Research Article

Photophysical, Photochemical, and BQ Quenching Properties of Zinc Phthalocyanines with Fused or Interrupted Extended Conjugation

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The effects of substituents and solvents on the photophysical and photochemical parameters of zinc(II) phthalocyanines containing four Schiff's base substituents attached directly and through phenyleneoxy-bridges on peripheral positions are reported. The group effects on peripheral position and the continual and intermittent conjugation of the phthalocyanine molecules on the photophysical and photochemical properties are also investigated. General trends are described for photodegradation, singlet oxygen, and fluorescence quantum yields of these compounds in dimethylsulfoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF). Among the different substituents, phthalocyanines with cinnamaldimine moieties (**1c** and **2c**) have the highest singlet oxygen quantum yields (Φ_{Δ}) and those with nitro groups (**1a** and **2a**) have the highest fluorescence quantum yields in all the solvents used. The fluorescence of the substituted zinc(II) phthalocyanine complexes is effectively quenched by 1,4-benzoquinone (BQ) in these solvents.

1. Introduction

Phthalocyanines (Pcs) are remarkable macrocyclic compounds having magnificent physical and chemical properties [1]. Metallophthalocyanines (MPc) have been investigated in detail for many years due to their high chemical and thermal stability, high degree of aromaticity, and synthetic flexibility [2, 3]. They have also found different applications in many fields ranging from industrial [4], technological [5, 6] to medical [7, 8]. Metallophthalocyanine (MPc) derivatives are photoactive and may be employed in photosensitization when the central metal ion is diamagnetic or a nontransition metal element [9, 10]. In this case, it is worth emphasizing the Pcs' application as photosensitizers in the photodynamic therapy (PDT) of tumours. MPcs could lead them to be more efficient sensitizers owing to their high triplet state quantum yields and long triplet lifetimes. The

photophysical properties of the Pc dyes are based on the presence and nature of the central metal ion. MPcs with paramagnetic metal centers produce low cytotoxic singlet oxygen. Closed shell and diamagnetic ions, like Zn^{2+} , Ga^{3+} and Si^{4+} , play important role in Pc complexes and bring excellent properties such as high singlet oxygen generation which is very important for PDT efficiency of photosensitizers [11–13]. ZnPcs have been widely studied because of closed shell d^{10} configuration of the central Zn^{2+} ion; they cause optical spectra that are not complicated by additional bands, as in partially filled transition-metal Pc complexes. Having intensive absorption in the low energy side (red) of visible region, high triplet yields, and efficient singlet oxygen generation makes ZnPcs valuable photosensitizers for PDT applications [14–17]. The general synthesis of organic solvent soluble substituted phthalocyanines is now well established. Pc complexes containing S, N, or O containing substituents

are known [18–20]. However the study of the photochemical and photophysical properties of such complexes is still very limited.

We have recently reported on the synthesis, characterization, and photophysical and photochemical properties of [2,9,16,23-tetra-(salicylaldimino)phthalocyaninatozinc(II)] and [2,9,16,23-Tetra-{8-hydroxyquinolino-salicydenaminatozinc(II)}phthalocyaninato-zinc(II)] [21]. In this work the photophysical and photochemical properties of tetrasubstituted zinc-phthalocyanines with unsaturated cinnamaldimine moieties attached to the inner core through phenoxy-bridges [22] and a new water-soluble tetracationic zinc phthalocyanine [23] which contains four conjugated Schiff's base groups at the peripheral positions are reported. The effect of the tetrasubstitution of zinc Pcs on their photophysical and photochemical properties will be evaluated in dimethylsulfoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF).

2. Experimental

2.1. Materials. Dimethylsulphoxide (DMSO), tetrahydrofuran (THF), and dimethylformamide (DMF) were dried before use as described in Perrin and Armarego [24]. Unsubstituted zinc phthalocyanine, 1, 3-diphenylisobenzofuran (DPBF), and 1,4-benzoquinone (BQ) were purchased from Sigma Aldrich. [2, 9, 16, 23-Tetra-(4-[4-nitrophenoxy])-phthalocyaninatozinc(II)] (**1a**) [22], [2,9,16,23-tetra-(4-[4-aminophenoxy])-phthalocyaninatozinc(II)] (**1b**) [22], [2, 9, 16, 23-tetra-(4-[4-((1Z,2E)-3-[4-(dimethylamino)phenyl]prop-2-en-1-ylideneimino)phenoxy])-phthalocyaninatozinc(II)] (**1c**) [22], tetrakis-([4-(trimethylamino)phenyl]prop-2-en-1-ylideneimino)phenoxy)-phthalocyaninatozinc(II)]tetra-iodide (**1d**) [22], [2(3),9(10),16(17),23(24)-tetra-nitro-phthalocyaninatozinc(II)] (**2a**) [23], [2(3),9(10),16(17),23(24)-tetraaminophthalocyaninato zinc(II)] (**2b**) [23], [2,9,16,23-tetra-(4-[(1E)-3-iminoprop-1-en-1-yl]phenyl}dimethylamino)phthalocyaninatozinc(II)] (**2c**) [23], and tetrakis-(4-[(1E)-3-iminoprop-1-en-1-yl]-N,N,N-trimethylphenylammonium)phthalocyaninato zinc(II)]tetraiodide (**2d**) [23] were synthesized and purified according to the literature procedures.

2.2. Equipment. Absorption spectra in the UV-visible region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Photoirradiations were done using a General Electric quartz line lamp (300 W). 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.

2.3. Photophysical Parameters

2.3.1. Fluorescence Quantum Yields. Fluorescence quantum yields (Φ_F) were determined by the comparative method (1) [29, 30], as follows:

$$\Phi_F = \Phi_{F(\text{Std})} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2}, \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the samples (**1a–1d** and **2a–2d**) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc (in DMSO) ($\Phi_F = 0.20$) [28] was employed as the standard. The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

2.3.2. Fluorescence Quenching by Benzoquinone (BQ). Fluorescence quenching experiments on the substituted zinc phthalocyanine derivatives (**1a–1d** and **2a–2d**) were carried out by the addition of different concentrations of BQ to a fixed concentration of the complexes, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm⁻³. The fluorescence spectra of substituted zinc phthalocyanine derivatives (**1a–1d** and **2a–2d**) at each BQ concentration were recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern-Volmer (S-V) equation [31] were shown in (2):

$$\frac{I_0}{I} = 1 + K_{\text{SV}} [\text{BQ}], \quad (2)$$

where I_0 and I are the fluorescence intensities of fluorophore in the absence and presence of quencher, respectively. The ratios of I_0/I were calculated and plotted against [BQ] according to (2), and K_{SV} is determined from the slope.

2.4. Photochemical Parameters

2.4.1. Singlet Oxygen Quantum Yields. Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the experimental setup described in the literature [32–34]. Typically, a 3 mL portion of the phthalocyanine derivatives, (absorbance ~ 1 at the irradiation wavelength) containing the singlet oxygen quencher, was irradiated in the Q band region with the photo-irradiation setup described in references [32–34]. Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method with ZnPc (in DMSO, DMF, and THF) as a reference. DPBF was used as chemical quencher for singlet oxygen in DMSO, DMF, and THF. Equation (3) was employed for the following calculations:

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{R \cdot I_{\text{abs}}^{\text{Std}}}{R^{\text{Std}} \cdot I_{\text{abs}}}, \quad (3)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yields for the standard unsubstituted ZnPc ($\Phi_\Delta^{\text{Std}} = 0.67$ in DMSO [35],

$\Phi_{\Delta}^{\text{Std}} = 0.56$ in DMF [36], and $\Phi_{\Delta}^{\text{Std}} = 0.53$ in THF [27]). R and R_{Std} are the DPBF photobleaching rates in the presence of the respective samples (**1a–1d** and **2a–2d**) and standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the samples (**1a–1d** and **2a–2d**) and standard, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen [36], the concentration of quencher (DPBF) was lowered to $\sim 3.10^{-5}$ M. Solutions of sensitizer ($C = 1 \times 10^{-5}$ M) containing DPBF were prepared in the dark and irradiated in the Q band region using the photo-irradiation setup. DPBF degradation at 417 nm was monitored. The light intensity 6.75×10^{15} photons $\text{s}^{-1} \cdot \text{cm}^{-2}$ was used for Φ_{Δ} determinations.

2.4.2. Photodegradation Quantum Yields. Photodegradation quantum yield (Φ_d) determinations were carried out using the experimental setup described in the literature [32–34]. Photodegradation quantum yields were determined using (4), as follows:

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

where C_0 and C_t are the samples (**1a–1d** and **2a–2d**) 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 (**1a–1d** and **2a–2d**). A light intensity of 2.24×10^{16} photons $\text{s}^{-1} \cdot \text{cm}^{-2}$ was employed for Φ_d determinations.

3. Results and Discussions

3.1. Ground State Electronic Absorption and Fluorescence Spectra. The UV-Vis spectra of the phthalocyanine complexes exhibits characteristic Q- and B-bands. Two-principle $\pi-\pi^*$ transitions are seen for phthalocyanines: a Q-band (~ 700 nm, a $\pi-\pi^*$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the complexes) and a B-band ($\sim 300\text{--}350$ nm, a deeper $\pi-\pi^*$ transition from the HOMO's (a_{1u} and a_{2u}) to the LUMO (e_g)) [37, 38]. The Q-band absorptions in the UV-Vis absorption spectra of the phthalocyanines (**1a–1d** and **2b–2d**) were observed as a single high intensity band due to a $\pi-\pi^*$ transition at around 677–686 and 685–720 nm in DMSO, 674–682 and 685–714 nm in DMF, and 672–679 [22] and 683–711 nm in THF, respectively, Table 1 and Figure 1. The other bands (B) in the UV region at 348–363 and 349–363 nm in DMSO, 350–378 and 338–368 nm in DMF and 348–383 [22] and 349–357 nm in THF were observed due to the transitions from the deeper π levels to the LUMO [39, 40].

Aggregation behavior of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, nature of solvent and substituents, metal ions, and temperature [41]. Aggregation is not desired in MPc complexes since aggregates are generally photoinactive. Aggregation is more

FIGURE 1: UV-Vis absorption spectra of complex **1a–1d** in DMF.

enhanced for peripherally substituted MPc complexes when compared to nonperipherally substituted ones.

When aggregation occurs, a band in the region of 630–645 nm is observed in the electronic absorption spectrum of MPcs as a result of the intramolecular interactions between the Pc units. Thus, the band at around 640 nm in DMSO for **2a** can be attributed to aggregation. Normally, DMSO is known to prevent aggregation since it is strong coordinating solvent. However, it has been observed before that aggregation occurs in DMSO for some MPc derivatives [42]. In the case of **2a**, where strong electron withdrawing nitro groups are placed as substituents, aggregation occurs in polar solvents. Depending on the polarity of the solvent, aggregated species are more dominant in DMSO, at appreciable level in DMF and hardly present in THF (Figure 2). In DMF, DMSO, and THF, the Q band positions of **1b** are red-shifted relative to those of **1a** with the same red-shifting being observed in all the solvents. The red shift as a consequence of the presence of amino groups on MPc spectra is well known [22, 23].

The fluorescence behavior of the phthalocyanine complexes (**1a–1d** and **2a–2d**) was studied in different solvents. Figure 2 shows fluorescence emission, absorption, and excitation spectra of complexes **1a** and **2a** in DMSO, DMF, and THF as examples of the studied zinc Pc complexes. Fluorescence emission and excitation peaks are listed in Table 1. The excitation spectra were similar to absorption spectra and both were mirror images of the fluorescent spectra for complexes **1a–1d**. The shapes of the excitation spectra of studied compounds were similar to their absorption spectra. This proximity of the wavelength of the Q band absorption to the Q band maxima of the excitation spectrum for phthalocyanine compounds suggests that the nuclear configurations of the ground and excited states are similar and not affected by excitation in Figure 2 even though the absorption and fluorescence excitation spectra are not completely similar for **2a–2d** due to conjugation effect of

TABLE 1: Spectral parameters of **1a–1d** and **2a–2d** in DMSO, DMF, and THF.

Solvent	Complex	Q band $\lambda_{\max}$, (nm)	Excitation λ_{Ex} , (nm)	Emission λ_{Em} , (nm)	Stokes shift Δ_{Stokes} , (nm)
DMSO	1a	677	678	689	12
DMF		674	676	686	12
THF		672 ^a	672	682	10
DMSO	1b	685	689	697	12
DMF		682	683	693	11
THF		679 ^a	687	694	15
DMSO	1c	686	690	696	10
DMF		682	685	691	9
THF		678 ^a	681	686	8
DMSO	1d	681	687	696	15
DMF		680	681	690	10
THF		679 ^a	681	690	11
DMSO	2a	685	707	717	32
DMF		685	699	718	33
THF		683 ^b	690	702	19
DMSO	2b	720	742	748	28
DMF		713	729	734	21
THF		708 ^b	713	710	2
DMSO	2c	718	720	728	10
DMF		710	712	721	9
THF		705 ^b	705	712	7
DMSO	2d	720 ^b	727	730	10
DMF		714 ^b	727	746	32
THF		711 ^b	725	730	19
DMSO	ZnPc	672 ^c	672 ^c	682 ^c	10
DMF	ZnPc	670 ^d	670 ^d	676 ^d	6
THF	ZnPc	666 ^e	666 ^e	673 ^e	7

^aReference [21].^bReference [22].^cReference [25].^dReference [26].^eReference [27].

these groups and aggregation. It is evident from Figure 3 that the emission peaks of the two species (**1a–1d** and **2a–2d**) are shifted to longer wavelength as a result of conversion of $-\text{NO}_2$ groups (**1a** and **2a**) into $-\text{NH}_2$ on phenoxy groups (**1b** and **2b**) in all solvents used. Spectral changes appearing as a result of enhanced conjugation have been clearly shown when the emission spectra of Pcs (**2a–2d**) are compared with those of analogous molecules (**1a–1d**) where identical substituents are attached not directly the Pc core but through phenylene-oxy bridges. As expected, emission bands of Pcs with conjugated cinnamalimine groups show bathochromic shifts (Table 1). The observed Stokes shifts were within the region ($\sim 5\text{--}35$ nm) observed for zinc Pc complexes (**1a–1d** and **2a–2d**).

3.2. Photophysical Studies

3.2.1. Fluorescence Quantum Yields. The fluorescence quantum yields (Φ_F) of zinc phthalocyanines (**1a–1d** and **2a–2d**)

were studied in DMSO, DMF, and THF. Fluorescence is strongly influenced by factors such as solvent polarity, viscosity, refractive index, temperature, and molecular structural features. Fluorescence quantum yields (Φ_F) were calculated in all solvents as shown in Table 2.

While fluorescence quantum yield (Φ_F) values for **1a–1d** and **2a–2d** in DMSO, DMF, and THF are lower than those for unsubstituted ZnPc ($\Phi_F = 0.20$ in DMSO [28], $\Phi_F = 0.17$ in DMF [25], and $\Phi_F = 0.25$ in THF [27], Table 2). This implies that the presence of the substituents (Scheme 1) caused low fluorescence of the parents ZnPc in DMSO, DMF, and THF. The continual conjugation of the substituents on the peripheral position of ZnPc increases electron density from Pc rings to substituents on peripheral position.

Higher Φ_F values were observed for the phthalocyanines including intermittent conjugation compared to the phthalocyanines including continual conjugation in DMSO, DMF, and THF except **1d** and **2d** in DMF and THF. Quaternized

TABLE 2: Photophysical and photochemical properties of **1a–1d** and **2a–2d** in DMSO, DMF, and THF.

Solvent	Complex	Φ_F	Φ_Δ	$\Phi_d (\times 10^{-5})$	Complex	Φ_F	Φ_Δ	$\Phi_d (\times 10^{-5})$
DMSO	1a	0.083	0.52	0.82	2a	0.006	0.21	1.56
DMF		0.103	0.36	51.20		0.035	0.35	20.36
THF		0.081	0.38	2.15		0.053	0.18	5.43
DMSO	1b	0.027	0.20	2.42	2b	0.005	0.10	30.06
DMF		0.011	0.12	42.15		0.008	0.08	13.16
THF		0.047	0.16	5.21		0.002	0.09	3.08
DMSO	1c	0.004	0.65	3.56	2c	0.003	0.54	26.32
DMF		0.009	0.58	40.56		0.007	0.51	31.42
THF		0.002	0.85	1.86		0.009	0.62	3.88
DMSO	1d	0.001	0.44	1.06	2d	0.001	0.36	31.14
DMF		0.004	0.18	62.25		0.026	0.11	52.32
THF		0.005	0.40	1.86		0.017	0.30	6.78
DMSO	Std-ZnPc	0.20 ^a	0.67 ^b	0.26 ^b				
DMF		0.17 ^c	0.56 ^c	0.023 ^c				
THF		0.25 ^d	0.53 ^d	0.002 ^d				

^aReference [28].^bReference [25].^cReference [26].^dReference [27].

group **2d** has higher Φ_F values than **1d** partners due to showing less aggregation tendency. The zinc phthalocyanine complexes bearing nitro group (**1a** and **2a**) are more fluorescent than other studied phthalocyanine complexes in all solvents used due to the nature of the electron withdrawing nitro group. The zinc phthalocyanine complexes (**1b** and **2b**) showed that lowest emission could be as a result of converted NO_2 group into NH_2 on the Pc ring. Complexes **1a** and **2a** have higher fluorescence quantum yield (Φ_F) values than the other complexes and in DMSO, DMF, and THF due to electron withdrawing group effect. Fluorescence quantum yield (Φ_F) values of phthalocyanines substituted Schiff base groups on peripheral positions (**1c** and **2c**) lowered when compared to **1b** and **2b** in DMSO and DMF **2c** except in THF. This effect can be explained by electron-donating feature of Schiff groups. Fluorescence quantum yield (Φ_F) of quaternized phthalocyanines (**1d** and **2d**) has the lowest values than the other complexes. Quaternized group quenched fluorescence quantum yield due to group effects. Comparing Φ_F values of complexes among the three solvents, complex **1a** has the highest fluorescence quantum yield Φ_F values in DMSO, DMF, and THF. Complexes **1d** and **2d** in DMSO, **1d** in DMF, and **1c** and **2b** in THF (Table 2) have the lowest values, respectively. The trend was reversed in DMSO, DMF, and THF Φ_F values were obtained for the Pc derivatives.

3.3. Photochemical Studies

3.3.1. Singlet Oxygen Quantum Yields. Singlet oxygen quantum yield Φ_Δ is a measure of singlet oxygen generation and the Φ_Δ values were obtained using (3). Singlet oxygen

quantum yields were studied in DMSO, DMF, and THF (for **1a–1d** and **2a–2d**) using a chemical method (using DPBF as a singlet oxygen quencher). Figure 4 shows spectral changes observed during photolysis of complexes **1b** and **2b** in THF in the presence of DPBF as an example. The disappearance of DPBF was monitored using UV-Vis spectral changes. There were no changes in the Q band intensities during the Φ_Δ determinations, confirming that complexes are not degraded during singlet oxygen studies [43]. The complexes (**1a–d** and **2a–d**) in this work were selected because they bore similar substituents; however they differed in their extended interrupted conjugation with phenoxy-bridges and continual conjugation bond linkages. We investigated the effect of this difference on the photophysicochemical properties. Phthalocyanines with fused extended conjugation (**2a–2d**) have lower singlet oxygen quantum yield when compared to phthalocyanines with interrupted extended conjugation (**1a–1d**) due to conjugation effect. Interrupted extended conjugation quenched singlet oxygen was generated. When the nature effect of groups on singlet oxygen quantum yields was investigated Schiff base groups (**1c** and **2c**) showed the highest values and quaternized groups (**1d** and **2d**) showed the lowest values in all solvents studied. The values of Φ_Δ are higher for ZnPc complexes including intermittent conjugation when compared to ZnPc complexes including continual conjugation in all studied solvents. The Φ_Δ values of complex **1c** were higher than all the substituted complexes (**1a–1d** and **2a–2d**) in DMSO, DMF and THF (Table 2). The values of Φ_Δ for **1c** (0.58 in DMF, and 0.85 in THF) and for **2c** (0.62 in THF) are higher when compared to unsubstituted ZnPc in DMF (0.56 [26]) and THF (0.53 [44]), Table 2. The values of Φ_Δ were the highest for **1a–1d** in DMSO except **1c** in THF.

FIGURE 2: Absorption, excitation, and emission spectra for complex **1a** in DMSO (a), DMF (b), and THF (c).

3.3.2. Photodegradation Studies. Photodegradation is a process where a phthalocyanine is degraded under light irradiation. It can be used to determine MPCs stability and this is especially important for those molecules intended for use as photocatalysts. The photobleaching stabilities of studied zinc phthalocyanine complexes (**1a–1d** and **2a–2d**) were determined in DMSO, DMF and THF by monitoring the decrease in the intensity of the Q band under irradiation with increasing time. The photodegradation quantum yield (Φ_d) values for the complexes are given in Table 2. All the complexes showed about the same stability with Φ_d of the order of 10^{-5} – 10^{-4} . These values show that the molecules are of moderate stability in all solvents used. Stable ZnPc molecules show values as low as 10^{-6} and for unstable molecules, values of the order 10^{-3} have been reported [45]. The

spectral changes observed for all the complexes (**1a–1d** and **2a–2d**) during irradiation confirmed that photodegradation occurred without phototransformation (Figure 5). Φ_d values of all complexes **1a–1d** are higher in DMF than in DMSO and THF, corresponding to the low Φ_d values in the former solvent, consistent with the notion that photodegradation is singlet oxygen mediated process. Complex **1a** is more stable than complexes **1b–1d** while complex **2a** showed the highest stability in DMSO (Table 2). Photobleaching quantum yield values of complexes **2a–2d** are lower than complexes **1a–1d** in both DMSO, DMF, and THF and hence complexes **2a–2d** are more stable than complexes **1a–1d** in the same solvents. In general photobleaching quantum yield values of phthalocyanines complexes are lower in DMSO than DMF. This trend was observed for our complexes **1a–1d** and

FIGURE 3: The emission peaks of the complexes (**1a–1d**) (a). FIGURE 4: A typical spectrum for the determination of singlet oxygen quantum yield. This figure was for complex **1b** (a) in THF at a concentration of $6 \times 10^{-6} \text{ mol dm}^{-3}$.

2a, but other complexes **2b–2d**. These complexes showed unexpected trend [46, 47].

3.4. Fluorescence Quenching Studies by Benzoquinone. The fluorescence quenching of zinc phthalocyanine complexes (**1a–1d** and **2a–2d**) by benzoquinone (BQ) in DMSO, DMF, and THF was found to obey Stern-Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Figure 6 shows the quenching of complex **1d** and **2d** by BQ in DMSO as an example. The slope of the plots shown in Figure 7 gave K_{SV} values of **1a–1d** in THF as an example, listed in Table 3. The Stern-Volmer plots for studied complexes (**1a–1d** and **2a–2d**) gave straight lines, depicting diffusion-controlled quenching mechanisms (Figure 7). Quinones have high electron affinities and their involvement in electron transfer processes is well documented [48]. The energy of the lowest excited state for quinones is greater than the energy of the excited singlet state of MPc complexes [49]; hence, energy transfer from the excited MPc to BQ is not likely

FIGURE 5: The photodegradation of compound **1d** (a) in DMF showing the disappearance of the Q band at 5 min intervals. FIGURE 6: Fluorescence emission spectral changes of **1d** (a) ($1.00 \times 10^{-5} \text{ mol dm}^{-3}$) on addition of different concentrations of BQ in THF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm^{-3} and saturated with BQ.

to occur. Moreover, MPcs are known to be easily reduced. Therefore MPc fluorescence quenching by BQ is via excited state electron transfer, from the MPc to the BQ [50]. The K_{SV} values for the BQ quenching of phthalocyanine complexes in different solvents are listed in Table 3. The K_{SV} values of the substituted phthalocyanine complexes (**1a–1d**) are lower than Std-ZnPc in DMF and THF, while the values of the complexes (**1a–1d**) are similar to the Std-ZnPc approximately in DMSO. Generally, the K_{SV} values of the substituted phthalocyanine complexes (**2a–2d**) are similar to the Std-ZnPc approximately in DMSO while the K_{SV} values are lower in DMF and higher in THF than Std-ZnPc. When compared the substituted complexes (**1a–1d** and **2a–2d**), the substitution with Schiff base Zn(II) complex group including continual conjugation seems to increase the K_{SV} values of the complexes in DMF and THF. The orders of K_{SV} values for substituted complexes (**1a–1d** and **2a–2d**) among the studied solvents are as follows: DMSO > DMF > THF except **1d** in DMSO and

SCHEME 1: Synthesis of zinc complexes. **1a-1d** and **2a-2d** ((i) Pd/C, hydrazine hydrate, dioxane, and reflux; (ii) 4-(dimethylamino) cinnamaldehyde, THF, and reflux; (iii) CH_3I , $CHCl_3$, and reflux) [22, 23].

THF > DMF > DMSO except **2d** in DMSO, respectively. In different solvents, the K_{SV} values for BQ quenching of phthalocyanine complexes vary directly with the solvents' polarity.

4. Conclusion

This work has described the spectral and photophysical properties of Zn(II) phthalocyanines with fused or interrupted extended conjugation. The photophysical and photochemical properties of the phthalocyanines (**1a-1d** and **2a-2d**) were investigated in DMSO, DMF, and THF. The effect of

the nature of substituent and solvents on the photophysical and photochemical parameters of the phthalocyanine complexes (**1a-1d** and **2a-2d**) are also reported in this study. The fluorescence quantum yields (Φ_F) values of complex **1a** were higher than all the substituted complexes (**1b-1d** and **2a-2d**) in DMSO, DMF, and THF. The highest singlet oxygen quantum yield values were obtained for only **1c** and **2c** among the all complexes synthesized in DMF, DMSO, and THF. These properties give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (type II mechanism), especially complexes **1c** and **2c** may be good candidate as a photosensitizer for PDT application.

TABLE 3: Fluorescence quenching data of substituted zinc phthalocyanine complexes (**1a–1d** and **2a–2d**) in DMSO, DMF, and THF.

Comp	$K_{SV} (M^{-1})$		
	DMSO	DMF	THF
1a	33,07	23,96	19,79
1b	44,64	24,36	9,21
1c	32,54	31,82	30,21
1d	22,43	30,32	11,57
2a	31,61	42,43	77,04
2b	28,79	41,25	49,11
2c	33,65	48,03	63,28
2d	60,71	54,71	102,89
ZnPc	31.90 ^a	57.60 ^b	48.48 ^c

^aReference [25].^bReference [26].^cReference [27]. FIGURE 7: Stern-Volmer plots for benzoquinone (BQ) quenching of substituted zinc phthalocyanine complexes **1a–1d** in THF. [MPC] $\sim 1.00 \times 10^{-5} \text{ mol dm}^{-3}$ in DMSO, DMF, and THF. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, and 0.040 mol dm^{-3} in all solvents used.

Conflict of Interests

Gulsah Gumrukcu, Gulnur Keser Karaoglan, Ali Erdogmus, Ahmet Gül, and Ulvi Avcıata report no financial relationships to Merck or any companies.

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