Photophysicochemical and Fluorescence Quenching Studies of Benzyloxyphenoxy Substituted Zinc Phthalocyanines

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Abstract

Photochemical and photophysical measurements were conducted on peripheral and non-peripheral tetrakis- and octakis(4-benzyloxyphenoxy) substituted zinc phthalocyanines (**1**, **2** and **3**). General trends are described for quantum yields of photodegradation, fluorescence quantum yields, triplet lifetimes and triplet quantum yields as well as singlet oxygen quantum yields of these compounds in dimethylsulphoxide (DMSO) and toluene. The fluorescence of the complexes is quenched by benzoquinone (BQ), and fluorescence quenching properties are investigated in DMSO and toluene. The effects of the solvents on the photophysical and photochemical parameters of the zinc(II) phthalocyanines (**1**, **2** and **3**) are also reported. Photophysical and photochemical properties of phthalocyanine complexes are very useful for PDT applications.

Keywords: Zinc phthalocyanine, triplet quantum yields, fluorescence quenching, fluorescence quantum yields

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1. Introduction

Phthalocyanines are a class of macrocyclic compounds possessing a system of conjugated π-electrons. Phthalocyanines exhibit a number of unique properties that make them of great interest in different scientific and technological areas. The important and extensive application of phthalocyanines is their use as colorants. Recently, they have also found applications in many fields in materials science, especially in nonlinear optical (NLO) devices, liquid crystals, Langmuir-Blodgett films, electrochromic devices, gas sensors, and as photosensitizers, to name a few [1,2]. A decisive disadvantage of metal-free and metalated phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the pheripheral and non-peripheral positions of the phthalocyanine framework [3]. Because of their lower degree of order in solid state, tetrasubstituted phthalocyanines are more soluble than the corresponding octasubstituted ones. In contrast to octa-substituted systems, tetra-substituted phthalocyanines are obtained as a mixture of constitutional isomers by statistical synthesis starting from mono-substituted phthalonitriles or corresponding diiminoisoindolines. Depending on their substituent positions two types (non-peripherally and peripherally substituted) of tetra-substituted macrocycles which show significant differences in their chemical and physical behaviour can be distinguished.

In recent years, remarkable progress has been made in the use of phthalocyanine derivatives as sensitizers for photodynamic therapy (PDT) of cancer [4-6]. PDT employs the combination of light and photosensitizer. Photosensitizer gets excited after the absorption of light of proper wavelength. This is followed by a singlet oxygen production by energy transfer from activated photosensitizer. Metallophthalocyanines (MPcs) have proved to be highly promising as photosensitizers due to their intense absorption in the red region of visible light. High triplet state quantum yields and long lifetimes are required for efficient sensitization and these criteria may be fulfilled by the incorporation of a diamagnetic metal. Zinc, aluminium and silicon phthalocyanine complexes, in particular, have good photosensitizing properties for PDT [7-10].

Zinc phthalocyanine complexes have attracted much interest because of their appreciably long triplet lifetimes and quantum yields [11-13]. Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplet excited state and ground state molecular oxygen increases with the lifetime of the excited state. The introduction of peripheral and non-peripheral substituents onto the MPc ring is expected to affect both the triplet quantum yield and lifetime, hence it is desirable to carry out studies on the effects of substituents on these parameters.

In this work, we report on the effects of tetra- (peripheral and non-peripheral) and octa- substitutions on the photophysical and photochemical parameters of zinc phthalocyanine derivatives in DMSO and toluene. Aggregation behaviour, photophysical (triplet state lifetimes and quantum yields, and fluorescence quantum yields) and photochemical (singlet oxygen and photodegradation quantum yields) properties were investigated. This work also explores the effects of ring substitutions and solvent on the fluorescence properties of the zinc phthalocyanines and on the quenching of the zinc phthalocyanines by benzoquinone (BQ) using the Stern-Volmer relationship. Since PDT activity is mainly based on singlet oxygen, its production was determined by the dye-sensitised photooxidation of 1,3-diphenylisobenzofuran (DPBF), a specific scavenger of this toxic species [14]. Studies of the photostability of zinc phthalocyanines during photosensitized reactions are also of immense importance.

2. Experimental

2.1. Materials and equipment

1,(4),8(11),15(18),22(25)-tetrakis(4-benzyloxyphenoxy) zinc phthalocyanine (**1**), 2,(3),9(10),16(17),23(24)-tetrakis(4-benzyloxyphenoxy) zinc phthalocyanine (**2**) and 2,3,9,140,16,17,23,24-octakis(4-benzyloxyphenoxy) zinc phthalocyanine (**3**) were prepared, purified and characterised according to literature procedures.[15] (Fig.1) Zinc phthalocyanine (**ZnPc**), 1,3-diphenylisobenzofuran (DPBF), benzoquinone (BQ), dimethylsulphoxide (DMSO) and dichloromethane (DCM), toluene were obtained from Aldrich. All other reagents and solvents were of reagent-grade quality and were dried as described in Perrin and Armarego [16] before use.

The electronic absorption spectra were recorded with a Varian 500 UV-Vis/NIR spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter using 1 cm pathlength cuvettes at room temperature.

Photo-irradiations were done 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 (Molelectron detector incorporated) power meter. Triplet-triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda -Physik FL3002 dye (Pyridin 1 dye in methanol). Single pulse energy was 2 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses.

2.2. Photophysical parameters

2.2.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by the comparative method (Eq. 1) [17,18]:

$$\Phi_F = \Phi_F(\text{Std}) \frac{F \,.\, A_{Std} \,.\, \eta^2}{F_{Std} \,.\, A \,.\, \eta^2_{Std}} \qquad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**1**, **2** or **3**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelength, respectively, η and η_{Std} are the refractive indexes of solvents ($\eta_{toluene}$ = 1.496 and η_{DMSO}=1.477) used for the samples and standard, respectively. The refractive indices of the solvents were employed in calculating fluorescence quantum yields in different solvents. Unsubstituted **ZnPc** (in DMSO) (Φ_F = 0.18) [19] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

2.2.2. Triplet quantum yields and lifetimes

The de-aerated solutions of the respective tetra- and octa-substituted ZnPc (**1**, **2** and **3**) complexes were introduced into a 1 cm pathlength spectrophotometric cell and irradiated at the Q band maxima with the laser system described above. Triplet quantum yields (Φ_T) were determined by a comparative method using triplet decay [20], Eq. 2.

$$\Phi_T^{Sample} = \Phi_T^{Std} \frac{\Delta A_T^{Sample} . \varepsilon_T^{Std}}{\Delta A_T^{Std} . \varepsilon_T^{Sample}} \qquad (2)$$

where ΔA_T^{Sample} and ΔA_T^{Std} are the changes in the triplet state absorbances of the samples (**1**, **2** or **3**) and standard, respectively; ε_T^{Sample} and ε_T^{Std}, the triplet state extinction coefficients for the samples (**1**, **2** or **3**) and standard, respectively. **ZnPc** was was employed as the standard. The triplet quantum yield (Φ_T^{Std}) for the **ZnPc** standard is Φ_T^{Std} = 0.65 in DMSO [21] and Φ_T^{Std} =0.65 in toluene [13].

Quantum yields of internal conversion (Φ_{IC}) were obtained using Eq. 3, which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of tetra- and octa-substituted **ZnPc** complexes.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \qquad (3)$$

Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

2.3. Photochemical parameters

Singlet oxygen (Φ_Δ) and photodegradation (Φ_d) quantum yield determinations were carried out using the experimental set-up described above and reported before [22,23]. Typically, a 2 ml portion of the respective tetra- and octa-substituted ZnPc (**1**, **2** and **3**) solutions (absorbance ~ 1 at the irradiation wavelength) containing the singlet oxygen quencher was irradiated in the Q band region with the photo-irradiation set-up described above. Φ_Δ values were determined in air using the relative method with DPBF as a singlet oxygen chemical quencher in DMSO and toluene (Eq. 4):

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{R \cdot I_{abs}^{Std}}{R^{Std} \cdot I_{abs}} \qquad (4)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standards (Φ_Δ^{Std} = 0.67 for **ZnPc** in DMSO [24] and 0.58 for **ZnPc** in toluene [25]. R and R_{Std} are the DPBF photobleaching rates in the presence of the respective substituted **ZnPc** complexes (**1**, **2** or **3**) and standard, respectively; I_{abs} and I_{abs}^{Std} are the rates of light absorption by the substituted **ZnPc** complexes (**1**, **2** or **3**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [26], the concentration of DPBF was lowered to ~3 x 10^{-5} mol dm^{-3}. Solutions of sensitizers (absorbance below 1 at the irradiation wavelength) containing DPBF were prepared in the dark and irradiated in the Q band region using the setup described above. DPBF degradation at 417 nm was monitored. The light intensity used for

Φ_Δ determinations was found to be 9.33 x 10^{15} photons s^{-1} cm^{-2}. Photodegradation quantum yields were determined using Eq. 5,

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

where C_0 and C_t are the substituted **ZnPc** complexes (**1**, **2** or **3**) 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 samples (**1**, **2** or **3**). A light intensity of 3.11 x 10^{16} photons s^{-1} cm^{-2} was employed for Φ_d determinations.

2.4. Fluorescence quenching by benzoquinone(BQ)

Fluorescence quenching experiments on the tetra- and octa-substituted zinc phthalocyanine complexes (**1**, **2** or **3**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complex, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032, 0.040 and 0.048 mol.dm^{-3}. The fluorescence spectra of tetra- and octa-substituted zinc phthalocyanine complexes (**1**, **2** or **3**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern-Volmer (S-V) equation [27]:

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \qquad (6)$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively; [Q] is the concentration of the quencher, and

K_{SV} is the Stern-Volmer constant. The ratios $\frac{I_0}{I}$ were calculated and plotted against [Q] using Eq. 6 and K_{SV} determined from the slope.

3. Results and Discussion

3.1 Spectroscopic studies

The electronic spectra of the tetra- and octa-substituted phthalocyanine derivatives (**1**, **2** and **3**) has been reported before [15], Table 1 summarizes the absorption spectral data. It was reported before [15] that although the octasubstituted (**3**) and peripherally tetrasubstituted (**2**) complexes have a typical spectral pattern in the visible region for the phthalocyanines, the non-peripheral complex (**1**) showed a new absorption band in toluene at 747 nm in addition to the main Q band, Fig. 2, due to protonation in solvents such as DCM and chloroform which contain small amounts of acid.

Complex **2** showed narrow Q bands and there were no new peaks (normally blue shifted [28]) in all solvents studied, thus complex **2** did not show aggregation in these solvents. Complex **3**, although did not show aggregation in chloroform, THF and toluene, it showed broad band around 620 nm due to aggregation in DMSO and in DCM (Fig. 3). DMSO is known to prevent aggregation since it is strong coordinating solvent. However, it has been observed [29] before that aggregation occurs in DMSO and not in less coordinating solvents for some MPc complexes.

The phthalocyanine derivatives (**1** and **2**) did not show aggregation in DMSO at different concentrations. Beer-Lambert law was obeyed for these compounds in the concentrations ranging from 1.4×10^{-5} to 4×10^{-6} mol. dm^{-3}.

All the complexes (**1**, **2 a**nd **3**) showed similar fluorescence behaviour in DMSO. Fig. 4 shows the absorption, fluorescence emission and excitation spectra for complexes (**1**, **2** and **3**) in DMSO. Fluorescence emission peaks were observed at: 709 nm for **1**, 693 nm for **2** and 691 nm for **3** in DMSO (Table 1). The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra in DMSO for complexes **1** and **2** (Fig. 4). For complex **3** the emission spectrum shows less broadening when compared to excitation and absorption spectra, confirming that the aggregate does not fluoresce. The proximity of the wavelength of each component of the Q-band absorption to the Q band maxima of the excitation spectra for all complexes suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in DMSO. The observed Stokes shifts (Table 1) were typical of MPc complexes in DMSO.

3.2. Photophysical properties

3.2.1. Fluorescence Quantum Yields

The fluorescence quantum yields (Φ_F) of all complexes were similar and typical of MPc complexes, Table 2. The Φ_F values of the substituted complexes (**1** and **2**) are similar to unsubstituted **ZnPc** in DMSO. All three complexes show marginally larger Φ_F values in toluene than unsubstituted **ZnPc** in toluene. Φ_F values of ZnPc and complex **2** are larger in DMSO than in toluene. Fluorescence quantum yields are related to the viscosity (η) of the solvent, by the Förster-Hoffmann equation (Eq. 8) [30] which shows that increased viscosity results in increased Φ_F value.

$$\text{Log}\,\Phi_F = C + x\text{Log}\eta \qquad (8)$$

Hence toluene with a lower viscosity than DMSO is expected to have lower Φ_F values. However these values are similar for complex **1**, and the Φ_F value for **3** is lower in DMSO compared to toluene, due to aggregation in the former solvent.

Peripherally tetrasubstituted complex (**2**) shows the largest (Φ_F) value in DMSO compare to the other complexes. The octasubstituted complex (**3**) shows lowest Φ_F value in DMSO. The very low Φ_F value for **3** in DMSO can be explained by the aggregation tendencies of the molecules in this solvent (Fig.3). Aggregation reduces the likelihood of radiative deactivation (fluorescence) through dissipation of energy by the aggregates.

Complex **3** showed larger quantum yield for internal conversion (Φ_{IC}, Table 2) in DMSO when compared to unsubstituted **ZnPc**, and complexes **1** and **2**, most likely due to aggregation. Complexes (**1** and **2**) showed lower Φ_{IC} values than unsubstituted **ZnPc**.

3.2.2. Triplet Lifetimes and Quantum Yields

Transient spectrum for complex **3** in toluene is shown in Fig. 5, and shows a maximum at 510 nm, hence the triplet life times and yields were determined at this wavelength for complexes **1**, **2** and **3**. Fig. 6 shows the triplet decay curves of the complexes (using complex **2** in DMSO as an example). The triplet life times (τ_T) for complexes **1** (210 μs), **2** (210 μs) and **3** (200 μs) are lower than for unsubstituted **ZnPc** (350 μs) in DMSO. This suggests that the substituents quench the triplet state.

The triplet quantum yields (Φ_T) for substituted complexes (**1**, **2** and **3**) in toluene are high compared to **ZnPc** standard in toluene (Φ_T = 0.65 for **ZnPc** in DMSO and toluene). The high values of Φ_T in toluene suggest efficient intersystem crossing (ISC) in the presence of the substituents for substituted complexes (**1**, **2** and **3**). Complex **3** showed low Φ_T value in DMSO due to the aggregation in this solvent.

3.3. Photochemical properties

3.3.1. Singlet Oxygen Quantum Yields

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO and toluene using a chemical method (1,3-diphenylisobenzofuran, DPBF). The disappearance of DPBF was monitored using UV-vis spectrophotometer. Many factors are responsible for the magnitude of the determined quantum yields of singlet oxygen including; triplet excited state energy, ability of substituents and solvents to quench the singlet oxygen, the triplet excited state lifetime and the efficiency of the energy transfer between the triplet excited state and the ground state of oxygen.

Fig. 7 shows spectral changes observed during photolysis of complex **2** in DMSO in the presence of DPBF. There was no change in the Q band intensity during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies. The Φ_Δ values of non-peripherally tetrasubstituted complex **1** were higher when compared to unsubstituted **ZnPc** in both of DMSO and toluene. The Φ_Δ values of peripheral tetrasubstituted (**2**) and octasubstituted (**3**) complexes were lower when compared to unsubstituted **ZnPc** in DMSO, but were similar in toluene (Table 2). The Φ_Δ values for **1** are larger than for the other complexes, probably due to less aggregation at non-peripheral positions. The magnitude of the S_Δ (= Φ_Δ/Φ_T) represents the efficiency of quenching of the triplet excited state by singlet oxygen. Complexes **1**, **2** and **3** showed S_Δ of near unity (Table 2), suggesting efficient quenching of the triplet state by singlet oxygen more so in DMSO than toluene for complexes **2** and **3**.

3.3.2. Photodegradation Studies

Degradation of the molecules under irradiation can be used to study their stability and this is especially important for those molecules intended for use as photo catalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation to other species absorbing in the visible region. The spectral changes observed for all the complexes **1**, **2** and **3** during irradiation are as shown in Fig. 8 (using complex **3** as an example in toluene) and hence confirms that photodegradation occurred without phototransformation.

Table 2 shows that all substituted complexes (**1**, **2** and **3**) were marginally more stable to degradation compared to unsubstituted **ZnPc** in DMSO while they showed approximately the same stability in toluene (except for **3**). Thus the substitution of **ZnPc** with 4-benzyloxyphenoxy group seem to increase the stability of the complexes in DMSO. All substituted complexes (**1**, **2** and **3**) were less stable in toluene compared to in DMSO. The order of stability among the substituted complexes was **3** > **2** > **1** in both of DMSO and toluene.

3.4. Fluorescence Quenching Studies by Benzoquinone (BQ)

Addition of BQ to **ZnPc** derivatives **2** and **3**, did not show any ground state electronic absorption spectral changes, hence there was no evidence of formation of ground state complex between BQ and complexes **2** and **3**. For complex **1**, spectral changes shown in Fig.9 were observed on addition of BQ to solutions of **1** in toluene. These changes are typical of loss of symmetry in MPc complexes and have been observed on protonation of these complexes [15,23,31]. The loss of symmetry suggests that addition of BQ to **1**, protonates this complex, as a result of the acidity of BQ. Again protonation occurred only for the non-peripherally substituted complex **1** due to the more basic nature of the nitrogens at the alpha position in this complex when compared to **2** and **3**. Fig. 10 shows the quenching of complex **2** by BQ in toluene as an example. This figure shows the quenching behaviour of zinc phthalocyanine complexes (**2** and **3**) typical of the non-aggregated complexes. The fluorescence quenching of zinc phthalocyanine complexes by benzoquinone (BQ) in DMSO and toluene was found to obey Stern-Volmer kinetics, Fig. 11 for complexes **2** and **3**, which is consistent with diffusion-controlled bimolecular reactions. However for complex **1**, the quenching of the MPc complexes was affected by protonation discussed above. Fluorescence spectral changes observed on addition of BQ to complex **1** are shown in Fig. 12. These changes show the fluorescence quenching at 712 nm, but the formation of a new compound with a fluorescence peak at 758 nm, whose fluorescence is not quenched by BQ. This new complex could be due to the low symmetry one whose spectra is shown in Fig.9. The slope of the plots shown at Fig. 11 gave K_{SV} values. Stern-Volmer plots for complex **1** showed a positive deviation from Stern-Volmer relationship at higher BQ concentrations. However, the linear part at low concentrations was employed for calculations of K_{SV} values for **3**. The K_{SV} values for the BQ quenching of zinc phthalocyanine complexes are listed in Table 3 in both of DMSO and toluene. The K_{SV} values of the substituted zinc phthalocyanine complexes (**1**, **2** and **3**) are lower than unsubstituted **ZnPc** in toluene or DMSO. The K_{SV} values were found to be larger in toluene compared to DMSO. The K_{SV} values of complex **1** and **2** were similar in both of DMSO and toluene. Complex **3** has the lowest K_{SV} value in DMSO because of aggregation.

4. Conclusions

In conclusion, the substituted complexes (**1**, **2** and **3**) showed similar and typical fluorescence quantum yields for MPcs in DMSO, except for complex **3** due to the aggregation. Complex **3** has a low triplet quantum yield due to aggregation. Triplet lifetimes are higher in DMSO than in toluene for substituted complexes (**1**, **2** and **3**). The substituted complexes (**1**, **2** and **3**) have good singlet oxygen quantum yields especially complex **1** which has the highest value in both solvents. The singlet oxygen quantum yields (Φ_Δ), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.46 to 0.77. Thus, these complexes show potential as Type II photosensitizers. On addition of BQ, loss of symmetry was observed in the ground state absorption spectrum of non-peripherally substituted complex **1**, due to protonation. The fluerescence of the protonated complex was not quenched by BQ. The K_{SV} values of the substituted zinc phthalocyanine complexes (**1**, **2** and **3**) are lower than unsubstituted **ZnPc** in toluene or DMSO.

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Figure Captions:

Fig. 1. Structure of zinc(II) phthalocyanine derivatives.

Fig. 2. Absorption spectra of the compound **1**, **2** and **3** in toluene. Concentration = 4 x 10^{-6}mol.dm^{-3}.

Fig. 3. Absorption spectra of the compound **3** in different solvents. Concentration = 4 x 10^{-6}mol.dm^{-3}.

Fig. 4. Absorption, Excitation and Emission spectra of the for compound **1** (a), **2** (b) and **3** (c) in DMSO. Excitation wavelength = 665 nm for **1** and 650 nm for **2** and **3**.

Fig. 5. Transient differential spectrum of complex **3** in toluene.

Fig. 6. Triplet decay curve of **2** in DMSO at 510 nm. Excitation wavelength = 681nm.

Fig. 7. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **2** in DMSO at a concentration of $3x10^{-5}$ mol.dm^{-3}.

Fig. 8. The photodegredation of compound **3** in toluene showing the disappearance of the Q-band at ten minutes intervals.

Fig. 9. Absorption spectral changes of **1** (1.20 x 10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.00228, 0.00436, 0.00626……. 0.018 mol dm^{-3}.

Fig. 10. Fluorescence emission spectral changes of **2** (1.10 x 10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm^{-3}.

Fig. 11. Stern-Volmer plots for benzoquinone (BQ) quenching of **1**, **2** and **3**. [MPc]~1.00 x10^{-5} mol dm^{-3} in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 mol dm^{-3}.

Fig. 12. Fluorescence emission spectral changes of **1** (1.20 x 10^{-5}mol dm^{-3}) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.00228, 0.00436, 0.00626……. 0.018 mol dm^{-3}

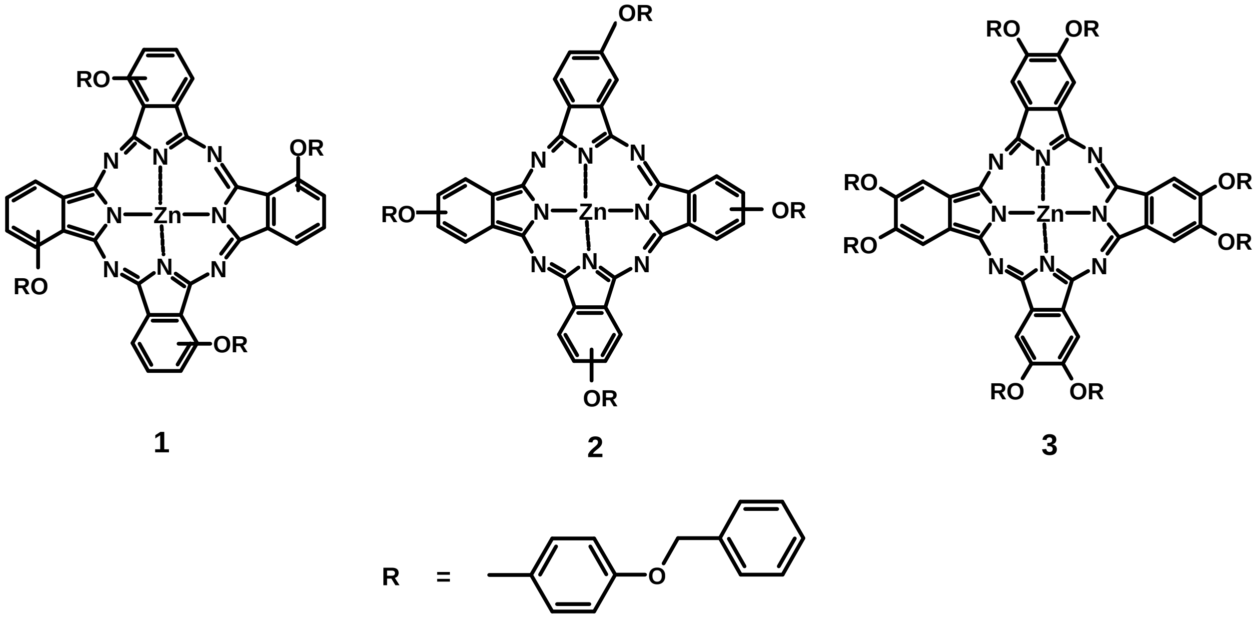


Fig. 1. Structure of zinc(II) phthalocyanine derivatives.

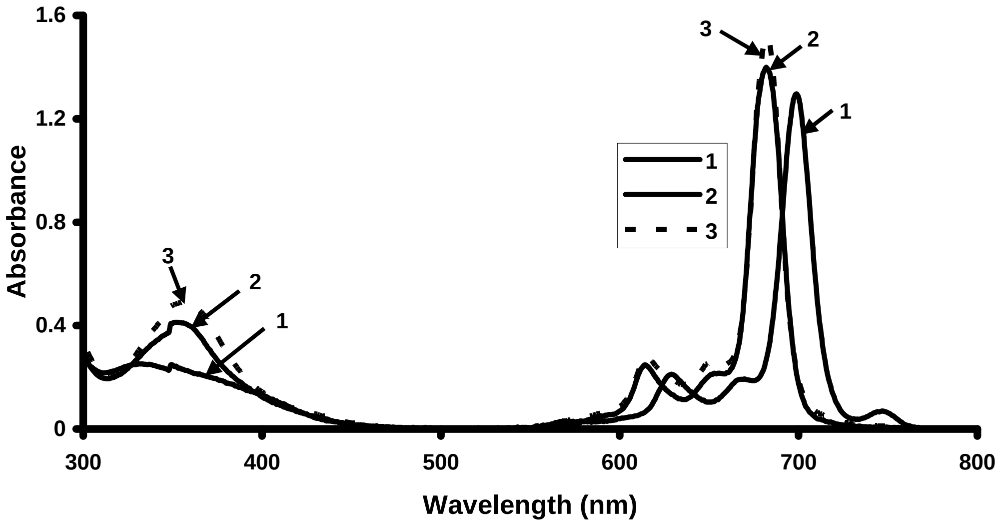


Fig. 2. Absorption spectra of the compound **1**, **2** and **3** in toluene. Concentration = 4 x 10^{-6}mol.dm^{-3}.

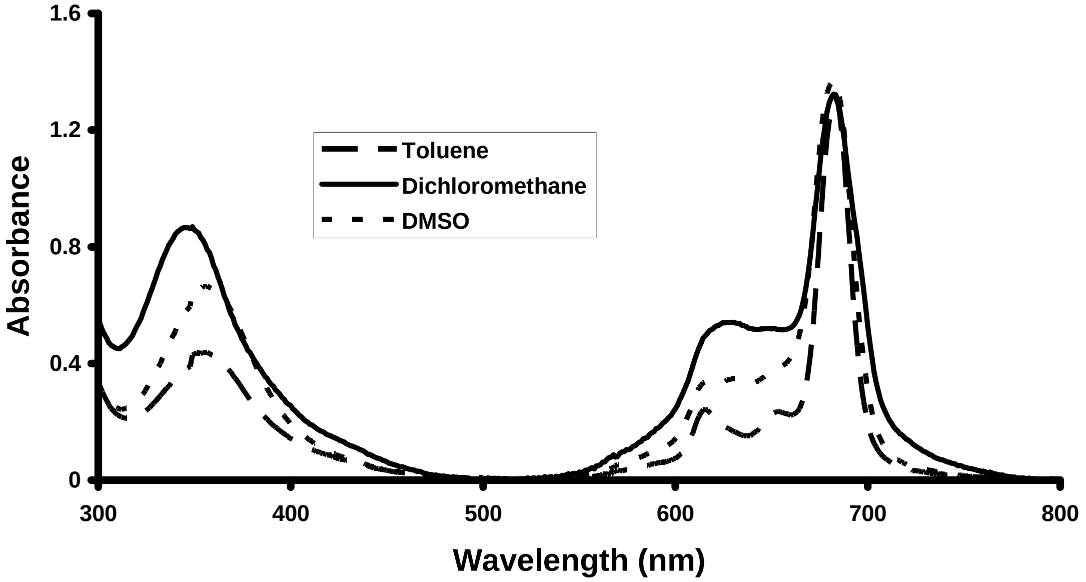
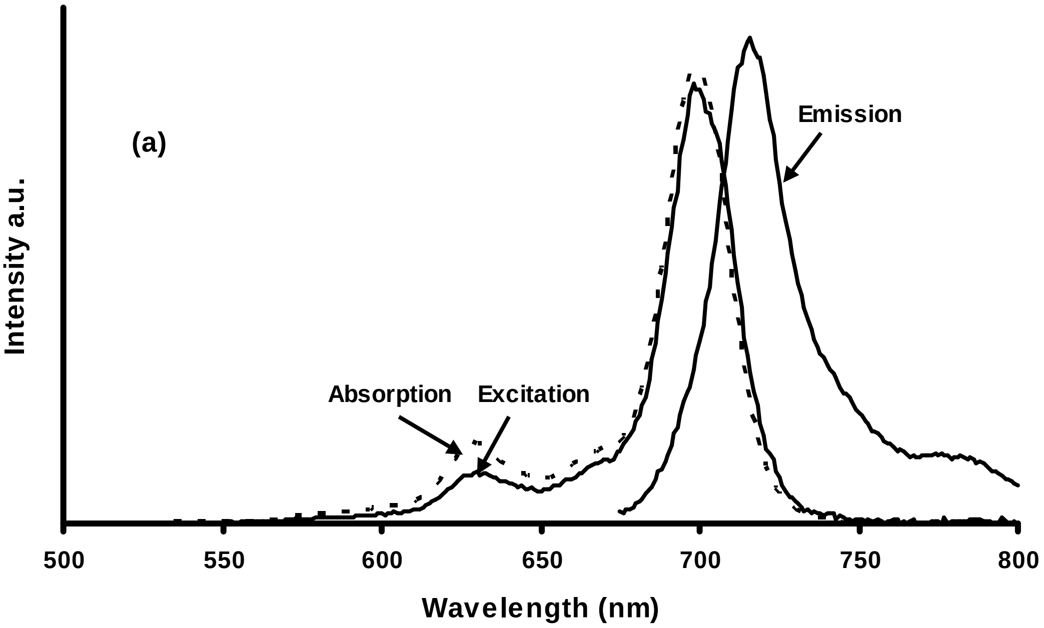
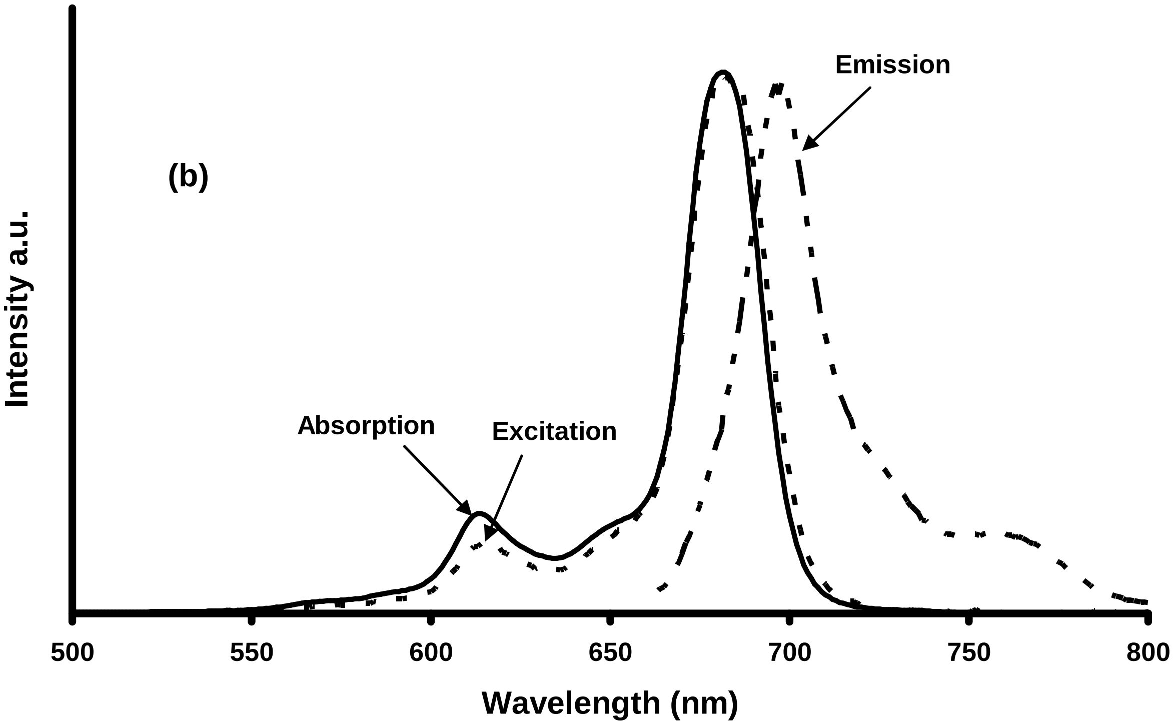


Fig. 3. Absorption spectra of the compound **3** in different solvents. Concentration = 4 x 10^{-6}mol.dm^{-3}.





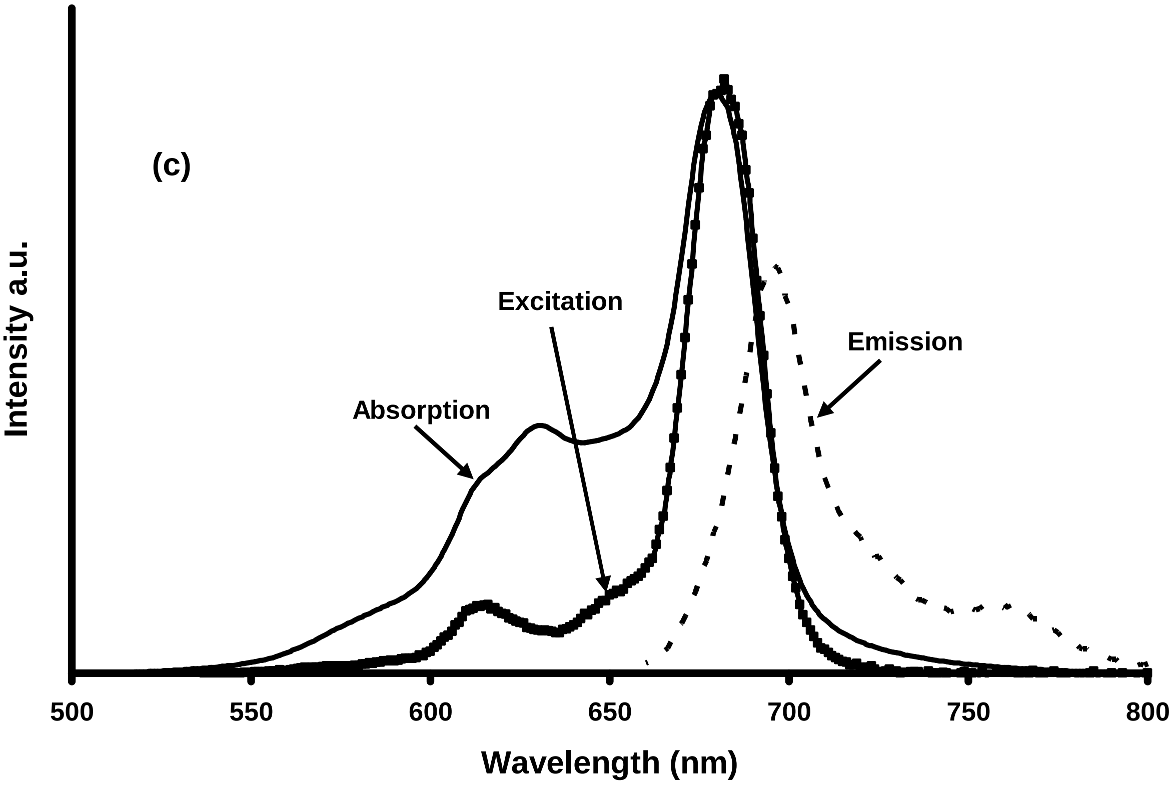


Fig. 4. Absorption, Excitation and Emission spectra of the for compound **1** (a), **2** (b) and **3** (c) in DMSO. Excitation wavelength = 665 nm for **1** and 650 nm for **2** and **3**.

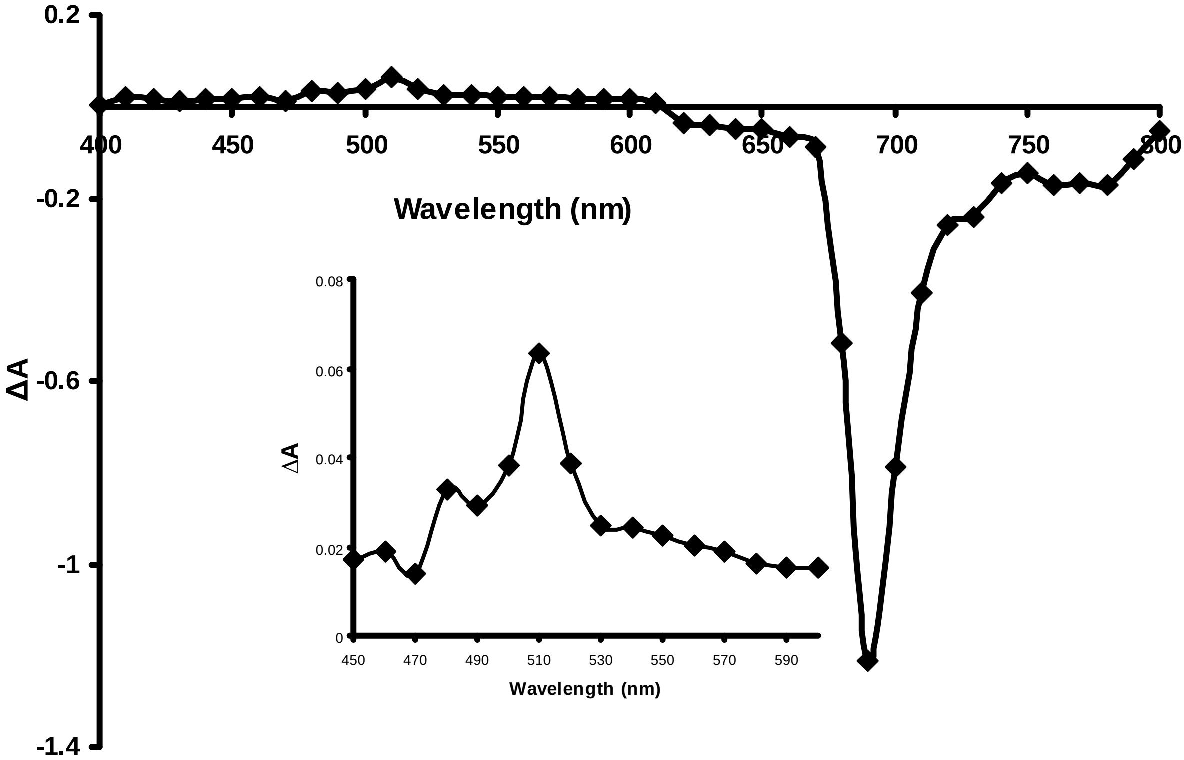


Fig. 5. Transient differential spectrum of complex **3** in toluene.

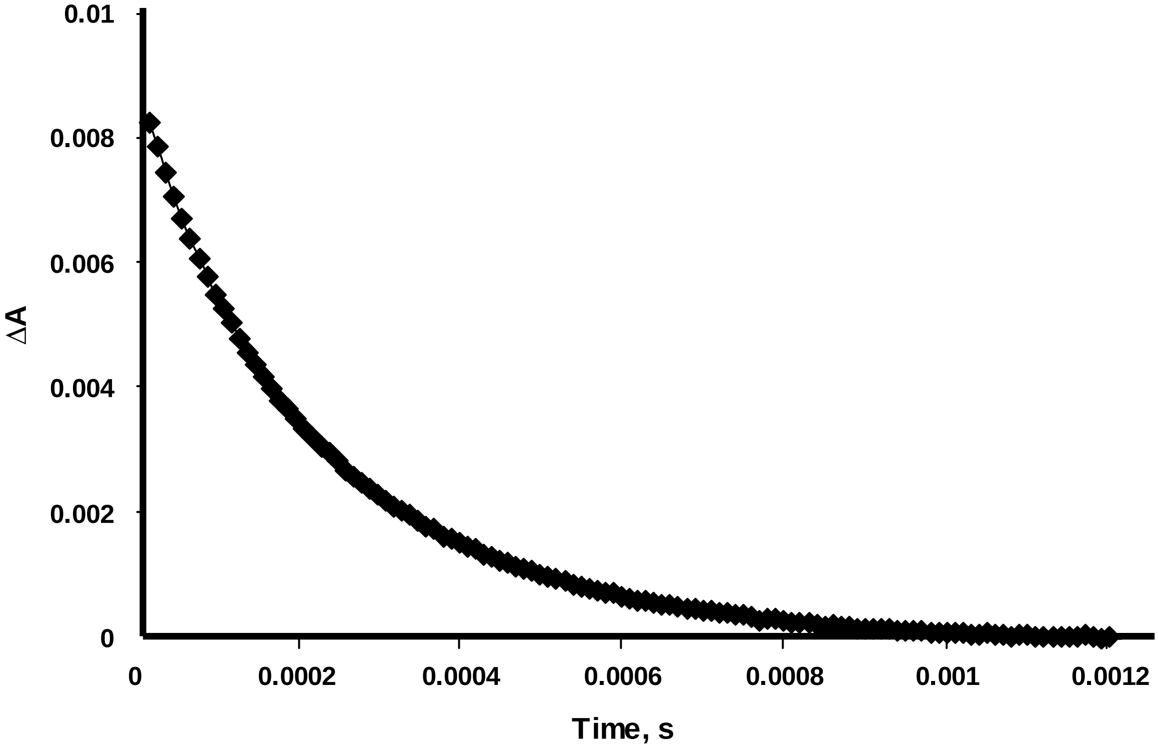


Fig. 6. Triplet decay curve of **2** in DMSO at 510 nm. Excitation wavelength = 681nm.

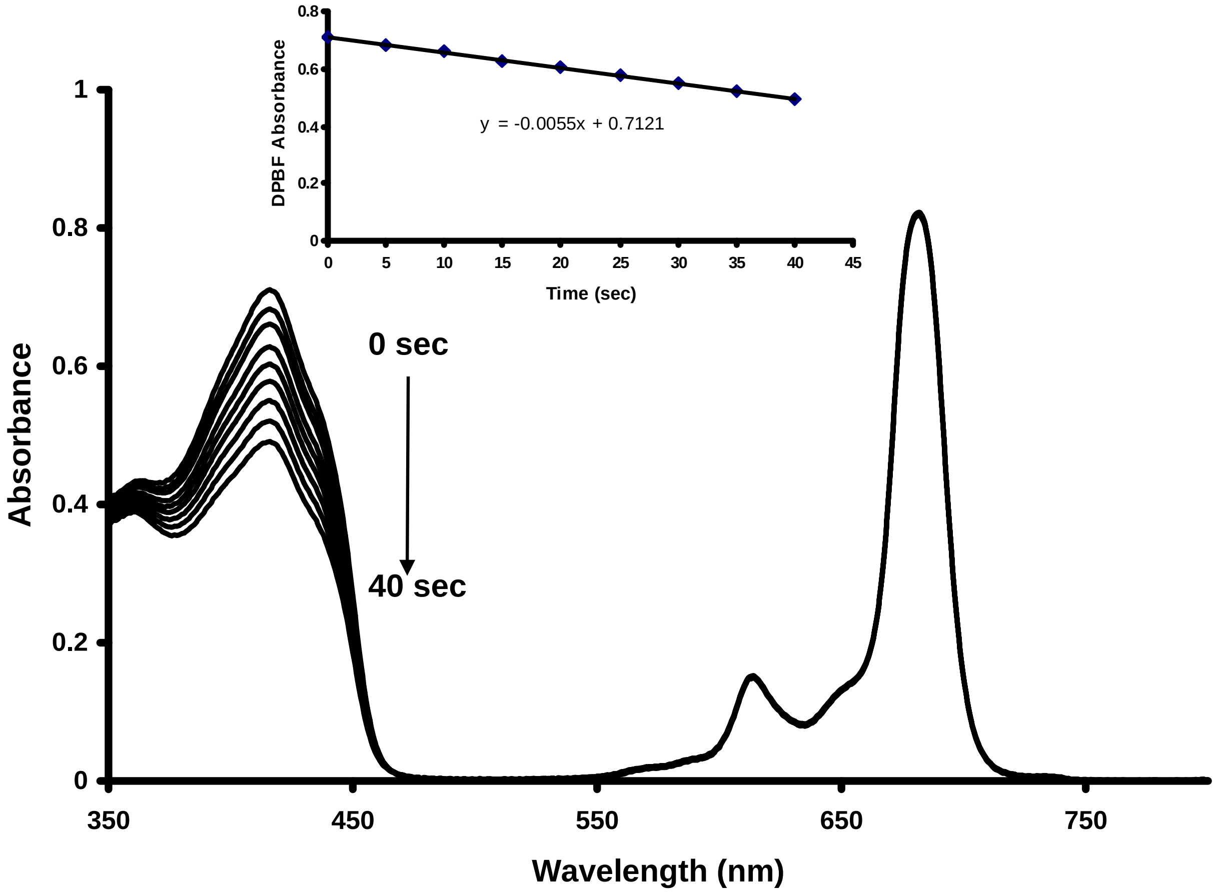


Fig. 7. A typical spectrum for the determination of singlet oxygen quantum yield. This determination was for compound **2** in DMSO at a concentration of $3x10^{-5}$ mol.dm^{-3}.

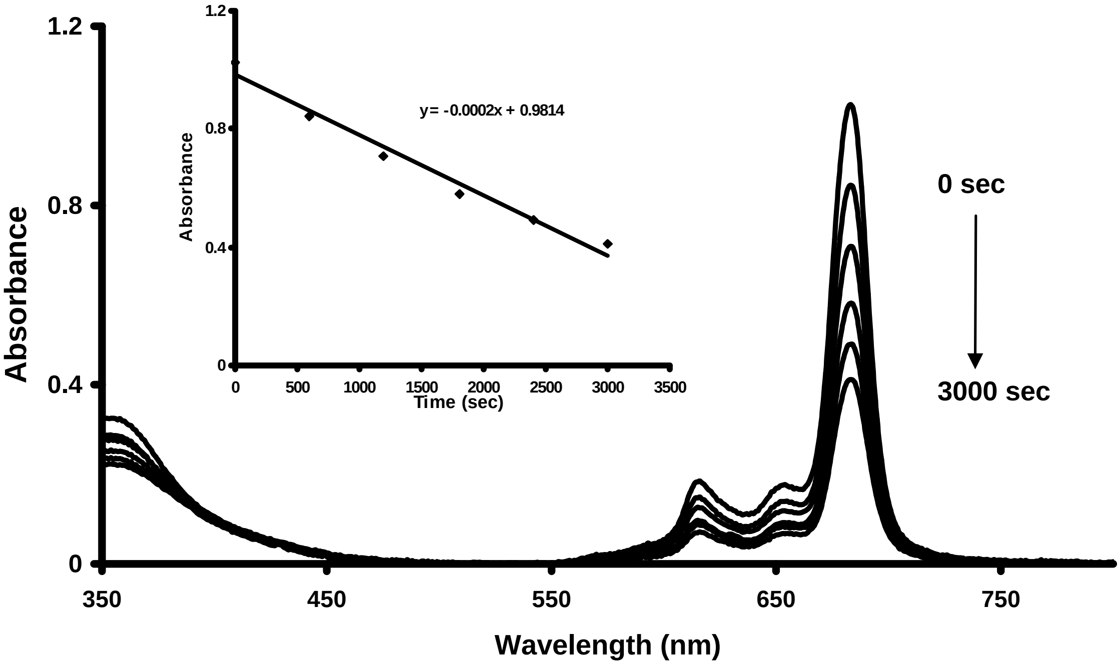


Fig. 8. The photodegredation of compound **3** in toluene showing the disappearance of the Q-band at ten minutes intervals.

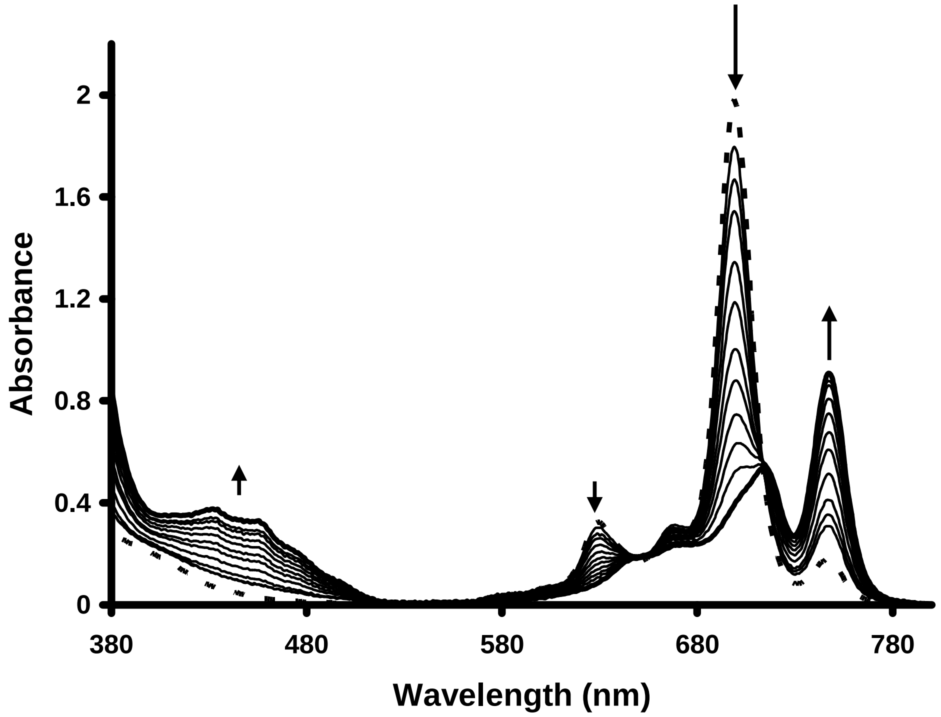


Fig. 9. Absorption spectral changes of **1** (1.20 x 10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.00228, 0.00436, 0.00626……. 0.018 mol dm^{-3}.

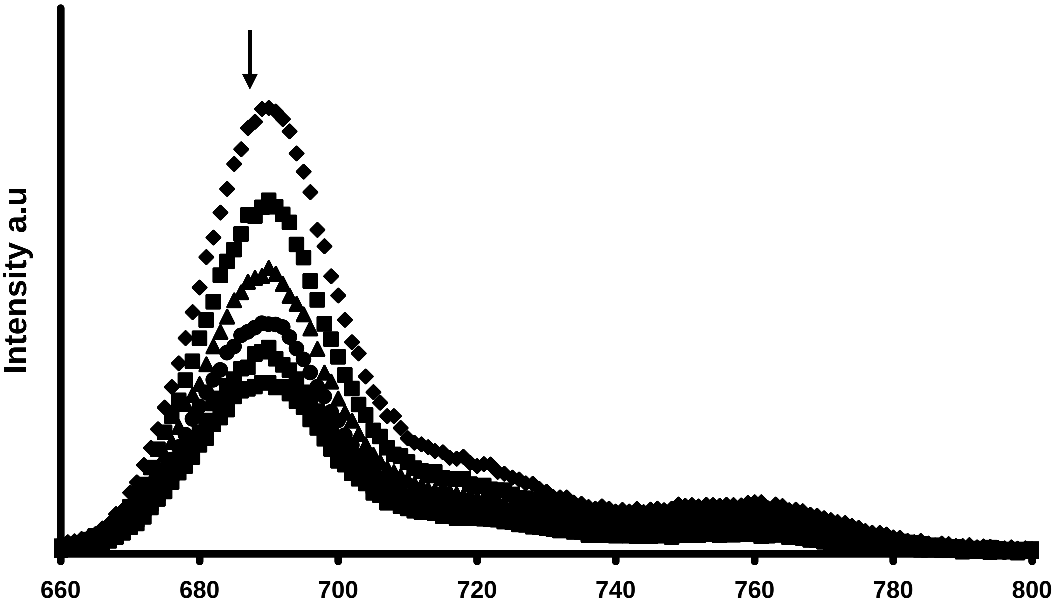


Fig. 10. Fluorescence emission spectral changes of **2** (1.10 x 10^{-5} mol dm^{-3}) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm^{-3}.

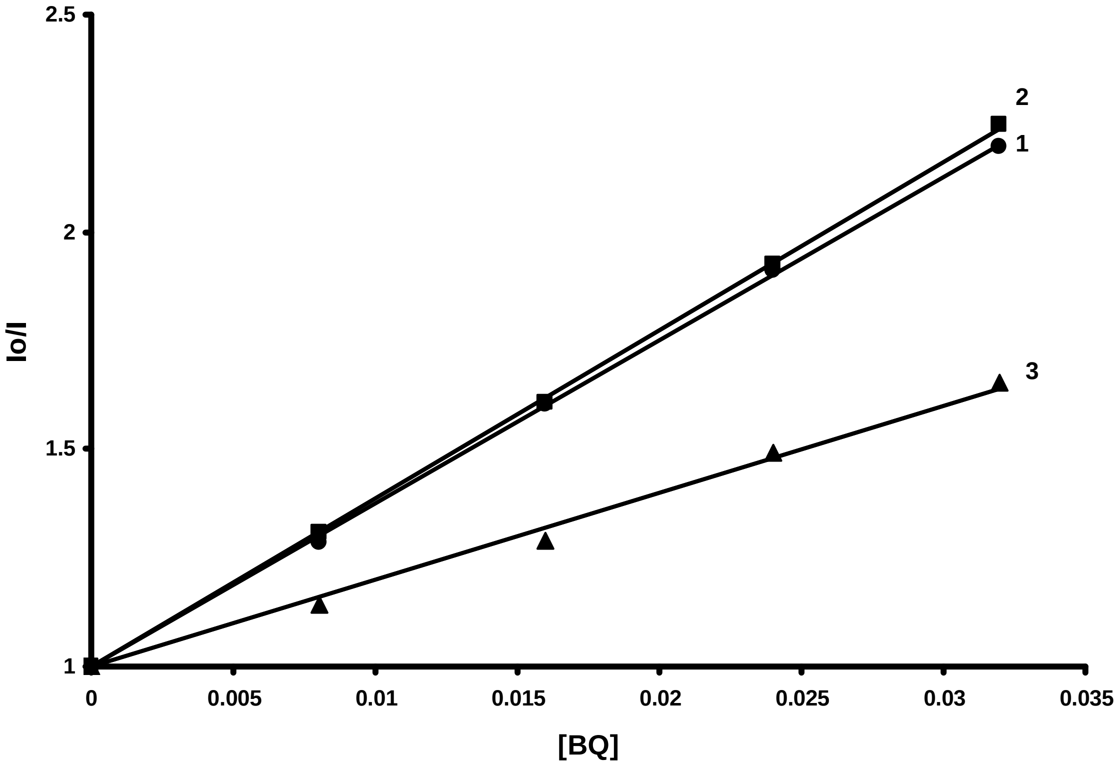


Fig. 11. Stern-Volmer plots for benzoquinone (BQ) quenching of **1**, **2** and **3**. [MPc]~1.00 x10^{-5} mol dm^{-3} in toluene. [BQ] = 0, 0.008, 0.016, 0.024, 0.032 mol dm^{-3}.

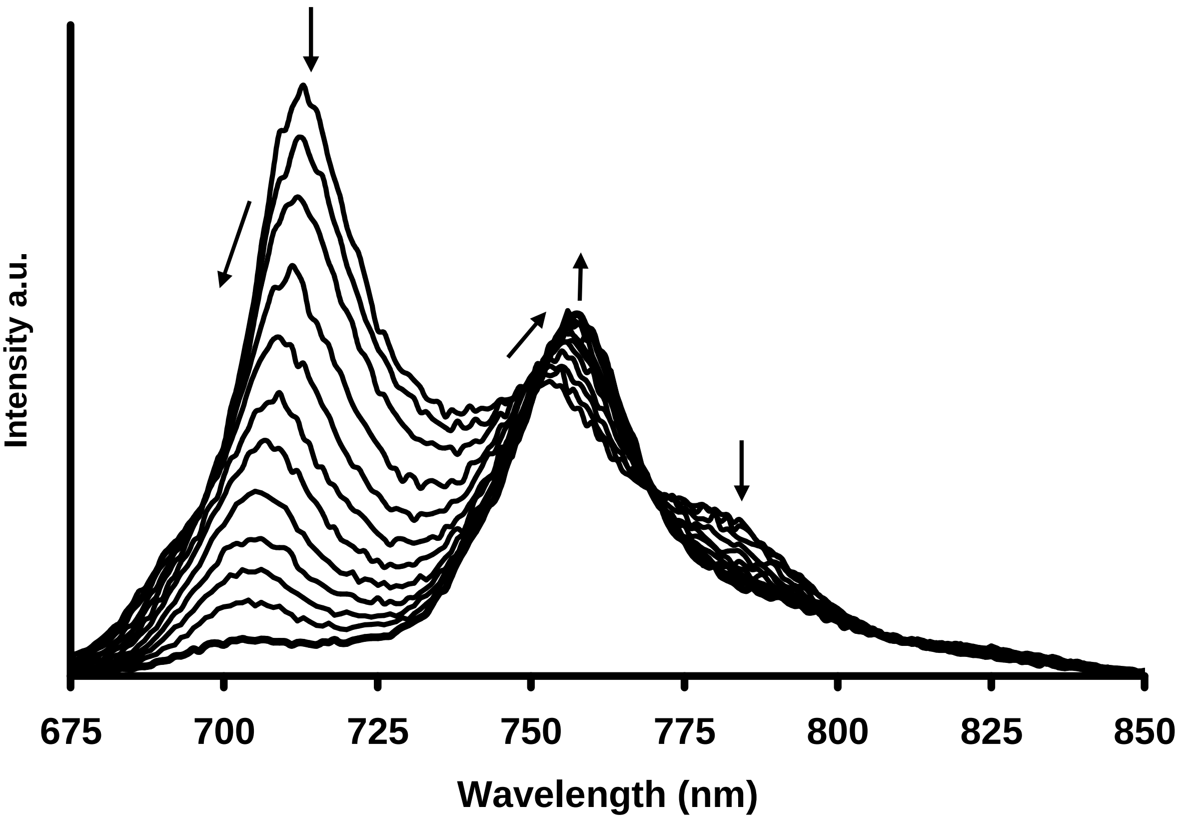


Fig. 12. Fluorescence emission spectral changes of **1** (1.20 x 10^{-5}mol dm^{-3}) on addition of different concentrations of BQ in toluene. [BQ] = 0, 0.00228, 0.00436, 0.00626……. 0.018 mol dm^{-3}.

Table 1 Absorption, excitation and emission spectral data for tetra- and octasubstituted zinc phthalocyanine complexes(**1**, **2** and **3**) in DMSO and toluene.

Compound	Solvent	Q band λ_{max}, (nm)	(log ε)	Excitation λ_{Ex}, (nm)	Emission λ_{Em}, (nm)	Stokes shift Δ_{Stokes}, (nm)
1	**DMSO**	**699**	**5.24**	**698**	**709**	**10**
	Toluene	**699**	**5.19**	**698**	**710**	**11**
2	**DMSO**	**681**	**5.23**	**682**	**693**	**12**
	Toluene	**682**	**5.23**	**682**	**693**	**11**
3	**DMSO**	**680**	**5.18**	**682**	**691**	**11**
	Toluene	**682**	**5.35**	**684**	**694**	**12**

Table 2 Photophysical and photochemical parameters of tetra- and octasubstituted phthalocyanines(**1**, **2** and **3**) in DMSO and toluene.

Compound	Solvent	Φ_F	Φ_T	Φ_{IC}	Φ_d (x 10^{-5})	Φ_Δ	S_Δ
1	**DMSO**	**0.18**	**0.81**	**0.01**	**0.50**	**0.76**	**0.93**
	Toluene	**0.18**	**0.81**	**0.01**	**6.70**	**0.77**	**0.95**
2	**DMSO**	**0.23**	**0.60**	**0.17**	**0.33**	**0.52**	**0.86**
	Toluene	**0.19**	**0.80**	**0.01**	**5.39**	**0.58**	**0.72**
3	**DMSO**	**0.08**	**0.47**	**0.45**	**0.13**	**0.46**	**0.97**
	Toluene	**0.18**	**0.78**	**0.04**	**2.87**	**0.58**	**0.74**
ZnPc[a]	**DMSO**	**0.18**[19]	**0.65**[21]	**0.17**	**2.61**	**0.67**[32]	**1.03**
	Toluene	**0.07**[33]	**0.65**[13]	**0.28**	**6.19**	**0.58**[32]	**0.89**

[a] References given as superscripts

Table 3 Fluorescence quenching data for tetra- and octasubstituted zinc phthalocyanine complexes (**1**, **2** and **3**) in DMSO and toluene.

Compound	**Solvent**	**K_{SV} (M^{-1})**
1	**DMSO**	**24.95**
	Toluene	**37.57**
2	**DMSO**	**26.70**
	Toluene	**38.74**
3	**DMSO**	**19.38**
	Toluene	**20.02**
ZnPc	**DMSO**	**31.90**
	Toluene	**61.53**