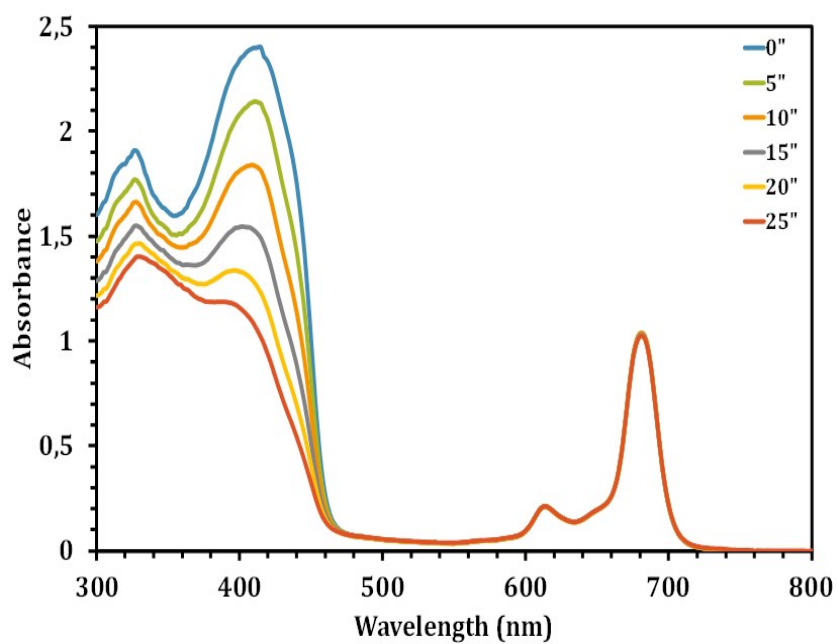


Figure S12. UV–Vis electronic absorption spectra of **2** for the determination of singlet oxygen quantum yield (Φ_{Δ}) by chemical method using DPBF in DMSO.

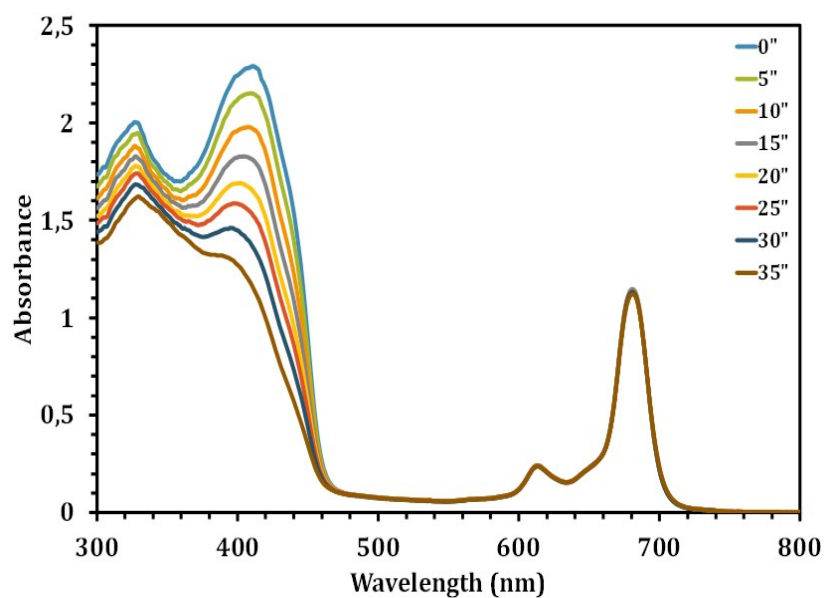


Figure S13. UV-Vis electronic absorption spectra of **3** for the determination of singlet oxygen quantum yield (Φ_{Δ}) by chemical method using DPBF in DMSO.

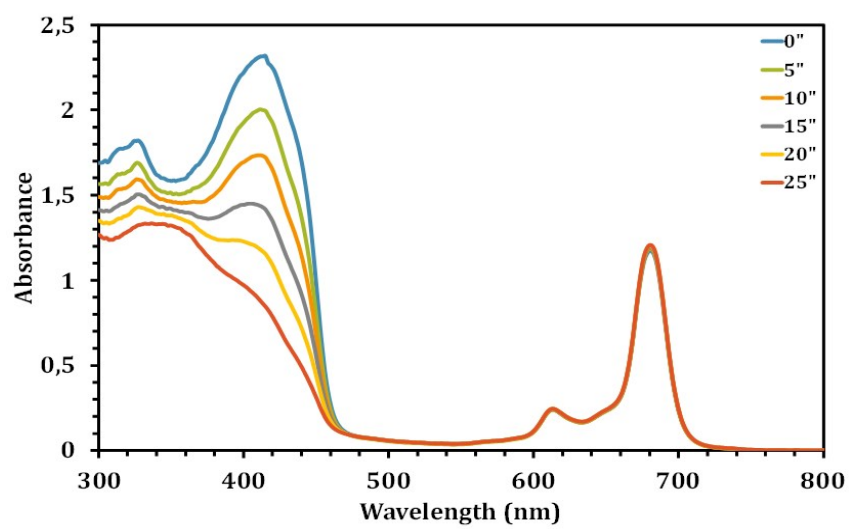


Figure S14. UV-Vis electronic absorption spectra of compound **5** for the determination of singlet oxygen quantum yield (Φ_{Δ}) by chemical method using DPBF in DMSO.

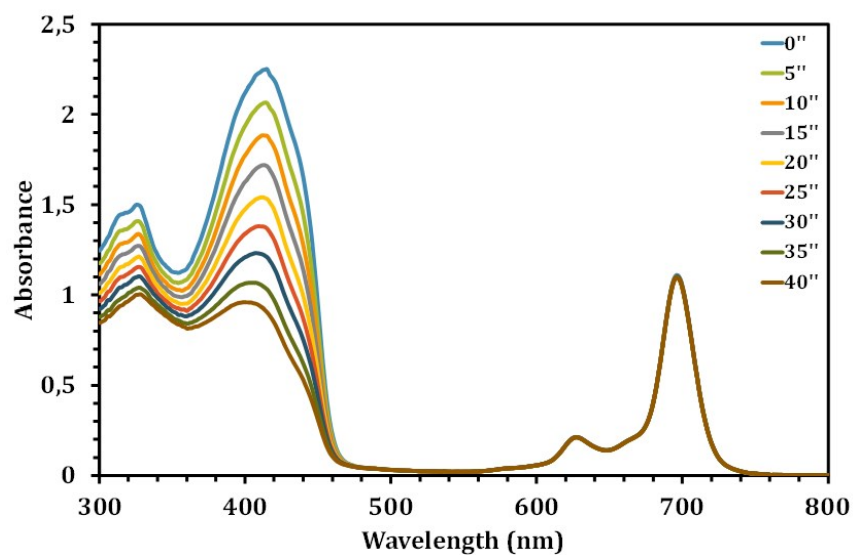


Figure S15. UV-Vis electronic absorption spectra of compound **6** for the determination of singlet oxygen quantum yield (Φ_{Δ}) by chemical method using DPBF in DMSO.

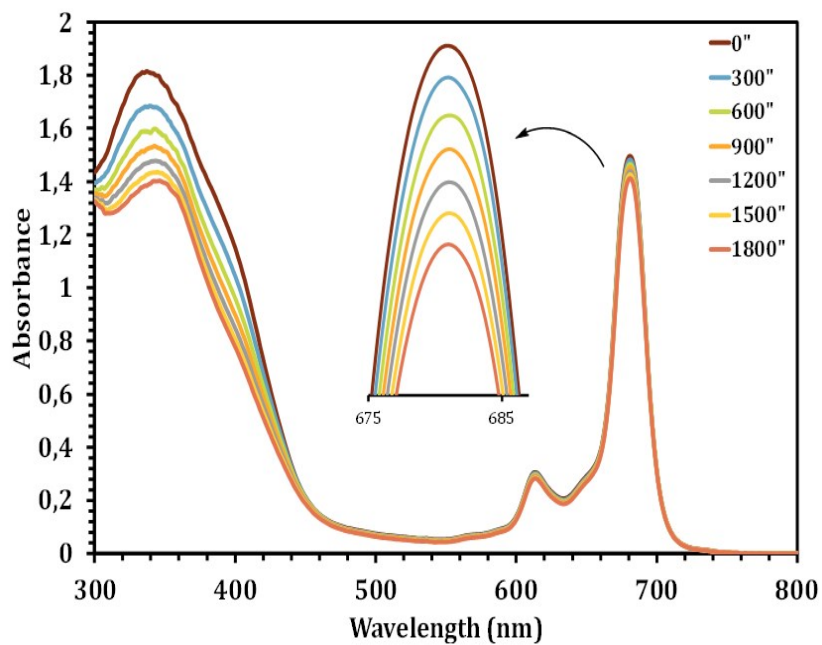


Figure S16. UV-Vis electronic absorption spectra of compound **2** under light irradiation with increasing time in DMSO.

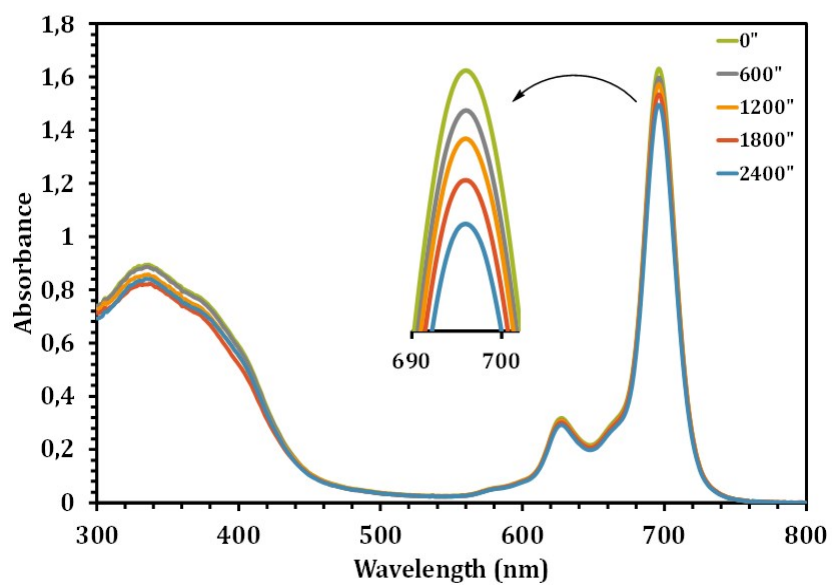


Figure S17. UV-Vis electronic absorption spectra of compound **4** under light irradiation with increasing time in DMSO.

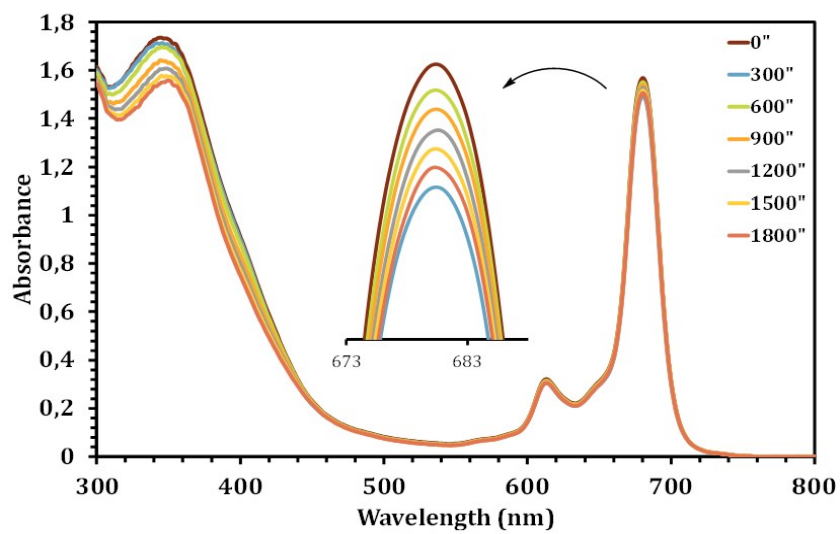


Figure S18. UV-Vis electronic absorption spectra of compound **5** under irradiation with light at increasing times in DMSO.

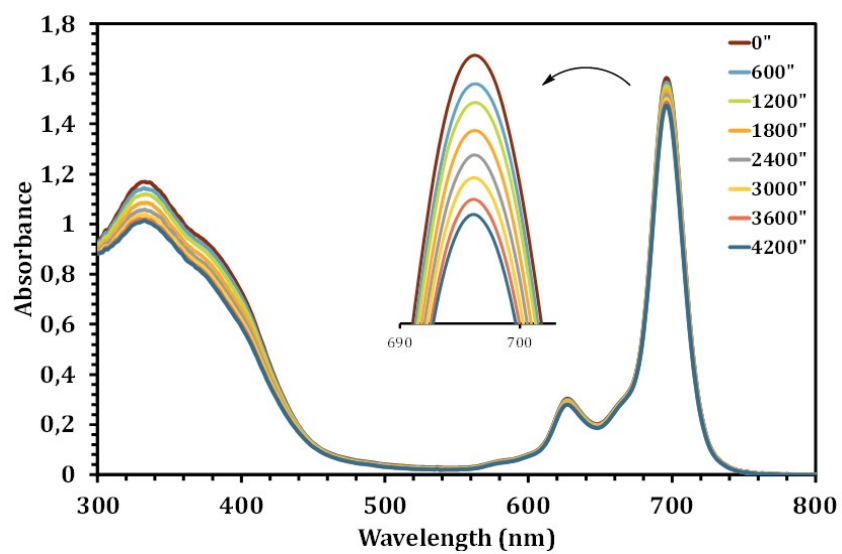


Figure S19. UV-Vis electronic absorption spectra of compound **6** under irradiation with light at increasing times in DMSO.

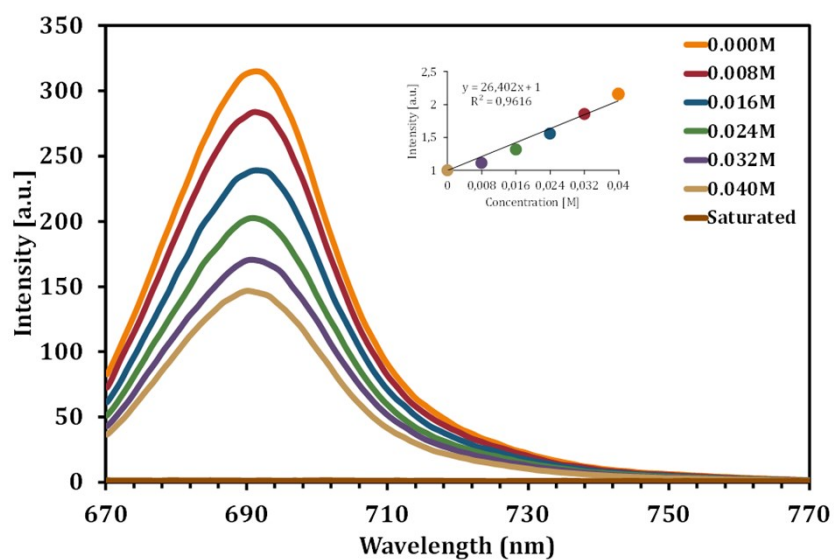


Figure S20. Fluorescent emission quenching of **3** (concentration $\sim 5 \times 10^{-6}$ M) by the addition of different concentrations of 1,4-benzoquinone in DMSO.

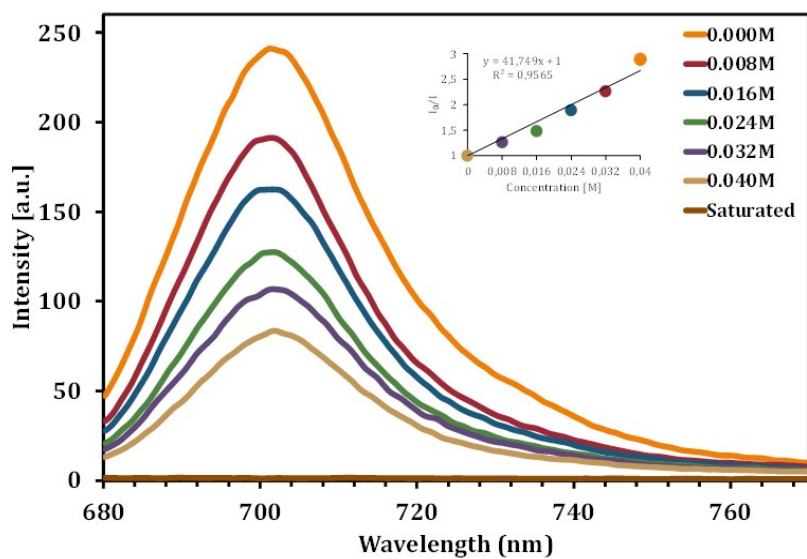


Figure S21. Fluorescence emission quenching of 4 (concentration $\sim 5 \times 10^{-6}$ M) by the addition of different concentrations of 1,4-benzoquinone in DMSO.

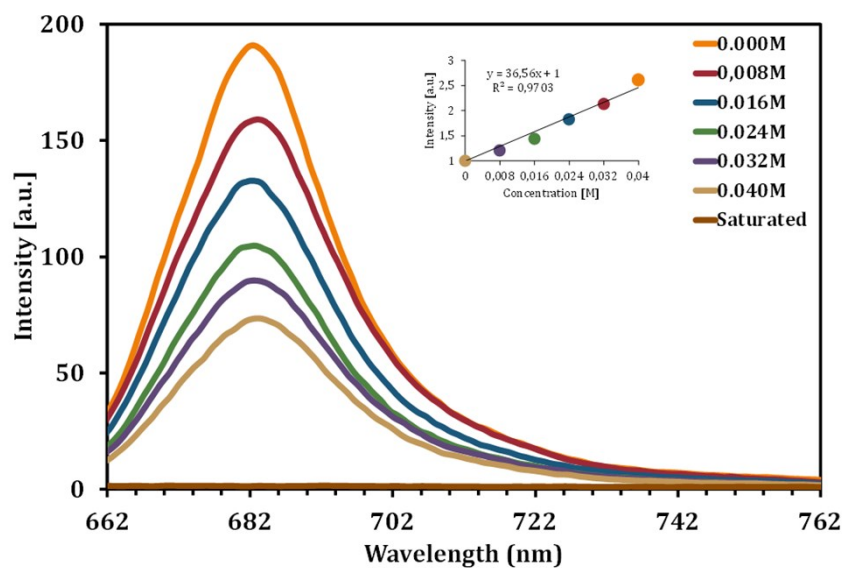


Figure S22. Fluorescence emission quenching of **5** (concentration $\sim 5 \times 10^{-6}$ M) by the addition of different concentrations of 1,4-benzoquinone in DMSO.

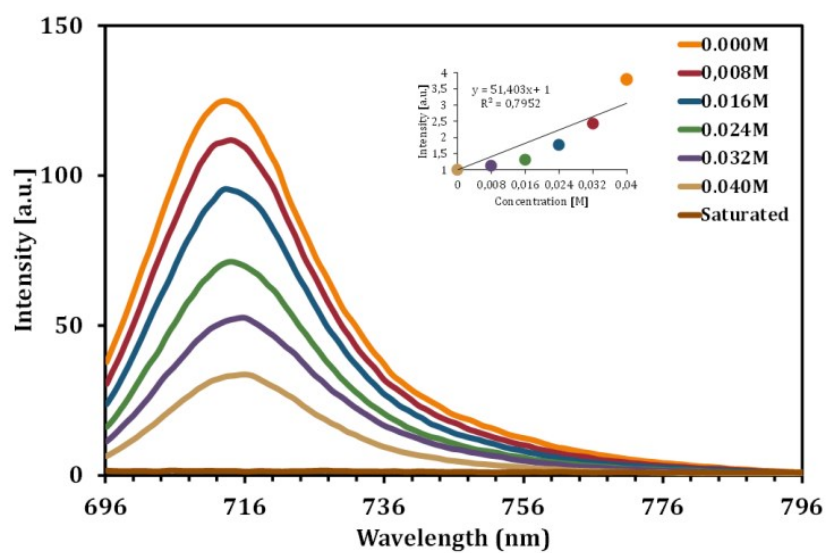


Figure S23. Fluorescence emission quenching of **6** (concentration $\sim 5 \times 10^{-6}$ M) by the addition of different concentrations of 1,4-benzoquinone in DMSO.

References

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