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# Photophysical and Photochemical Properties of Fluorinated and Nonfluorinated *n*-Propanol-Substituted Zinc Phthalocyanines

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**Keywords:** Phthalocyanines / Photodynamic therapy / Fluorinated ligands / Zinc / Photophysics / Photochemistry

The synthesis of symmetrical fluorinated and nonfluorinated zinc(II) phthalocyanine derivatives obtained from 4,5-dichlorophthalonitrile, 4-nitrophthalonitrile and 3-nitrophthalonitrile substituted with 2,2,3,3-tetrafluoro-1-propanol and *n*-propanol are described. The comparison of the photophysicochemical properties of fluorinated and nonfluorinated substituted zinc(II) phthalocyanines is reported for the first time. The new compounds have been characterized by elemental analysis, IR, $^1$H NMR and $^{19}$F NMR spectroscopy, electronic spectroscopy and mass spectra. The photophysical and photochemical properties of the compounds were studied in dimethyl sulfoxide (DMSO). The complexes were quenched with benzoquinone (BQ), and their fluorescence-quenching properties were investigated in the same solvent. The effects of the number of the substitution and the position on the photophysical and photochemical parameters of the zinc(II) phthalocyanines **1a**–**7a** are also reported. Photophysical and photochemical properties of phthalocyanine complexes are very useful for photodynamic therapy (PDT) of cancer applications. In particular, high singlet-oxygen quantum yields are very important for Type II mechanisms. These complexes have good singlet-oxygen quantum yields and show potential as Type-II photosensitizers.

## Introduction

Phthalocyanine (Pc) derivatives have found wide application both in traditional fields of technology and in some new ones: as functional dyes, for information recording, in laser techniques, medicine, as semiconductors, catalysts, chemical sensors, liquid crystals, nonlinear optics and electrochromic displays.[1] Although phthalocyanines that carry electron-donating substituents have frequently been described, those with electron-withdrawing groups that contain fluorine atoms especially are currently receiving a great deal of attention due to their interesting electron-transporting characteristics.[2–12]

Metallophthalocyanines (MPcs), particularly the aluminium and zinc derivatives, are also currently undergoing clinical trials for use in the photodynamic therapy (PDT) of cancer.[13–19] MPcs have a much higher extinction coefficient of the Q band near 700 nm, which makes them efficiently excitable directly through tissue. Therefore, MPcs have been widely thought to be ideal photosensitizers for PDT of cancer. ZnPcs in particular have been extensively studied since the $d^{10}$ configuration of the central $Zn^{2+}$ ion results in optical spectra that are not complicated by additional bands, as in transition-metal complexes. ZnPcs have intensive red-visible region absorption and high singlet and triplet yields, which makes them valuable photosensitizers for PDT applications.

Recently, we reported that ZnPc derivatives functionalized with substituents such as polyoxyethylene and benzyloxyphenoxy groups in peripheral and nonperipheral positions on the phthalocyanine ring possessed PDT properties due to their interesting photophysical properties.[20–23]

In this paper, we describe the synthesis of new octa- and tetrasubstituted zinc(II) phthalocyanines through the substitution of Pc with fluorinated and nonfluorinated *n*-propanol in peripheral and nonperipheral positions. We studied the photophysical (fluorescence lifetime and quantum yields) and photochemical (singlet-oxygen and photodegradation quantum yields) properties of these $Zn^{II}$ phthalocyanines in DMSO. The fluorescence-quenching behaviour of these $Zn^{II}$–phthalocyanine complexes by benzoquinone in DMSO are also reported.

## Results and Discussion

### Synthesis

Fluorophthalonitriles **1** and **3** are starting compounds for the synthesis of fluoroalkoxy-tetrasubstituted Pcs and they have been prepared by nucleophilic substitution of the nitro group in 4-nitrophthalonitrile or 3-nitrophthalonitrile on 2,2,3,3-tetrafluoro-1-propanol. The fluorinated phthalonitriles **5** and **6** were prepared by the reaction of 2,2,3,3-tetrafluoro-1-propanol with 4,5-dichlorophthalo-

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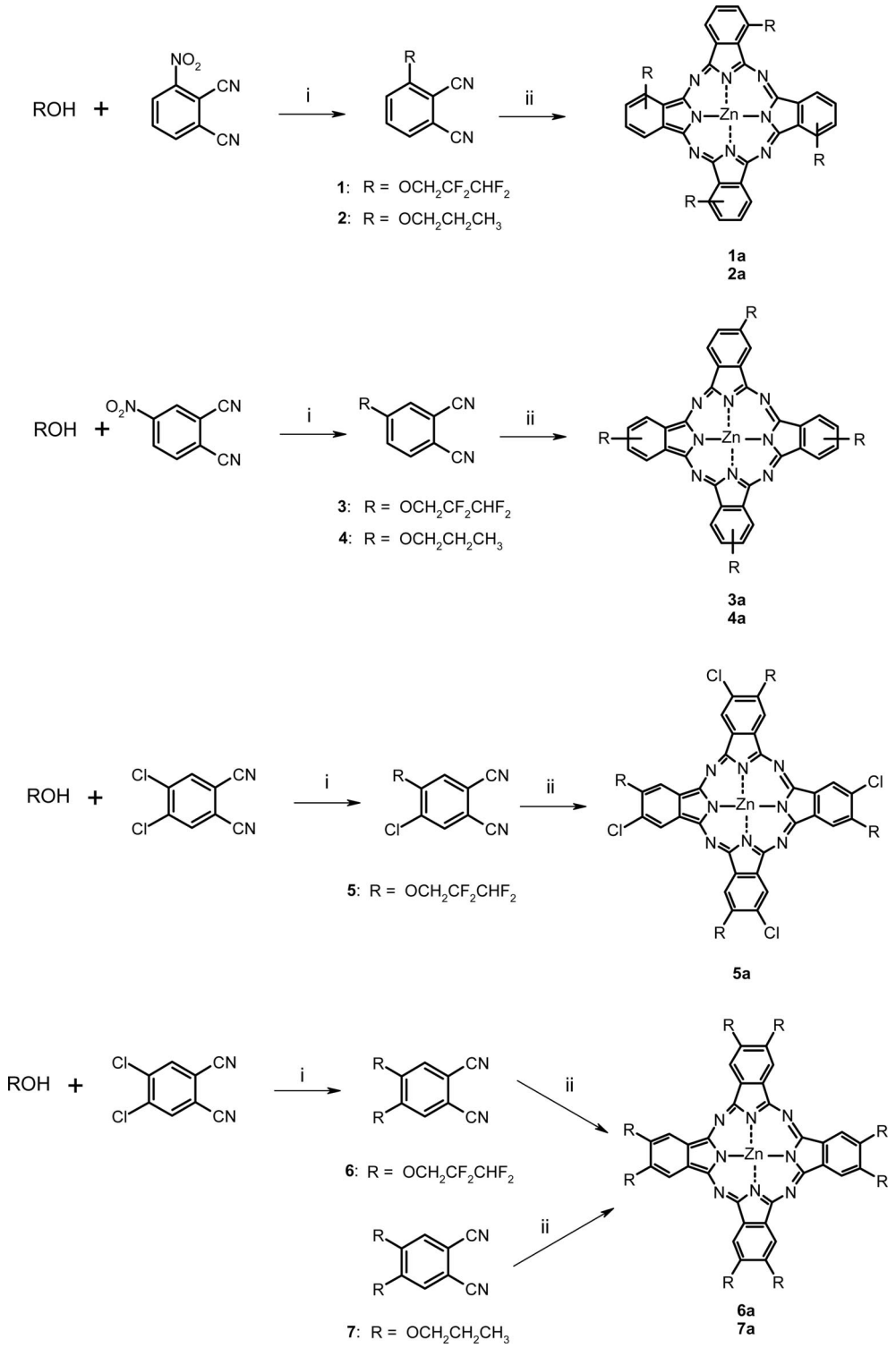
nitrile under the same conditions but in different proportions. On the contrary, the substituted phthalonitrile **7** was unobtainable from *n*-pentanol with 4,5-dichlorophthalonitrile under the same conditions. During the first step, catechol was alkylated during a Williamson etherification reaction with the desired alkyl bromide (2 equiv.) and $K_2CO_3$ (2 equiv.). For the second step, the bisalkylated product was brominated in $CH_2Cl_2$. The third step consisted of a Rosenmund–von Braun substitution reaction of the bromo groups by cyano groups. The bromo compounds




Scheme 1. Chemical pathway used to synthesize the tetra- (**1a**, **2a**, **3a**, **5a**) and octasubstituted (**6a**, **7a**) phthalocyanine derivatives; (i) $K_2CO_3$, DMSO, room temperature, 24 h; (ii) *n*-amyl alcohol, DBU, zinc acetate, reflux.

were heated to reflux with copper(I) cyanide in DMF. The pure product was obtained by crystallization from *n*-hexane. We did not succeed in obtaining 4-chloro-5-(propoxy)-phthalonitrile and its zinc phthalocyanine derivative.

The zinc phthalocyanines were synthesized according to the reported methods.[9,24–30] Both octa- and tetrasubstituted $Zn^{II}$–phthalocyanine reactions were achieved in anhydrous *n*-amyl alcohol and 1,5-diazabicylo[4.3.0]non-5-ene (DBU) as base in the presence of anhydrous zinc acetate at 140 °C under an argon atmosphere (Scheme 1). All the phthalocyanines were obtained by the cyclotetramerization of the phthalonitrile compounds. The tetrasubstituted phthalocyanines obtained by the cyclotetramerization of mono-substituted phthalonitrile derivatives naturally exist as four structural isomers, but the isolation and characterization of all four of them are difficult. Our attempts to separate these isomers by chromatographic techniques in this study have been unsuccessful. The new intermediate products and phthalocyanine complexes were characterized by $^1H$ and $^{19}F$ NMR spectroscopy, mass spectrophotometry, FTIR spectrophotometry, UV/Vis spectrophotometry and elemental analysis.

For all of the studied ZnPc complexes, after a reaction period of 8 h, the product was precipitated in *n*-hexane and filtered. Further purification was done by multiple column chromatography over silica gel and using a mixed solvent system of $CH_2Cl_2$/MeOH as eluent.

The solubility of MPcs is affected by the type of the peripheral substituents. Whereas the nonfluorinated derivatives **2a**, **4a** and **7a** show high solubility in nonpolar organic solvents (e.g., chloroform), the fluorinated derivatives **1a**, **3a**, **5a** and **6a** show high solubility only in more polar organic solvents (e.g., acetone). Generally, fluoroalkyl-substituted compounds are known for their high solubility in polar solvents. This increasing solubility may be due to the fact that the fluorinated atom has the highest electronegativity of all elements and also has an isoelectronic structure with an oxygen atom in the hydroxy group.[19,31]

### Characterization

The IR spectra of all the phthalonitrile compounds **1**–**7** clearly indicate the presence of C≡N groups by the intense stretching bands at around 2235 $cm^{-1}$. The characteristic C–F bands of **1**, **3**, **5** and **6** appeared at 1080–1100 $cm^{-1}$. The $^1H$ NMR spectra of phthalonitrile compounds **1**–**7** were recorded in $CDCl_3$. $^1H$ NMR signals of aliphatic CH and $CH_2$ protons of fluorinated phthalonitriles **1**, **3**, **5** and **6** were observed as a triplet due to effect of the fluorine atoms. $^2J_{H,F}$ geminal and $^3J_{H,F}$ vicinal coupling constants were observed, as expected, at 52 and 23 Hz, respectively. The $^{19}F$ NMR spectroscopy signals for $CF_2$ groups for fluorinated phthalonitriles **1**, **3**, **5** and **6** appeared as a triplet in the range of –123 to –124 ppm, and a doublet was observed for $CF_2H$ in the range of –138 to –139 ppm.

In the mass spectra of compounds **1**–**7**, the presence of the characteristic molecular ion peaks confirmed the proposed structure.

The formation of phthalocyanines from the phthalonitrile derivatives was verified by the disappearance of the C≡N stretching vibration band at around 2235 $cm^{-1}$. The IR spectra of fluorinated Zn–phthalocyanines **1a**, **3a**, **5a** and **6a** are very similar to the nonfluorinated Zn–phthalocyanines **2a**, **4a** and **7a**; only a C–F stretching band appears at around 1100 $cm^{-1}$ for **1a**, **3a**, **5a** and **6a**. The $^1H$ NMR spectra of fluorinated ZnPc complexes **1a**, **3a**, **5a** and **6a** were recorded in [$D_6$]acetone, but [$D_6$]DMSO was used for nonfluorinated ZnPc. The $^1H$ NMR spectra of the fluorinated ZnPcs show the resonance of the fluorine and proton interactions of the side chains at lower field than the corresponding phthalonitriles. The $^1H$ NMR spectra of tetrasubstituted ZnPc **1a**, **2a**, **3a**, **4a** and **5a** showed the phthalocyanine ring protons as unresolved multiplets (most likely due to the presence of isomers).

Two different resonances were observed in the $^{19}F$ NMR spectra of the fluorinated phthalocyanines due to chemical nonequivalency of the fluoro groups in these compounds. The chemical shift of the fluorine atoms is slightly influenced by the aromatic systems. In the $^{19}F$ NMR spectra of fluorinated ZnPcs **1a**, **3a**, **5a** and **6a**, the resonances that belonged to the $CF_2$ groups were observed in the range –126 to –127 ppm as multiplets, and the resonances that belonged to the $CF_2H$ group were observed in the range –140 and –141 ppm as multiplets.

A close investigation of the mass spectra of the Pcs compounds confirmed the proposed structure. The mass spectra of all ZnPcs were obtained by ESI techniques; the molecular-ion peaks were observed as expected (see Figure 1, which offers complex **6a** as an example).

### Ground-State Electronic Absorption and Fluorescence Spectra

The electronic spectra of the complexes showed characteristic absorption in the Q-band region at 696 nm for **1a**, 706 nm for **2a**, 678 nm for **3a**, 683 nm for **4a**, 677 nm for **5a**, 673 nm for **6a** and 678 nm for **7a** in DMSO (Table 1). The B-band region was observed around 350–360 nm in DMSO (Figure 2). The spectra showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for **1a** to **7a** in DMSO.[32] The Q-band positions of the substituted Zn–phthalocyanine complexes **1a**–**7a** are red-shifted relative to that of unsubstituted ZnPc, thus implying that the HOMO–LUMO energy gap of the phthalocyanine ring is reduced upon the introduction of the substituents. The Q bands of the fluorinated substituted Zn–phthalocyanine complexes **1a**, **3a**, **5a** and **6a** were blue-shifted relative to the corresponding nonfluorinated substituted Zn–phthalocyanine complexes **2a**, **4a** and **7a** in DMSO due to the electron-withdrawing properties of the fluorine atoms. The Q-band positions of the octasubstituted Zn–phthalocyanine complex (**6a**) are blueshifted relative to the corresponding octachloro-substituted Zn–phthalocyanine complex (**5a**) in DMSO due to the increase in the electron-withdrawing

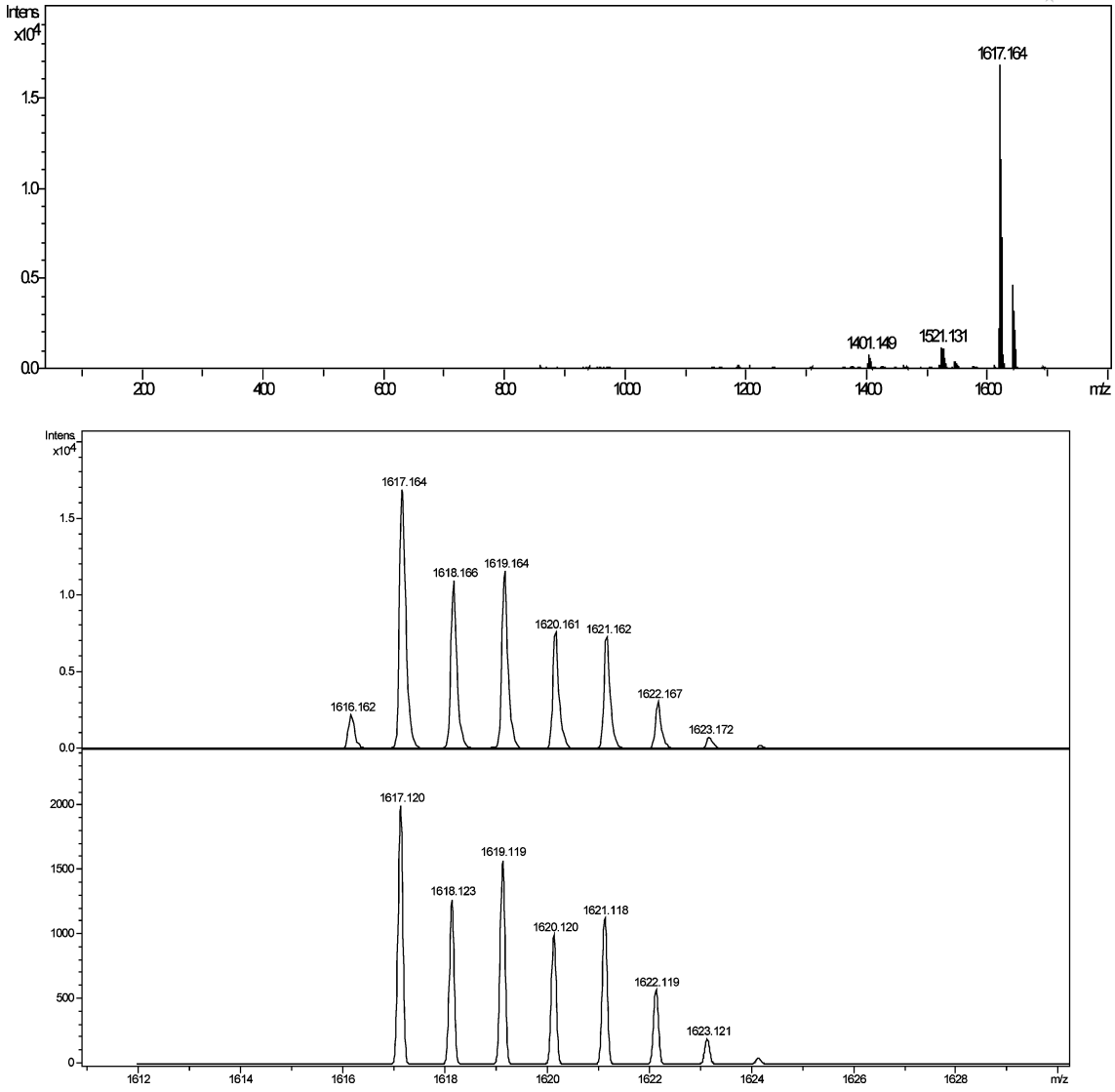



Figure 1. The mass spectrum of compound **6a**.

fluorine atoms on the substituents for complex **6a** (Table 1). The B bands are broad due to the superimposition of the B1 and B2 bands in the 350 to 360 nm region.

Table 1. Absorption, excitation and emission spectroscopic data for unsubstituted and substituted zinc(II) phthalocyanine complexes in DMSO.

| Compound | Q band $\lambda_{max}$ [nm] | log$\varepsilon$ | Excitation $\lambda_{Ex}$ [nm] | Emission $\lambda_{Em}$ [nm] | Stokes shift $\Delta_{Stokes}$ [nm] |
|---|---|---|---|---|---|
| **1a** | 696 | 5.24 | 697 | 708 | 12 |
| **2a** | 706 | 5.08 | 707 | 717 | 11 |
| **3a** | 678 | 5.13 | 680 | 690 | 12 |
| **4a** | 683 | 5.10 | 685 | 697 | 14 |
| **5a** | 677 | 5.08 | 679 | 686 | 9 |
| **6a** | 673 | 5.32 | 674 | 681 | 8 |
| **7a** | 678 | 4.99 | 678 | 686 | 8 |
| ZnPc[a] | 672 | 5.14 | 672 | 682 | 10 |

[a] Ref.[20]

Aggregation is usually depicted as a coplanar association of rings that progresses from monomer to dimer and higher order complexes. It is dependent upon the concentration, the nature of the solvent, the nature of the substituents, complexed metal ions and temperature.[33] In the aggregated state, the electronic structure of the complexed phthalocyanine rings are perturbed, thereby resulting in alternation of the ground- and excited-state electronic structures.[34] Generally in MPc complexes, the peak due to aggregation is blueshifted with respect to the monomer. In this study, the aggregation behaviour of the phthalocyanine complexes **1a**–**7a** was investigated in different solvents [DMSO, toluene, chloroform, THF, DMF and methanol (MeOH)] (Figure 3 for complex **4a**). Whereas the nonperipheral substituted complexes **1a** and **2a** did not show aggregation in MeOH, the peripheral tetra- and octa-substituted complexes **3a**–**7a** showed a broad band around 630 nm in MeOH, thus suggesting aggregation of the latter group of

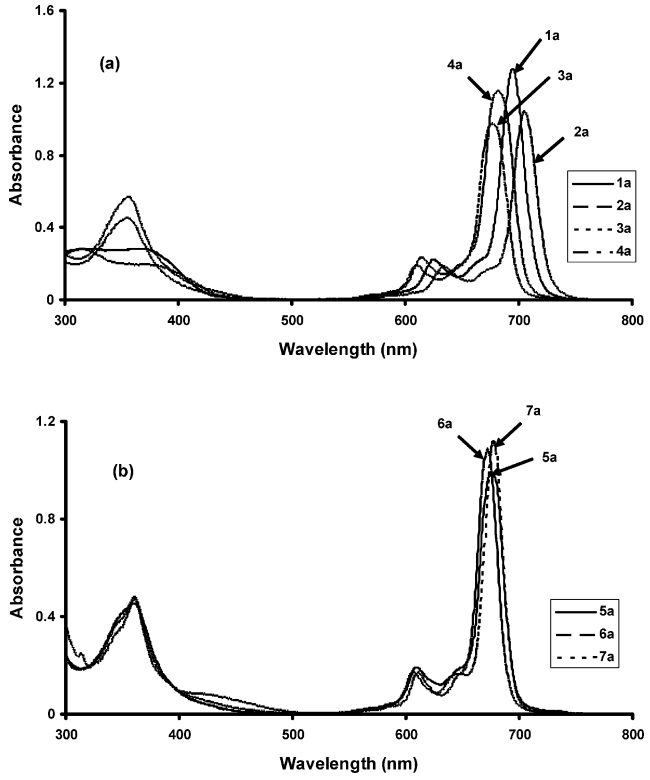



Figure 2. Absorption spectra of (a) tetrasubstituted (**1a**, **2a**, **3a** and **4a**) and (b) octasubstituted (**5a**, **6a** and **7a**) phthalocyanines in DMSO. Concentration: approximately $4 \times 10^{-6}$ mol dm$^{-3}$.

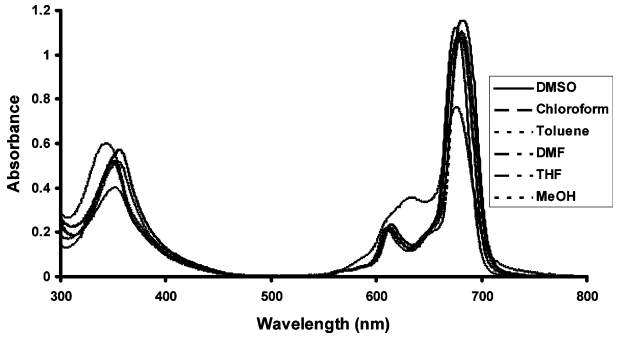



Figure 3. Absorption spectra of **4a** in different solvents. Concentration: $4.00 \times 10^{-6}$ mol dm$^{-3}$.

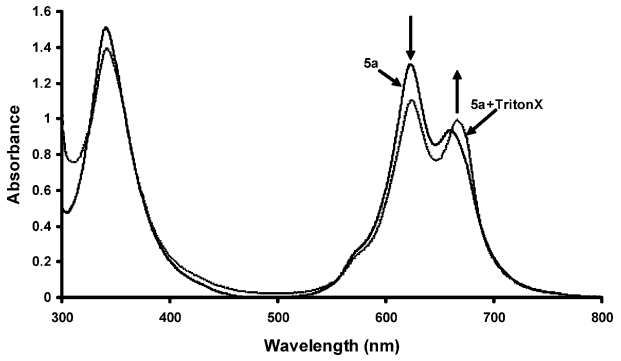



Figure 4. Absorption spectral changes for complex **5a** observed upon addition of Triton X-100 in methanol.

complexes in this solvent. For instance, complex **4a** has two nonvibrational bands at 630 and 674 nm (Figure 3), with the higher energy band being assigned to the aggregate in MeOH. This is typical of aggregation behaviour in MPc complexes.[32] The nonperipherally substituted phthalocyanines are known to show less aggregation than peripherally substituted phthalocyanines.[35] The addition of Triton X-100 (a surfactant) to the solutions of the aggregated complexes **3a**–**7a** in MeOH resulted in a decrease in the aggregation, as was evident from the increase in the intensity of the monomer peak and decrease in the intensity of the aggregate peak (Figure 4 for complex **5a**). We suggest that the high aggregation in MeOH is due to the hydrogen bonds between -OH groups of the solvent and oxygen atoms of the Zn–phthalocyanine complexes. However, whereas the tetrasubstituted Zn–phthalocyanine complexes **1a**–**4a** did not show aggregation in chloroform and toluene, the octasubstituted complexes **5a**–**7a** showed a broad band around 630 nm in these solvents, thereby suggesting aggregation of the latter complexes in chloroform and toluene. Toluene and chloroform are noncoordinating solvents, so would not be axially ligated by the zinc central atom, thereby giving room for π–π stacking between adjacent rings.

The aggregation behaviour of the Zn–phthalocyanine complexes **1a**–**7a** was also investigated at different concentrations in DMSO (Figure 5 for complex **7a**). In DMSO, as the concentration was increased, the intensity of absorption of the Q band also increased for all complexes **1a**–**7a** (Figure 5 for complex **7a**). The Beer–Lambert law was obeyed for all of these complexes in the concentrations ranging from $1.8 \times 10^{-5}$ to $8 \times 10^{-6}$ mol dm$^{-3}$.

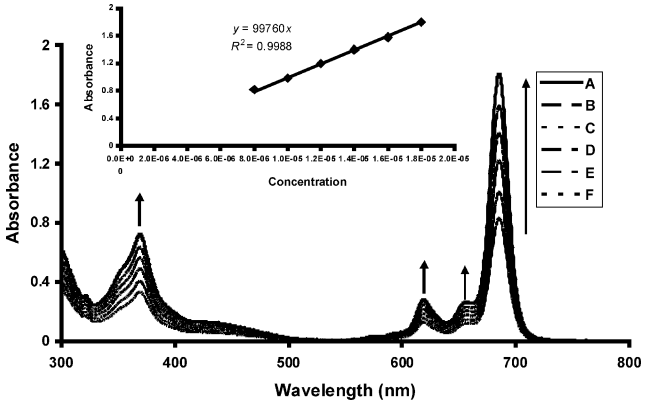



Figure 5. Aggregation behaviour of **7a** in DMSO at different concentrations: $18 \times 10^{-6}$ (A), $16 \times 10^{-6}$ (B), $14 \times 10^{-6}$ (C), $12 \times 10^{-6}$ (D), $10 \times 10^{-6}$ (E), $8 \times 10^{-6}$ (F) mol dm$^{-3}$. Inset: plot of absorbance versus concentration.

All of the studied Zn–phthalocyanine complexes **1a**–**7a** showed similar fluorescence behaviour in DMSO. Figure 6 shows the absorption, fluorescence emission and excitation spectra for complex **1a** in DMSO by way of example. Fluorescence emission peaks were observed at 708 nm for **1a**, 717 nm for **2a**, 690 nm for **3a**, 697 nm for **4a**, 686 nm

for **5a**, 681 nm for **6a** and 686 nm for **7a** in DMSO (Table 1). The excitation spectra were similar to the absorption spectra and both were mirror images of the fluorescence spectra in DMSO (Figure 6, as an example for complex **1a**). 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 are typical of MPc complexes in DMSO (Table 1).

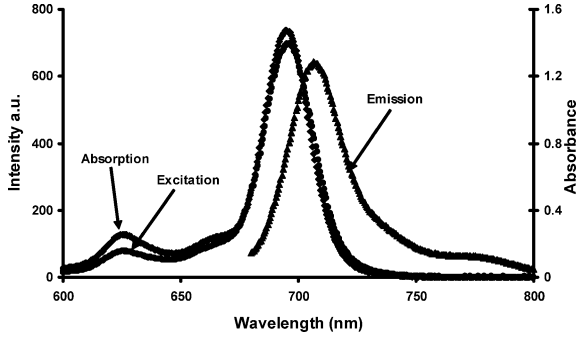



Figure 6. Absorption, excitation and emission spectra for compound **1a** in DMSO. Excitation wavelength = 670 nm.

## Photophysical and Photochemical Properties

### *Fluorescence Lifetimes and Quantum Yields*

The fluorescence quantum yields ($\Phi_F$) of all Zn–phthalocyanine complexes are typical for MPc complexes (Table 2). Whereas the $\Phi_F$ values of the nonperipheral tetrasubstituted Zn–phthalocyanine complexes **1a** and **2a** are lower, the other studied Zn–phthalocyanine complexes **3a** to **7a** are higher than unsubstituted ZnPc in DMSO. Complex **5a** showed the highest and complex **2a** showed the lowest $\Phi_F$ values among the studied Zn–phthalocyanine complexes.

Table 2. Photophysical and photochemical parameters of unsubstituted and substituted zinc(II) phthalocyanine complexes in DMSO.

| Compound | $\Phi_F$ | $\tau_F$ [ns] | $\tau_0$ [ns][a] | $k_F$ [$s^{-1}$] ($\times 10^8$)[b] | $\Phi_d$ ($\times 10^{-5}$)[c] | $\Phi_\Delta$[d] |
|---|---|---|---|---|---|---|
| **1a** | 0.13 | 1.35 | 6.94 | 1.38 | 1.45 | 0.85 |
| **2a** | 0.10 | 0.95 | 9.49 | 1.05 | 2.78 | 0.88 |
| **3a** | 0.31 | 2.50 | 8.07 | 1.23 | 1.46 | 0.53 |
| **4a** | 0.26 | 2.00 | 7.42 | 1.34 | 2.74 | 0.68 |
| **5a** | 0.32 | 3.02 | 9.42 | 1.06 | 1.43 | 0.55 |
| **6a** | 0.20 | 2.77 | 13.88 | 0.71 | 1.53 | 0.79 |
| **7a** | 0.27 | 2.71 | 9.05 | 1.10 | 3.16 | 0.71 |
| ZnPc[e] | 0.18 | 1.22 | 6.80 | 1.47 | 2.61 | 0.67 |

[a] $\tau_0$ is the natural radiative lifetime. [b] $k_F$ is the rate constant for fluorescence. Values were calculated using $k_F = \Phi_F/\tau_F$, in which $\tau_F$ is the fluorescence lifetime. [c] $\Phi_d$ is the photodegradation quantum yield. [d] $\Phi_\Delta$ is the singlet-oxygen quantum yield. [e] Ref.[20]

Generally, the $\Phi_F$ values of the studied fluorinated Zn–phthalocyanine complexes are higher than those of the nonfluorinated Zn–phthalocyanine complexes in DMSO. As described elsewhere,[36] the halogenation of the phthalocyanine complexes on the phthalocyanine skeleton decreases the $\Phi_F$ values. This observation is consistent with the notion that the aromatic fluorine groups are part of the phthalocyanine π system and thus increase the reactant–product intersystem crossing. As a result, intersystem crossing is favoured. An increase in the fluorescence quantum yield is noticed when aromatic fluoro groups on the phthalocyanine skeleton are replaced by fluoro-aliphatic groups. The fluoro-aliphatic substituents are not able to participate in π backbonding, unlike the aromatic fluoro groups; thus, they are not conjugated with the π-ring system.

Lifetimes of fluorescence ($\tau_F$) were calculated using the Strickler–Berg equation.[37] By using this equation, a good correlation has been[38] found for the experimentally and theoretically determined fluorescence lifetimes for the unaggregated molecules, as is the case in this work. Thus, we suggest that the values obtained using this equation are a good measure of the fluorescence lifetimes. The $\tau_F$ value of complex **2a** is lower than that of unsubstituted ZnPc in DMSO, thereby suggesting a lower $\Phi_F$ value. The $\tau_F$ values for nonperipheral tetrasubstituted Zn–phthalocyanine complexes **1a** and **2a** are lower than those of other studied Zn–phthalocyanine complexes **3a** to **7a** in DMSO (Table 2). Complex **5a** showed the highest and complex **2a** showed the lowest $\tau_F$ values among the studied complexes. The natural radiative lifetime ($\tau_0$) values of substituted complexes **1a** to **7a** are larger than that of the unsubstituted complex (ZnPc) in DMSO. The $\tau_0$ values among substituted Zn–phthalocyanine complexes decrease as follows: **6a** > **2a** > **5a** > **7a** > **3a** > **4a** > **1a** > **ZnPc** (Table 2). The rate constants for fluorescence ($k_F$) values of the substituted complexes (**1a** to **7a**) are lower than that of the unsubstituted ZnPc complex in DMSO. The $k_F$ values among substituted Zn–phthalocyanine complexes decrease as follows: **ZnPc** > **1a** > **4a** > **3a** > **7a** > **5a** > **2a** > **6a** (Table 2).

### *Singlet-Oxygen Quantum Yields*

Singlet-oxygen quantum yields ($\Phi_\Delta$) were determined for samples in DMSO using a chemical method and 1,3-diphenylisobenzofuran (DPBF) as a quencher. The disappearance of DPBF was monitored with a UV/Vis spectrophotometer. Many factors are responsible for the magnitude of the determined quantum yield of singlet oxygen; these include: triplet excited-state energy, the 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.

There was no change in the Q-band intensity during the $\Phi_\Delta$ determinations (Figure 7, using complex **3a** in DMSO as an example), thus confirming that complexes are not degraded during singlet-oxygen studies. The $\Phi_\Delta$ values of peripheral tetrasubstituted complex **3a** and tetrachloro-substituted complex **5a** were lower, and those of the other substituted complexes **1a**, **2a**, **4a**, **6a** and **7a** were higher when compared with unsubstituted ZnPc in DMSO (Table 2). The $\Phi_\Delta$ values of the nonperipheral tetrasubstituted Zn–phthalocyanine complexes **1a** and **2a** were higher than pe-

ripheral tetra- (**3a** and **4a**) and octasubstituted (**5a**, **6a** and **7a**) Zn–phthalocyanine complexes in DMSO. This suggests that the higher $\Phi_\Delta$ values of nonperipheral tetrasubstituted phthalocyanine complexes (**1a** and **2a**) could be due to red-shifting of the Q bands for these complexes relative to the peripheral tetra- (**3a** and **4a**) and octasubstituted (**5a**, **6a** and **7a**) Zn–phthalocyanine complexes. Complex **2a** showed the highest and complex **3a** showed the lowest $\Phi_\Delta$ values between the studied complexes. The $\Phi_\Delta$ values among substituted complexes decreases as follows: **2a** > **1a** > **6a** > **7a** > **4a** > **ZnPc** > **5a** > **3a** (Table 2).

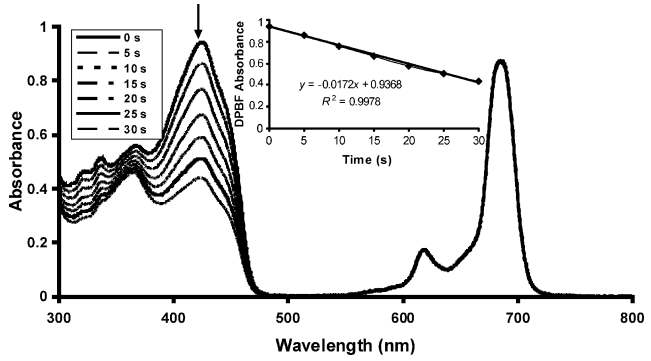



Figure 7. A typical spectrum for the determination of the singlet-oxygen quantum yield. This determination was for compound **3a** in DMSO at a concentration of $1 \times 10^{-5}$ mol dm$^{-3}$. Inset: plot of DPBF absorbance versus time.

### *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 photocatalysts. The collapse of the absorption spectra without any distortion of the shape confirms clean photodegradation not associated with phototransformation. The spectral changes observed for all the Zn–phthalocyanine complexes **1a** to **7a** during irradiation are as shown in Figure 8 (using complex **6a** in DMSO as an example) and hence confirms that photodegradation occurred without phototransformation.

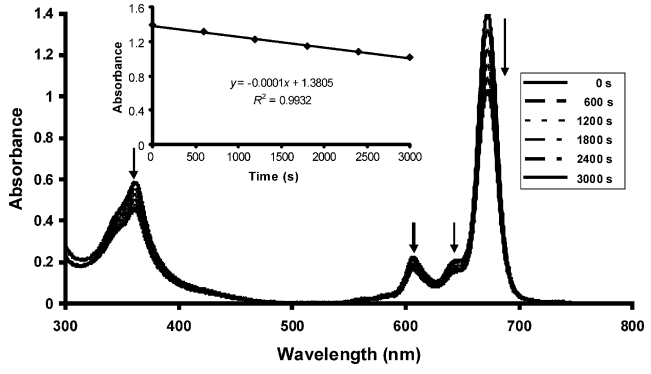



Figure 8. The photodegredation of compound **6a** in DMSO showing the disappearance of the Q band at 10 min intervals. Inset: plot of absorbance versus time.

Table 2 shows that whereas the fluorinated complexes **1a**, **3a**, **5a** and **6a** were more stable to degradation than unsubstituted ZnPc, the nonfluorinated Zn–phthalocyanine complexes **2a**, **4a** and **7a** were less stable to degradation in DMSO. Thus the substitution of the fluorinated propanol groups on ZnPc seems to increase the stability of the complexes in DMSO. Complex **5a** was more stable and complex **7a** was less stable than other substituted Zn–phthalocyanine complexes.

### *Fluorescence Quenching Studies with Benzoquinone (BQ)*

In the presence of the BQ quencher, a reaction takes place between the excited Zn–phthalocyanine complexes and the BQ molecules. The fluorescence quenching of Zn–

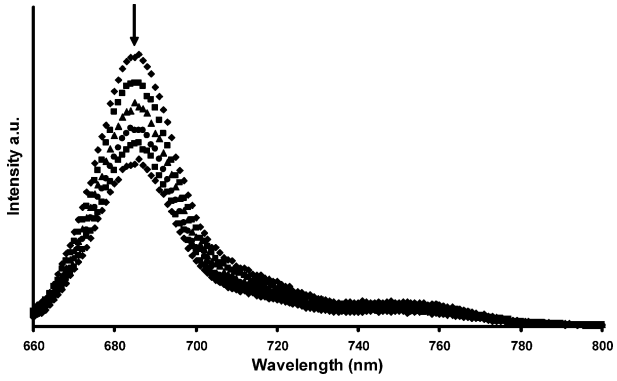



Figure 9. Fluorescence emission spectral changes of **5a** ($1.00 \times 10^{-5}$ mol dm$^{-3}$) upon addition of different concentrations of BQ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm$^{-3}$.

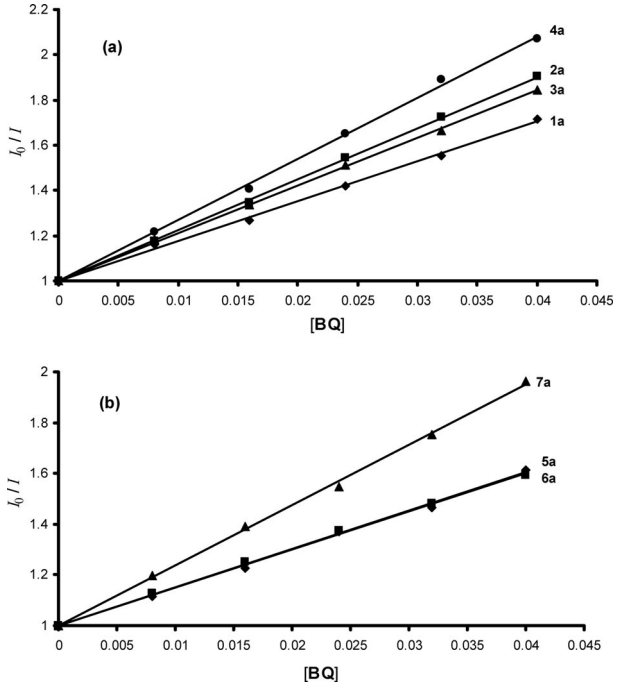



Figure 10. Stern–Volmer plots for benzoquinone (BQ) quenching of (a) **1a**, **2a**, **3a**, **4a** and (b) **5a**, **6a**, **7a**. [MPc] = approximately $1.00 \times 10^{-5}$ mol dm$^{-3}$ in DMSO. [BQ] = 0, 0.008, 0.016, 0.024, 0.032, 0.040 mol dm$^{-3}$.

phthalocyanine complexes by BQ in DMSO was found to obey Stern–Volmer kinetics, which is consistent with diffusion-controlled bimolecular reactions. Figure 9 shows the quenching of complex **5a** by BQ in DMSO as an example. The slope of the plots shown in Figure 10 give Stern–Volmer constant ($K_{SV}$) values. The $K_{SV}$ and bimolecular quenching constant ($k_q$) values for the BQ quenching of zinc phthalocyanine complexes in DMSO are listed in Table 3. The $K_{SV}$ values of the substituted Zn–phthalocyanine complexes **1a** to **7a** are lower than that of unsubstituted ZnPc in DMSO. The $K_{SV}$ values among the substituted complexes decreased as follows: **4a** > **7a** > **2a** > **3a** > **1a** > **6a** > **5a** in DMSO. The $k_q$ values of the substituted Zn–phthalocyanine complexes (**1a** to **7a**) are also lower than that for unsubstituted ZnPc in DMSO. The bimolecular quenching rate constants were found to be close to the diffusion-controlled limits, approximately $10^{10}$ $M^{-1}s^{-1}$. The $k_q$ values among the substituted complexes decreased as follows: **2a** > **6a** > **4a** > **1a** > **3a** > **7a** > **5a** in DMSO (Table 3).

Table 3. Fluorescence quenching data for unsubstituted and substituted zinc(II) phthalocyanines in DMSO.

| Compound | $K_{SV}$ [$M^{-1}$] | $k_q/10^{10}$ [$dm^3 mol^{-1} s^{-1}$] |
|---|---|---|
| **1a** | 17.61 | 1.30 |
| **2a** | 22.53 | 2.37 |
| **3a** | 21.09 | 0.88 |
| **4a** | 27.05 | 1.35 |
| **5a** | 15.00 | 0.49 |
| **6a** | 15.12 | 1.82 |
| **7a** | 23.74 | 0.87 |
| ZnPc[a] | 31.90 | 2.61 |

[a] Ref.[20]

## Conclusion

In conclusion, we have prepared and characterized new 2,2,3,3-tetrafluoro-1-propanol and *n*-propanol-substituted Zn–phthalocyanine complexes for the first time. In DMSO, the compounds produced spectra that showed monomeric behaviour evidenced by a single (narrow) Q band, typical of metallated phthalocyanine complexes for all the complexes **1a** to **7a** in this study. We also studied the aggregation behaviour of these new complexes **1a** to **7a** in different solvents and in different concentrations in DMSO. The substituted complexes showed similar and typical fluorescence behaviour in DMSO. Generally, the $\Phi_F$ values of the fluorinated Zn–phthalocyanine complexes were higher than non-fluorinated Zn–phthalocyanine complexes in DMSO. The substituted Zn–phthalocyanine complexes **1a** to **7a** have good singlet-oxygen quantum yields, especially nonperipheral substituted complexes **1a** and **2a**, which have the highest values. The $\Phi_\Delta$ values, which give an indication of the potential of the complexes as photosensitizers in applications in which singlet oxygen is required (Type II mechanism), ranged from 0.53 to 0.88. Thus, these complexes show potential as Type II photosensitizers. The substitution of ZnPc with 2,2,3,3-tetrafluoro-1-propanol groups seemed to increase the photostability of the complexes, but the substitution of ZnPc with *n*-propanol groups seemed to decrease the photostability of the complexes in DMSO. The substituted Zn–phthalocyanines **1a** to **7a** showed lower $K_{sv}$ and $k_q$ values than the unsubstituted ZnPc in DMSO.

## Experimental Section

**Materials:** Quinoline, dimethyl sulfoxide (DMSO), *n*-hexane, chloroform ($CHCl_3$), methanol (MeOH), *N*,*N*′-dimethylformamide (DMF) and dichloromethane ($CH_2Cl_2$) were dried as described by Perrin and Armarego[39] before use. Zinc acetate, $K_2CO_3$, $Na_2CO_3$, anhydrous $Na_2SO_4$, 1,3-diphenylisobenzofuran (DPBF), 1,5-diazabicylo[4.3.0]non-5-ene (DBU), [$D_6$]DMSO, $CDCl_3$, [$D_6$]acetone, 2,2,3,3-tetrafluoro-1-propanol and *n*-propanol were purchased from commercial suppliers. 3-Nitrophthalonitrile (**1**),[40] 4-nitrophthalonitrile (**2**)[41] and 4,5-dichlorophthalonitrile (**3**)[42] were synthesized and purified according to literature procedures.

**Equipment:** Elemental analyses were obtained with a Thermo Finnigan Flash 1112 instrument. Infrared spectra in KBr pellets were recorded with a Perkin–Elmer FTIR System Spectrum BX. $^1H$ and $^{19}F$ NMR spectra were recorded in [$D_6$]DMSO, [$D_6$]acetone or $CDCl_3$ with Bruker and Varian 500 MHz spectrometers. Absorption spectra in the UV/Vis region were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded with a Varian Eclipse spectrofluorometer using cuvettes (1 cm path length) at room temperature. The mass spectra were acquired with a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated in positive ion mode using an *m*/*z* range of 50–3000. The capillary voltage of the ion source was set at 6000 V and the capillary exit at 190 V. The nebulizer gas flow was 1 bar and drying gas flow 8 mL $min^{-1}$.

Photoirradiation was done with a General Electric quartz line lamp (300 W). A 600 nm glass cutoff filter (Schott) and a water filter were 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 MAX5100 (Molelectron detector incorporated) power meter.

**Photophysical Parameters**

***Fluorescence Quantum Yields and Lifetimes*:** Fluorescence quantum yields ($\Phi_F$) were determined by the comparative method; see Equation (1).[38,43]

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

$F$ and $F_{Std}$ are the areas under the fluorescence curves of the samples (**1a**–**7a**) and the standard, respectively. $A$ and $A_{Std}$ are the respective absorbances of the sample and standard at the excitation wavelengths. The $n$ and $n_{Std}$ values are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc in DMSO ($\Phi_F$ = 0.18)[20] was employed as the standard.

Natural radiative lifetimes ($\tau_0$) were determined with the PhotochemCAD program,[37] which uses the Strickler–Berg equation, and fluorescence lifetimes ($\tau_F$) were given by Equation (2).

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

By using the $\tau_F$ values, rate constants for fluorescence ($k_f$), intersystem crossing ($k_{ISC}$), internal conversion ($k_{IC}$) and photodegradation ($k_d$) were estimated.

**Photochemical Parameters**

***Singlet-Oxygen Quantum Yields*:** Singlet-oxygen ($\Phi_\Delta$) quantum-yield determinations were carried out using the experimental setup described in the literature.[44,45] Typically, a 2 mL portion of the respective substituted ZnPc complex **1a**–**7a** solutions (absorbance ca. 1.5 at the irradiation wavelength) that contained the singlet-oxygen quencher was irradiated in the Q-band region with the photoirradiation setup described in the literature. The $\Phi_\Delta$ values were determined in air using the relative method with DPBF as a singlet-oxygen chemical quencher in DMSO; see Equation (3).

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

$\Phi_\Delta^{Std}$is the singlet-oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{Std}$ = 0.67 in DMSO[46]). $R$ and $R_{Std}$ are the DPBF photobleaching rates in the presence of the respective samples **1a**–**7a** and standard, respectively; $I_{abs}$ and $I_{abs}^{Std}$ are the rates of light absorption by the samples **1a**–**7a** and standard, respectively. The concentrations of DPBF in the solutions were calculated using the determined value of $\log \varepsilon$ = 4.36 at 417 nm (DPBF in DMSO). The light intensity used for $\Phi_\Delta$ determinations was found to be $9.27 \times 10^{15}$ photons $s^{-1}$ $cm^{-2}$.

***Photodegradation Quantum Yields*:** Photodegradation quantum yields ($\Phi_d$) were determined using Equation (4),

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

in which $C_0$ and $C_t$ are the concentrations of the samples **1a**–**7a** before and after irradiation, respectively; $V$ is the reaction volume; $N_A$ is 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 **1a**–**7a**. A light intensity of $3.09 \times 10^{16}$ photons $s^{-1}$ $cm^{-2}$ was employed for $\Phi_d$ determinations.

**Fluorescence Quenching with Benzoquinone (BQ):** Fluorescence-quenching experiments on the substituted ZnPc complexes **1a**–**7a** 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 ZnPc complexes **1a**–**7a** at each BQ concentration were recorded, and the changes in fluorescence intensity were related to BQ concentration by the Stern–Volmer (SV) equation[47]; see Equation (5).

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \quad (5)$$

$I_0$ 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. $K_{SV}$ is the product of the bimolecular quenching constant ($k_q$) and the fluorescence lifetime $\tau_F$; see Equation (6).

$$K_{SV} = k_q.\tau_F \quad (6)$$

The ratios $I_0/I$ were calculated and plotted against [BQ] according to Equation (5), and $K_{SV}$ was determined from the slope.

**Synthesis:** The routes for the synthesis of phthalonitrile and phthalocyanine compounds are given in Scheme 1. All the phthalonitrile and phthalocyanine compounds were prepared corresponding to the reported procedures.[48–51] 2,3-Octakis(propoxy)phthalocyaninatozinc(II) (**7a**) was prepared according to the procedure described in the literature.[24,52]

**3-(2,2,3,3-Tetrafluoropropoxy)phthalonitrile (1):** The 2,2,3,3-tetrafluoro-1-propanol (2.00 g, 11.55 mmol) was dissolved in dried DMSO (6 mL) under an argon atmosphere and 3-nitrophthalonitrile (1.53 g, 11.59 mmol) was added. After stirring for 10 min, finely ground anhydrous $K_2CO_3$ (2.55 g, 18.45 mmol) was added in portions over 2 h with efficient stirring. The reaction mixture was stirred under an argon atmosphere at room temperature for 24 h, and then the solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined extracts were treated first with $Na_2CO_3$ solution (5%), then with water and dried with anhydrous $Na_2SO_4$. $CH_2Cl_2$ was removed under reduced procedure. The pure product was obtained by crystallization from *n*-hexane. The product was soluble in $CH_2Cl_2$, $CHCl_3$, acetone and DMSO. Yield 1.00 g (51%) as a white powder; m.p. 120 °C. FTIR: $\tilde{\nu}_{max}$ = 3099 (ArCH), 2235 (CN), 1588, 1474, 1454 (C=C), 1082 (C–F) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.69 (t, 1 H, ArH), 7.44 (d, 1 H, ArH), 7.21 (d, 1 H, ArH), 6.19 (t, $^2J_{F,H}$ = 53 Hz, 1 H, CH), 4.50 (t, $^3J_{F,H}$ = 23 Hz, 2 H, $OCH_2$) ppm. $^{19}F$ NMR (500 MHz, $CDCl_3$): $\delta$ = –124.40 (m, 2 F, $CF_2$), –138.97 (dd, 2 F, $CF_2H$) ppm. $C_{11}H_6F_4N_2O$ (258.17): calcd. C 51.17, H 2.34, N 10.85; found C 51.02, H 2.24, N 10.35. EI-MS: $m/z$ = 258 $[M]^+$.

**3-Propoxyphthalonitrile (2):** Compound **2** was prepared according to the procedure described for **1**. Yield 0.64 g (59%) as a white powder; m.p. 123 °C. FTIR: $\tilde{\nu}_{max}$ = 3088 (ArCH), 2972–2883 (CH), 2237 (CN), 1580, 1565 (C=C), 1450 ($CH_2$) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.83 (t, 1 H, ArH), 7.39 (dd, 1 H, ArH), 7.34 (dd, 1 H, ArH), 3.89 (t, 2 H, Ar-$OCH_2$), 1.78 (m, 8 H, $OCH_2CH_2$), 0.87 (t, 12 H, $CH_3$) ppm. $C_{11}H_{10}N_2O$ (186.21): calcd. C 70.95, H 5.41, N 15.04; found C 70.43, H 5.14, N 14.55. EI-MS: $m/z$ = 186 $[M]^+$.

**4-(2,2,3,3-Tetrafluoropropoxy)phthalonitrile (3):** Compound **3** was prepared according to the procedure described for **1**. Yield 1.9 g (50%) as a white powder; m.p. 82 °C. FTIR: $\tilde{\nu}_{max}$ = 3035 (ArCH), 2235 (CN), 1600, 1567 (C=C), 1084 (C–F) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.74 (d, 1 H, ArH), 7.22 (d, 1 H, ArH), 7.20 (dd, 1 H, ArH), 6.06 (t, $^2J_{F,H}$ = 53 Hz, 1 H, CH), 4.44 (t, $^3J_{F,H}$ = 23 Hz, 2 H, $OCH_2$) ppm. $^{19}F$ NMR (500 MHz, $CDCl_3$): $\delta$ = –123.75 (t, 2 F, $CF_2$), –137.91 (d, 2 F, $CF_2H$) ppm. $C_{11}H_6F_4N_2O$ (258.17): calcd. C 51.17, H 2.34, N 10.85; found C 51.02, H 2.24, N 10.35. EI-MS: $m/z$ = 258 $[M]^+$.

**4-Propoxyphthalonitrile (4):** Compound **4** was prepared according to the procedure described for **1**. Yield 0.30 g (28%) as a white powder; m.p. 76 °C. FTIR: $\tilde{\nu}_{max}$ = 3082 (ArCH), 2974–2886 (CH), 2230 (CN), 1596 (C=C), 1495 ($CH_2$) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.86 (d, 1 H, ArH), 7.51 (d, 1 H, ArH), 7.38 (dd, 1 H, ArH), 3.92 (t, 2 H, Ar-$OCH_2$), 1.80 (m, 8 H, $OCH_2CH_2$), 0.88 (t, 12 H, $CH_3$) ppm. $C_{11}H_{10}N_2O$ (186.21): calcd. C 70.95, H 5.41, N 15.04; found C 70.45, H 5.49, N 14.69. EI-MS: $m/z$ = 186 $[M]^+$.

**4-Chloro-5-(2,2,3,3-tetrafluoropropoxy)phthalonitrile (5):** Synthesis and purification was as outlined for **1**. 4,5-Dichlorophthalonitrile was employed instead of 3-nitrophthalonitrile. The amounts of the reagents employed were as follows: 2,2,3,3-tetrafluoro-1-propanol (1.00 g, 7.57 mmol), 4,5-dichlorophthalonitrile (1.40 g, 7.65 mmol) and anhydrous $K_2CO_3$ (1.60 g, 11.60 mmol) in dried DMSO (5 mL). The reaction mixture was stirred under an argon atmosphere at room temperature for 24 h. Then the solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined extracts were treated first with $Na_2CO_3$ solution (5%), then with water and dried with anhydrous $Na_2SO_4$. $CH_2Cl_2$ was removed under reduced procedure. The pure product was obtained by crystallization from *n*-hexane. The product was soluble in $CH_2Cl_2$, $CHCl_3$, acetone and DMSO. Yield 0.9 g (41%) as a white powder; m.p. 101 °C. FTIR: $\tilde{\nu}_{max}$ = 3038 (ArCH), 2238 (CN), 1585 (C=C), 1098 (C–F), 788 (C–Cl) $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ = 7.66 (s, 1 H, ArH), 7.06 (s, 1 H, ArH), 6.00 (t, $^2J_{H,F}$ = 52 Hz, 1 H, CH), 4.36 (t, $^3J_{H,F}$ = 22 Hz, 2 H Ar-O-$CH_2$) ppm. $^{19}F$ NMR (500 MHz, $CDCl_3$): $\delta$ = –123.772 (t, 2 F, $CF_2$), –138.362 (d, 2 F, $CF_2H$) ppm. $C_{11}H_5ClF_4N_2O$ (292.62): calcd. C 45.15, H 1.72, N 9.57; found C 45.40, H 1.74, N 9.47. EI-MS: *m*/*z* = 292 $[M]^+$.

**4,5-Bis(2,2,3,3-tetrafluoropropoxy)phthalonitrile (6):** 2,2,3,3-Tetrafluoro-1-propanol (1.00 g, 7.57 mmol) and 4,5-dichlorophthalonitrile (0.69 g, 3.78 mmol) were added successively with stirring to dried DMSO (10 mL). After they were dissolved, anhydrous $K_2CO_3$ (1.05 g, 7.57 mmol) was added portionwise for 2 h, and the reaction mixture was stirred under an argon atmosphere at room temperature for 24 h. The solvent was evaporated under reduced pressure. Water (5 mL) was added and the aqueous phase was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined extracts were treated first with $Na_2CO_3$ solution (5%), then with water and dried with anhydrous $Na_2SO_4$. $CH_2Cl_2$ was removed under reduced procedure. The pure product was obtained by crystallization from *n*-hexane. The product was soluble in $CH_2Cl_2$, $CHCl_3$, acetone and DMSO. Yield 0.9 g (31%) as a white powder; m.p. 126 °C. FTIR: $\tilde{\nu}_{max}$ = 3058 (ArCH), 2235 (CN), 1595 (C=C), 1110 (C–F) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.16 (s, 1 H, ArH), 6.06–5.83 (t, $^2J_{H,F}$ = 53 Hz, 1 H, CH), 4.58 (t, $^3J_{H,F}$ = 23 Hz, 2 H Ar-O-$CH_2$) ppm. $^{19}F$ NMR (500 MHz, $CDCl_3$): $\delta$ = –123.754 (t, 4 F, $CF_2$), –138.035 (d, 4 F, $CF_2H$) ppm. $C_{14}H_8F_8N_2O_2$ (388.21): calcd. C 43.31, H 2.08, N 7.22; found C 43.33, H 1.94, N 7.20. EI-MS: *m*/*z* = 388 $[M]^+$.

**4,5-Bis(propoxy)phthalonitrile (7):** Compound **7** was prepared according to the procedure described in the literature.[52] Yield 1.1 g (36%) as a white powder; m.p. 250 °C. FTIR: $\tilde{\nu}_{max}$ = 3058 (ArCH), 2967–2878 (CH), 2226 (CN), 1589 (C=C) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ = 7.37 (s, 2 H, ArH), 4.00–3.96 (t, 4 H, $ArCH_2$), 1.81–1.74 (m, 4 H, $OCH_2CH_2$), 1.02–0.98 (t, 6 H, $CH_3$) ppm. $C_{14}H_{16}N_2O_2$ (244,29): calcd. C 68.83, H 6.60, N 11.47; found C 68.79, H 6.59, N 11.39. EI-MS: *m*/*z* = 244 $[M]^+$.

**1,(4)-Tetrakis(2,2,3,3-tetrafluoropropoxy)phthalocyaninatozinc(II) (1a):** A mixture of **1** (500 mg, 1.94 mmol), anhydrous zinc(II) acetate (89 mg, 0.485 mmol), *n*-amyl alcohol (10 mL) and DBU (0.5 mL) were heated to reflux for 8 h under an argon atmosphere in a round-bottomed flask. The resulting green suspension was cooled and the product was precipitated by the addition of *n*-hexane. The green crude product was purified by passing through a silica gel column with $CH_2Cl_2$/MeOH (10:1) elution. Yield 210 mg (40%) as a green powder; m.p. >200 °C. FTIR: $\tilde{\nu}_{max}$ = 3040 (ArCH), 2934 ($CH_2$), 1586 (C=C), 1489, 1335, 1080 (C–F) $cm^{-1}$. $^1H$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = 8.28–8.07 (d, 4 H, ArCH), 7.98–7.07 (m, 8 H, ArCH), 5.80–5.74 (m, $^2J_{H,F}$ = 56 Hz, 4 H CH), 4.88–4.83 (m, $^3J_{H,F}$ = 24 Hz, 8 H Ar-O-$CH_2$) ppm. $^{19}F$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = –125.878 to –127.427 (m, 8 F, $CF_2$), –141.271 to –142.077 (m, 8 F, $CF_2H$) ppm. $C_{44}H_{24}F_{16}N_8O_4Zn$ (1096.13): calcd. C 47.78, H 2.92, N 10.13; found C 47.73, H 2.87, N 10.03. ESI-MS: *m*/*z* = 1097.40 $[M + H]^+$.

**1,(4)-Tetrakis(propoxy)phthalocyaninatozinc(II) (2a):** Compound **2a** was prepared according to the procedure described for **1a**. The amounts of reagents employed were as follows: **2** (300 mg, 1.611 mmol), anhydrous zinc(II) acetate (74 mg, 0.403 mmol) and DBU (0.4 mL) in *n*-amyl alcohol (10 mL). Yield 70 mg (22%) as a green powder; m.p. >200 °C. FTIR: $\tilde{\nu}_{max}$ = 3040 (ArCH), 2960–2875 ($CH_2$), 1605 (C=C), 1488, 1385, 1340, 1228, 1050 (C–F) $cm^{-1}$. $^1H$ NMR (500 MHz, [D$_6$]DMSO): $\delta$ = 8.16 (b, 4 H, ArCH), 7.64 (b, 4 H, ArCH), 6.98 (b, 4 H, ArCH), 4.16 (m, 8 H, Ar-O-$CH_2$), 2.05 (m, 8 H, O-$CH_2CH_2$), 1.12 (t, 12 H, $CH_3$) ppm. $C_{44}H_{40}N_8O_4Zn$ (807.21): calcd. C 65.23, H 4.98, N 13.83; found C 64.88, H 4.92, N 13.01. ESI-MS: *m*/*z* = 808.60 $[M + H]^+$.

**2,(3)-Tetrakis(2,2,3,3-tetrafluoropropoxy)phthalocyaninatozinc(II) (3a):** A mixture of **3** (500 mg, 1.94 mmol), anhydrous zinc(II) acetate (89 mg, 0.485 mmol), *n*-amyl alcohol (10 mL) and DBU (0.5 mL) were heated to reflux for 8 h under an argon atmosphere in a round-bottomed flask. The resulting green suspension was cooled and the product was precipitated by the addition of *n*-hexane. The green crude product was purified by passing through a silica gel column with $CH_2Cl_2$/MeOH (10:1) elution. Yield 300 mg (56%) as a green powder; m.p. >200 °C. FTIR: $\tilde{\nu}_{max}$ = 3040 (ArCH), 1608 (C=C), 1488, 1455, 1340, 1069 (C–F) $cm^{-1}$. $^1H$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = 8.45–8.28 (d, 4 H, ArCH), 7.96 (s, 4 H, ArCH), 7.48–7.36 (d, 4 H, ArCH), 6.94–6.73 (t, $^2J_{H,F}$ = 52 Hz, 4 H CH), 4.98 (s, 8 H, Ar-O-$CH_2$) ppm. $^{19}F$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = –126.288 (s, 8 F, $CF_2$), –140.499, –140.611 (d, 8 F, $CF_2H$) ppm. $C_{44}H_{24}F_{16}N_8O_4Zn$ (1096.13): calcd. C 47.78, H 2.92, N 10.13; found C 48.23, H 2.57, N 9.23. ESI-MS: *m*/*z* = 1097.40 $[M + H]^+$.

**2,(3)-Tetrakis(propoxy)phthalocyaninatozinc(II) (4a):** Compound **4a** was prepared according to the procedure described for **3a**. The amounts of reagents employed were as follows: **4** (300 mg, 1.611 mmol), anhydrous zinc(II) acetate (74 mg, 0.403 mmol), DBU (0.4 mL) in amyl alcohol (10 mL). Yield 147 mg (45%) as a green powder; m.p. >200 °C. FTIR: $\tilde{\nu}_{max}$ = 3040 (ArCH), 2961–2880 (CH), 1600 (C=C), 1487, 1470, 1380 $cm^{-1}$. $^1H$ NMR (500 MHz, [D$_6$]DMSO): $\delta$ = 8.11 (b, 4 H, ArCH), 7.70 (b, 4 H, ArCH), 6.93 (d, 4 H, ArCH), 3.91 (s, 8 H, Ar-O-$CH_2$) 1.83 (m, 8 H, O-$CH_2$-$CH_2$), 1.11 (t, 12 H, $CH_3$) ppm. $C_{44}H_{40}N_8O_4Zn$ (807.0): calcd. C 65.23, H 4.98, N 13.83; found C 64.99, H 4.89, N 13.65. ESI-MS: *m*/*z* = 808.60 $[M + H]^+$.

**Octakis-2,9,16,23-chloro-3,10,17,24-(2,2,3,3-tetrafluoropropoxy)-phthalocyaninatozinc(II) (5a):** A mixture of **5** (250 mg, 0.85 mmol), anhydrous zinc(II) acetate (39 mg, 0.21 mmol), *n*-amyl alcohol (10 mL) and DBU (0.5 mL) were heated to reflux for 8 h under an argon atmosphere in a round-bottomed flask. The resulting green suspension was cooled and the product was precipitated by the addition of *n*-hexane. The green crude product was purified by passing through a silica gel column with $CH_2Cl_2$/MeOH (10:1) elution. Yield 63 mg (24%) as a green powder; m.p. >200 °C. FTIR: $\tilde{\nu}_{max}$ = 3040 (ArCH), 2934 ($CH_2$), 1605 (C=C), 1488, 1439, 1386, 1080 (C–F) $cm^{-1}$. $^1H$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = 8.30 (b, 4 H, ArCH), 7.86 (b, 4 H, ArCH), 6.75 (b, $^2J_{H,F}$ = 53 Hz, 4 H CH), 4.96 (b, $^3J_{H,F}$ = 23 Hz, 8 H Ar-$CH_2$-O) ppm. $^{19}F$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = –126.191 (b, 8 F, $CF_2$), –140.602 (b, 8 F, $CF_2H$) ppm. $C_{44}H_{20}Cl_4F_{16}N_8O_4Zn$ (1236.0): calcd. C 42.76, H 1.63, N 9.07; found C 42.48, H 1.57, N 8.25. ESI-MS: *m*/*z* = 1237.0 $[M + H]^+$.

**2,3-Octakis(2,2,3,3-tetrafluoropropoxy)phthalocyaninatozinc(II) (6a):** A mixture of **6** (250 mg, 0.64 mmol), anhydrous zinc(II) acetate (30 mg, 0.16 mmol), *n*-amyl alcohol (10 mL) and DBU (0.5 mL) were heated to reflux for 8 h under an argon atmosphere. The resulting green suspension was cooled, the reaction mixture was poured into an adequate amount of *n*-hexane, and the resulting precipitate was collected. The crude product was dissolved in acetone and was purified by passing through a silica gel column with $CH_2Cl_2$/MeOH (10:1) elution. Yield 99 mg (38%) as a green powder; m.p. >200 °C. FTIR: $\tilde{\nu}_{max}$ = 3045 (ArCH), 1600 (C=C), 1500, 1460, 1380, 1110 (C–F) $cm^{-1}$. $^1H$ NMR ([D$_6$]acetone): $\delta$ = 8.53 (s, 8 H, ArH), 6.89–6.68 (t, $^2J_{H,F}$ = 52 Hz, 8 H, CH), 5.14 (s, 16 H, Ar-OCH$_2$) ppm. $^{19}F$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = –126.756 (m, 16 F, $CF_2$), –140.903 (m, 16 F, $CF_2H$) ppm. $C_{56}H_{32}F_{32}N_8O_8Zn$ (1616.25): calcd. C 41.56, H 1.99, N 6.92; found C 41.19, H 1.84, N 6.77. ESI-MS: *m*/*z* = 1617.2 $[M + H]^+$.

**2,3-Octakis(propoxy)phthalocyaninatozinc(II) (7a):** Compound **7a** was prepared according to the procedure described in the literature.[24,25]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