Solvent effects on the photochemical and fluorescence properties of zinc phthalocyanine derivatives

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Abstract

The effects of solvents on the singlet oxygen, photobleaching and fluorescence quantum yields for zinc phthalocyanine (ZnPc) and its derivatives; (pyridino)zinc phthalocyanine ((py)ZnPc), zinc octaphenoxyphthalocyanine (ZnOPPc) and zinc octaestronephthalocyanine (ZnOEPc), is presented. The effects of the solvents on the ground state spectra are also discussed. The largest red shift of the Q band was observed in aromatic solvents, the highest shift being observed for 1-chloronaphthalene. Higher singlet fluorescence quantum yields were observed in THF for ZnPc and ZnOPPC. Also in the same solvent phototransformation rather than photobleaching was observed for ZnOPPc. Split Q band in the emission and excitation spectra of ZnOPPc was observed in some solvents and this is explained in terms of the lowering of symmetry following excitation.

1. Introduction

Metallophthalocyanines (MPcs) have been a subject of extensive study because of their increasing diverse applications from industrial (catalysts, photoconductors, etc.) to biomedical (photodynamic therapy, PDT) [1]. Zinc (II) phthalocyanine (ZnPc), complexes have in particular been intensively studied with respect to their photosensitizing properties [2, 3, 4, 5, 6, 7, 8, 9 and 10]. Metallophthalocyanine complexes tend to aggregate in solution [11, 12 and 13] and aggregation diminishes the photosensitising ability of MPc complexes. Addition of groups to the peripheral positions of MPc complexes is known to influence the properties of the MPc to a large degree [14, 15, 16, 17 and 18]. For instance, the peripheral substituents increase the distance between the planar macrocycle rings carrying the $\pi$-electrons thereby making solvation easier. Solvents affect aggregation in phthalocyanine complexes. Organic solvents are known to reduce aggregation whereas aqueous solvents result in highly aggregated complexes. However, many phthalocyanine complexes remain aggregated even in non-aqueous solutions [10, 19 and 20]. Aromatic solvents such as benzene or toluene are known to give narrow Q bands in phthalocyanines whereas broadening is observed in other non-aromatic solvents [21]. Solvents also affect the photophysical and photochemical properties of MPc complexes [19, 20, 21 and 22].

It is believed that during PDT, the photosensitiser is excited to its triplet state, and then transfers the energy to ground state oxygen, $O_2$ ($^3\Sigma_g$) generating excited state oxygen, $^1O_2$ ($^1\Delta_g$) which is the chief cytotoxic species, through the so-called Type II mechanism [23]. Studies on the photostability of MPcs

during photosensitized reactions as well as their ability to generate the singlet oxygen are of immense importance.

In this work we report on the effects of a series of solvents on the singlet oxygen, photobleaching and fluorescence quantum yields for zinc phthalocyanine (ZnPc) and its derivatives; (pyridino)zinc phthalocyanine ((py)ZnPc), zinc octaphenoxyphthalocyanine (ZnOPPc) and zinc octaestronephthalocyanine (ZnOEPc), Fig. 1. Peripheral or axial substitution of the zinc phthalocyanine complexes increases solubility. Also zinc phthalocyanine complexes peripherally substituted with estrone result in photosensitisers which may be selective towards certain tumour cells, the so called third generation type of photosensitisers.
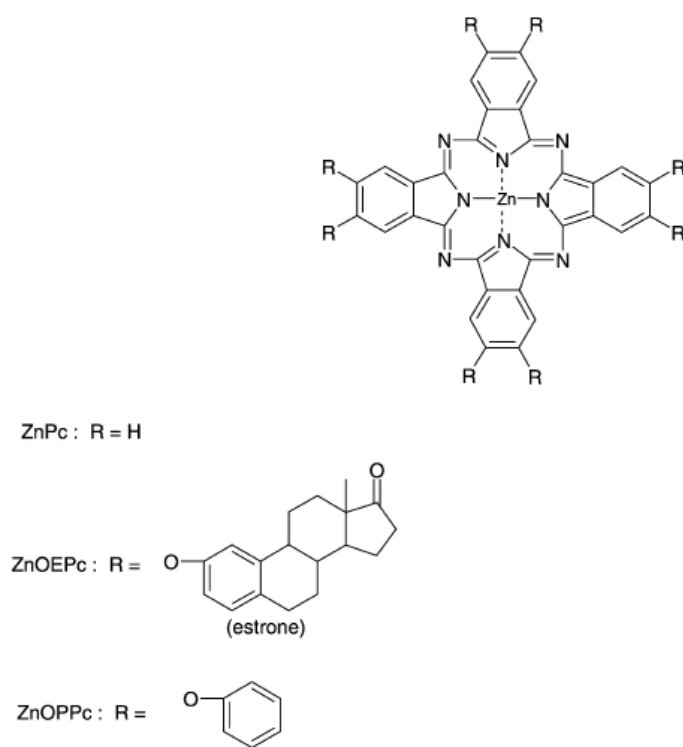


Fig. 1. Molecular structure of the zinc phthalocyanine (ZnPc) and its derivatives; (pyridino)zinc phthalocyanine ((py)ZnPc), zinc octaphenoxyphthalocyanine (ZnOPPc) and zinc octaestronephthalocyanine (ZnOEPc).

## 2. Experimental
### 2.1. Materials

Zinc phthalocyanine (ZnPc) was obtained from Aldrich. Zinc octaphenoxy-phthalocyanine (ZnOPPc) and zinc octaestronephthalocyanine (ZnOEPc) were synthesised as described before [10]. Axially ligated (pyridino)zinc phthalocyanine was synthesised using established procedures for the synthesis of axially ligated phthalocyanines by refluxing ZnPc in pyridine for 3 h. The solvent was then evaporated in air at 60 °C. The resulting solid was washed with hexanes. The complex formed is represented as (py)ZnPc since ZnPc is known to form a five coordinate complex with pyridine [24]. 1,3-Diphenylisobenzofuran

(DPBF) was purchased from Aldrich and used as received. *N,N′*-dimethylformamide (DMF, SAARCHEM) was freshly distilled. Dimethylsulphoxide (DMSO, SAARCHEM) was dried in alumina before use. All other solvents were obtained from SAARCHEM and used without further purification.

2.2. Photobleaching and singlet oxygen quantum yields

Photobleaching ($\Phi_p$) and singlet oxygen ($\Phi_\Delta$) quantum yields determinations were carried out using the experimental set-up which has been described in detail elsewhere [10, 25 and 26]. $\Phi_\Delta$ was determined using DPBF as a singlet oxygen quencher. The relative method shown by Eq. (1) was employed for calculations of $\Phi_\Delta$ values

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{W I_{abs}^{Std}}{W^{Std} I_{abs}} \tag{1}$$

where $\Phi_\Delta^{Std}$ is the singlet oxygen quantum yield for the standards used in the various solvents. Table 1 gives the literature [6, 27 and 28] values of $\Phi_\Delta^{Std}$ in the various solvents used in this work. $W$ and $W^{Std}$ are the DPBF photobleaching rates in the presence of ZnPc derivatives under investigation and the respective standard (chlorophyll a or ZnPc, Table 1). $I_{abs}$ and $I_{abs}^{Std}$ are the rates of light absorption by the ZnPc derivatives and the standard, respectively. The initial DPBF concentrations were kept the same for both the standards and the samples. Molar extinction coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) of DPBF at $\lambda=417$ nm were determined to be $\varepsilon=23,000$ (DMSO); $\varepsilon=23,000$ (DMF); $\varepsilon=27,500$ (pyridine); $\varepsilon=18,000$ (benzene); $\varepsilon=18,000$ (toluene). All the experiments were carried out at room temperature.

Table 1. Singlet oxygen quantum yield ($\Phi_\Delta^{Std}$) standards employed in the various solvents

| Solvent | Standard | $\Phi_\Delta^{Std}$ | Reference |
|---|---|---|---|
| DMSO | ZnPc | 0.67 | [27] |
| DMF | ZnPc | 0.56 | [6] |
| Pyridine | Chlorophyll a | 0.59 | [28] |
| Benzene | Chlorophyll a | 0.60 | [28] |
| Toluene | Chlorophyll a | 0.60 | [28] |

The quantum yields for photobleaching were determined using the standard equation employed before [10, 25 and 26]. Fluorescence quantum yields were determined by the comparative method [29 and 30],

using chlorophyll a in ether ($\Phi_F$=0.32) [31] as the reference standard. The refractive indexes of the solvents were employed in calculating the $\Phi_F$ of the ZnPc derivatives.

UV–Vis spectra were recorded on a Varian 500 UV/visible/NIR spectrophotometer. Fluorescence spectra were recorded with the Varian Eclipse spectrofluorimeter.

## 3. Results and discussion
### 3.1. Effects of solvents on the ground state electronic absorption spectra

Table 2 shows that with the exception of chloroform, a larger red shift of the Q band was observed for ZnPc in aromatic solvents. The largest red shift was observed for 1-chloronaphthalene. The shift to longer wavelength could be due to either the destabilization of the highest occupied molecular orbital (HOMO) or the stabilization of the lowest unoccupied molecular orbital (LUMO). It has been suggested [19] that the interaction between coordinating solvents and the phthalocyanine molecule, stabilises the LUMO of the complexes. The observed red shift suggests that aromatic solvents stabilise the LUMO in MPc complexes, with the 1-chloronaphthalene containing a more extend $\pi$ system stabilizing the LUMO to a larger extent. It is known [32] that the Q band shifts to longer wavelengths with enlargement of $\pi$ conjugated system of the phthalocyanine ring. This work suggests that the presence of conjugation in solvents also shifts the Q band to the red.

Table 2. Polarization red shifts of ZnPc in various solvents. $\lambda_{Qband}$ for ZnPc VAPOUR=660 nm [24]

| Solvent | Dipole moment, $\mu$ | Refractive index, $n_D$ | Q-band, $\lambda_{max}$ (nm) | Polarization red shift, $\Delta\lambda$ (nm) |
|---|---|---|---|---|
| Triethylamine | 0.72 | 1.401 | 666 | 6 |
| 1,4-Dioxane | 0.45 | 1.422 | 666 | 6 |
| THF | 1.69 | 1.406 | 668 | 8 |
| n-Butylamine | 1.30 | 1.401 | 669 | 9 |
| DMF | 3.79 | 1.430 | 670 | 10 |
| Dichloromethane | 1.36 | 1.445 | 671 | 11 |
| DMSO | 3.96 | 1.479 | 672 | 12 |
| Toluene | 0.38 | 1.097 | 672 | 12 |
| Benzene | 0.00 | 1.501 | 672 | 12 |
| o-Xylene | 0.62 | 1.505 | 672 | 12 |
| Chloroform | 1.90 | 1.438 | 673 | 13 |
| Chlorobenzene | 1.72 | 1.524 | 673 | 13 |
| Pyridine | 2.21 | 1.509 | 674 | 14 |
| Benzonitrile | 3.50 | 1.528 | 674 | 14 |
| 1-Chloronaphthalene | 1.55 | 1.633 | 677 | 17 |

It has been reported before [19] that band positions in Ti(IV)Pc complexes were red shifted as the polarity of the solvent increased for non-coordinating solvents, with the magnitude of the red shift following the

order hexane<toluene<chloroform<1-chloronaphthalene. The trend observed in Table 2 for these solvents is as follows: BENZENE=toluene˜chloroform<1-chloronaphthalane.

Table 2 shows that in general, as the refractive index of the solvent increased, the red shift of the Q band increased. The electronic absorption spectra of ZnPc in the various solvents was analysed by using the method described originally by Bayliss [19 and 33]. The plot of $(n^2-1)/(2n^2+1)$ (where $n$ is the refractive index) versus the red shift in the Q band (the polarization red shift) is shown in Fig. 2. The linear nature of the plot suggests that the red shifts in the Q band are mainly a result of solvation rather than coordination. The relationship for the solvents evaluated can be expressed by Eq. (2):

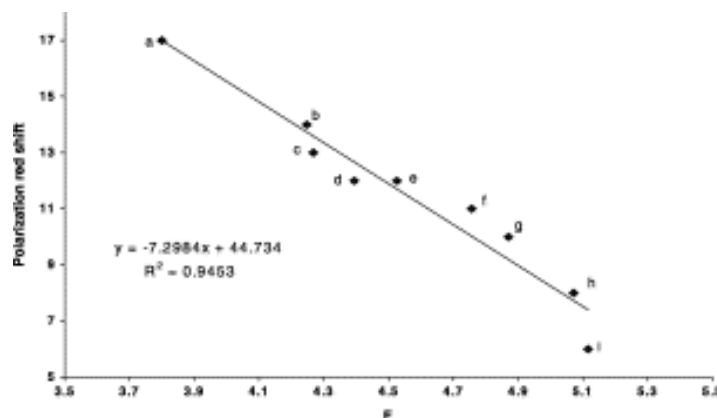$$\Delta\lambda_Q = -7.298F - 44.73 \tag{2}$$

with $R^2 = 0.945$.



Fig. 2. Plot of polarization red shift vs. $F$ (for ZnPc) where $F=(n^2-1)/(2n^2+1)$, and $n$ is the refractive index of the solvent: (a) 1-chloronaphthalene, (b) benzonitrile, (c) chlorobenzene, (d) benzene, (e) DMSO, (f) dichloromethane, (g) DMF, (h) THF, (i) triethylamine.

There is no correlation in Table 2 between the coordinating strength of the solvent and the red shift. A coordinating solvent such as pyridine gives the same red shift as, for example, dichloromethane, confirming that coordination of the solvent does not play a significant role in the red shift. There was also no clear trend in the variation of the Q band with dipole moments considering all the solvents.

Except for ZnOEPc in DMSO, the ground state absorption spectra of the complexes was typical of monomeric species. ZnOEPc was found to show aggregation in DMSO even at very low concentrations $<1\times10^{-6}$ mol dm$^{-3}$, this was evidenced by broadening of the Q band and the appearance of the band associated with aggregates at the higher energy side (629 nm) of the Q band, Fig. 3a. But in all the other

solvents investigated for ZnOEPc, such broadening was not observed, Fig. 3b. The ZnOPPc species showed the presence of an extra band at 698 nm in THF, Fig. 3c. Observation of two bands in the Q band region of MPc complexes is normally associated with the presence of monomeric and aggregated species. However, comparison with the spectra for systems where monomer/dimer equilibrium exists (e.g. Fig. 3a) shows that the main Q band at 674 nm in Fig. 3c is due to the monomer, there is no dimer peak evident to the higher energy side of this peak. The band at 698 nm needs some explanation. Charge transfer bands involving the central metal are not expected in ZnPc complexes. A similar band termed the 'X' band has been observed before in substituted ZnPc complexes [34]. This band was observed in non-polar or less polar solvents such as benzene and chloroform, but not in more polar solvents such as DMF, acetone and DMSO [34]. This band was observed more clearly only in THF in this work. The origin of the X band was explained in terms of the distortion of the Pc ring in substituted ZnPc complexes. Thus the presence of an extra band at 698 nm for the ZnOPPc complex in THF, suggests loss of symmetry in this molecule due to the distortion of the MPc molecule. Such departure from planarity is common in tetraphenyl porphyrins [35]. It is also known that the presence of eight phenyl groups on the peripheral positions of the phthalocyanine ring result in high distortion of the ring [36]. This distortion may be more pronounced in ZnOPPc due to the more flexible nature of the phenoxy rings compared to the estrone group. The reason why the 698 nm was clearly observable in THF may be due to the observation [34] that the presence of oxygen at the axial position of ZnPc complexes results in the distortion of the Pc ring. THF contains oxygen which may interact with the central Zn metal of the ZnOPPc molecule, enhancing the distortion. However solvents such as DMF and DMSO also contain oxygen, however the latter may be S-bonded in MPc complexes [37].
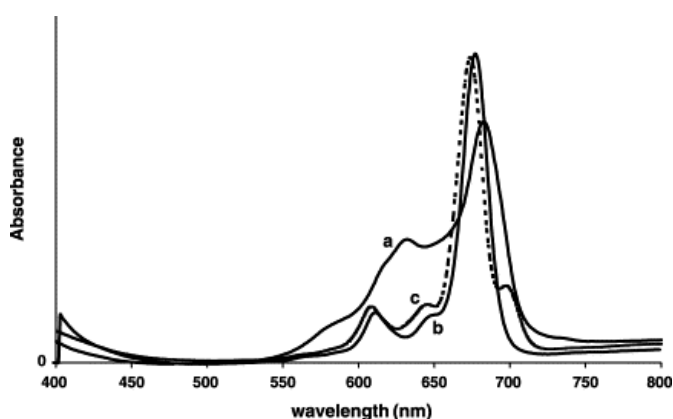


Fig. 3. Electronic absorption spectra of ZnOEPc in (a) DMSO and (b) THF. (c) Electronic absorption spectra of ZnOPPc in THF. Concentration=$\approx 1\times10^{-6}$ mol dm$^{-3}$.

## 3.2. Singlet oxygen quantum yields

Table 3 shows singlet oxygen quantum yields ($\Phi_\Delta$) values for ZnPc, (py)ZnPc, ZnOPPc and ZnOEPc in a variety of solvents. Interaction between vibrational levels of the solvent molecules and the electronic or vibrational levels of singlet oxygen results in the deactivation of singlet oxygen in some solvents, especially protic ones such as water and methanol [28]. Table 3 shows that $\Phi_\Delta$ values for ZnPc do not vary much with changes in solvent, with values ranging from 0.56 (DMF) to 0.67 (DMSO). The (py)ZnPc complex was prepared as explained in the experimental section in order to improve solubility of the ZnPc species. Indeed this complex is more soluble than the ZnPc species without an axial pyridine ligand. It was expected that the $\Phi_\Delta$ values would be higher based on solubility alone. However, there is a general lowering of the $\Phi_\Delta$ values for (py)ZnPc in the various solvents (except DMF), compared to ZnPc. This can only be explained by the possible quenching of the singlet oxygen by the pyridine when attached to the ZnPc complex, in a similar manner to singlet oxygen quenching by other amines. However, pyridine as a solvent does not seem to quench singlet oxygen significantly since $\Phi_\Delta$ values in pyridine are not lower than in the other solvents listed in Table 3. A larger variation in $\Phi_\Delta$ values is observed for the octa substituted ZnPc derivatives, (ZnOPPc and ZnOEPc). For ZnOPPc, the $\Phi_\Delta$ ranged from 0.45 (toluene) to 0.60 in DMSO, and for ZnOEPc $\Phi_\Delta$ ranged from 0.43 to 0.64. These complexes are known [10] to show aggregation at concentrations as low as $1 \times 10^{-5}$ mol dm$^{-3}$ in DMSO. The variation in $\Phi_\Delta$ values with solvent for each complex may reflect different extents of aggregation in this complex in the various solvents. The low $\Phi_\Delta$ for ZnOEPc in DMSO is due to its highly aggregated nature in this solvent as discussed above. Aggregation lowers $\Phi_\Delta$ values through dissipation of energy by the aggregates.

Table 3. Singlet oxygen quantum yield values of ZnPc and derivatives in five different solvents. References shown in square brackets where literature values were employed

| Solvent | ZnPc | ZnOEPc | ZnOPPc | (py)ZnPc |
|---|---|---|---|---|
| DMSO | 0.67 [27] | 0.43 | 0.60 | 0.63 |
| DMF | 0.56 [6] | 0.60 | 0.53 | 0.58 |
| Pyridine | 0.61 | 0.64 | 0.52 | |
| Benzene | 0.62 | 0.51 | 0.47 | 0.50 |
| Toluene | 0.58 | 0.54 | 0.45 | 0.49 |

## 3.3. Photobleaching quantum yields

Table 4 gives photobleaching (photodegradation) quantum yields ($\Phi_p$) for ZnPc, (py)ZnPc, ZnOEPc and ZnOPPc in the various solvents. Photobleaching is identified by a decrease in the spectra without formation of new peaks. The $\Phi_p$ value for ZnOEPc in DMSO has been reported before [10] and it is the highest in Table 4. Phthalocyanine molecules in general photodegrade oxidatively via attack by singlet

oxygen generated by them. Reductive photodegradation has been reported [25] for phthalocyanines containing pyridine rings (porphyrazines). In general, Table 4 shows that photodegradation is more pronounced in pyridine, DMF and DMSO for all the ZnPc derivatives, with the exception of ZnPc in benzonitrile and (py)ZnPc in DMSO. Comparing the photobleaching quantum yields in DMSO and pyridine, the largest photobleaching is observed for the ZnOEPc, containing the biological ring substituents. It has been observed before [10] that phthalocyanine molecules containing biological molecules on the peripheral positions are more easily degraded compared to other octasubstituted MPc complexes. For all the ZnPc derivatives, the lowest photobleaching quantum yields were observed when $n$-butylamine or THF were employed as solvents. $N$-butylamine is highly basic with $K_b=4.8\times10^{-4}$ [38], compared to $K_b=2.3\times10^{-9}$ for pyridine, hence the donor ability of $n$-butylamine may prevent oxidative degradation of MPc complexes. Pyridine, DMSO and DMF are less basic than $n$-butylamine, even though they have high donor numbers [39], Table 4. Thus pyridine, DMSO and DMF will be less efficient in stabilising the ring against oxidative attack than n-butylamine, resulting in higher photodegradation rates. THF has a low donor number, Table 4, compared to pyridine, DMSO and DMF, hence it would be expected to show high photodegradation quantum yield using the argument presented above, but this is not the case in Table 4. In THF, the ZnOPPc species underwent phototransformation rather than photobleaching, Fig. 4. The phototransformation process involved an increase in the low energy band at 698 nm and a very slow decrease in the main Q band for ZnOPPc in THF. As discussed above, the observation of the band at 698 nm may reflect loss of symmetry by distortions of the MPc molecule as photolysis progressed.

Table 4. Photobleaching quantum yield values of ZnPc derivatives in various solvents

| | Solvent | Solvent donor number | $10^{-5}/\varepsilon$ (dm³ mol⁻¹ cm⁻¹) Q band | $10^5/\Phi_p$ |
|---|---|---|---|---|
| ZnPc | DMSO | 29.8 | 2.38 | 2.61 |
| | DMF | 26.6 | 2.35 | 2.23 |
| | Pyridine | 33.1 | 2.65 | 5.85 |
| | THF (20.0) | 20 | 3.05 | 0.152 |
| | $n$-Butylamine | – | 2.9 | 0.543 |
| | Benzonitrile | 11.9 | 2.5 | 4.99 |
| ZnOEPc | DMF | 26.6 | 2.76 | 6.21 |
| | DMSO | 29.8 | 1.74 | 275[c] |
| | THF | 20 | 2.62 | 0.121 |
| | Pyridine | 33.1 | 2.18 | 6.15 |
| | Benzonitrile | 11.9 | 2.78 | 1.71 |
| | Benzene | 0.1 | 2.91 | 1.89 |
| | $n$-Butylamine | – | 2.35 | 0.643 |
| ZnOPPc | DMSO | 29.8 | 1.34 | 2.53 |
| | DMF | 26.6 | 1.26 | 12.1 |
| | Pyridine | 33.1 | 1.58 | 4.93 |
| | Benzonitrile | 11.9 | 1.67 | 2.16 |
| | Benzene | 0.1 | 1.7 | 1.39 |
| | $n$-Butylamine | – | 2.08 | 0.699 |
| (py)ZnPc | DMSO | 29.8 | 2.23 | 0.505 |
| | DMF | 26.6 | 2.32 | 9.43 |
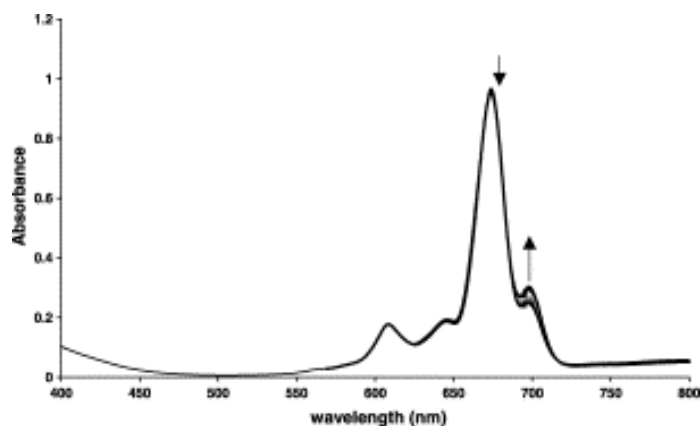
Fig. 4. Electronic absorption spectra observed during photolysis of ZnOPPc in THF. Photolysis wavelength ($\lambda_{Exc}$)=670 nm.

3.4. Fluorescence studies

Fig. 5a shows the excitation and fluorescence spectra of ZnOEPc in DMSO. The absorption spectra of this complex shows that it is aggregated in DMSO (Fig. 3a), but Fig. 5a shows that it is the monomeric species which fluoresces. Fluorescence and excitation spectra of the ZnOEPc complex shown in Fig. 5a were also observed in the other solvents shown in Table 5, and confirmed that it is the monomeric species which fluoresces. ZnPc and (py)ZnPc showed monomeric emission and absorption spectra. The fluorescence excitation and emission spectra for the ZnOPPc complex showed two bands, Fig. 5b, associated with the loss of symmetry as discussed above. The presence of two peaks in the excitation and fluorescence spectra was observed not only in THF, but also in pyridine, benzene and toluene, but not in the more polar solvents such as DMF or DMSO. This observation suggests that in the former group of solvents, loss of symmetry occurs following excitation. This loss of symmetry was observed only for THF in the ground state of ZnOPPc as discussed above.
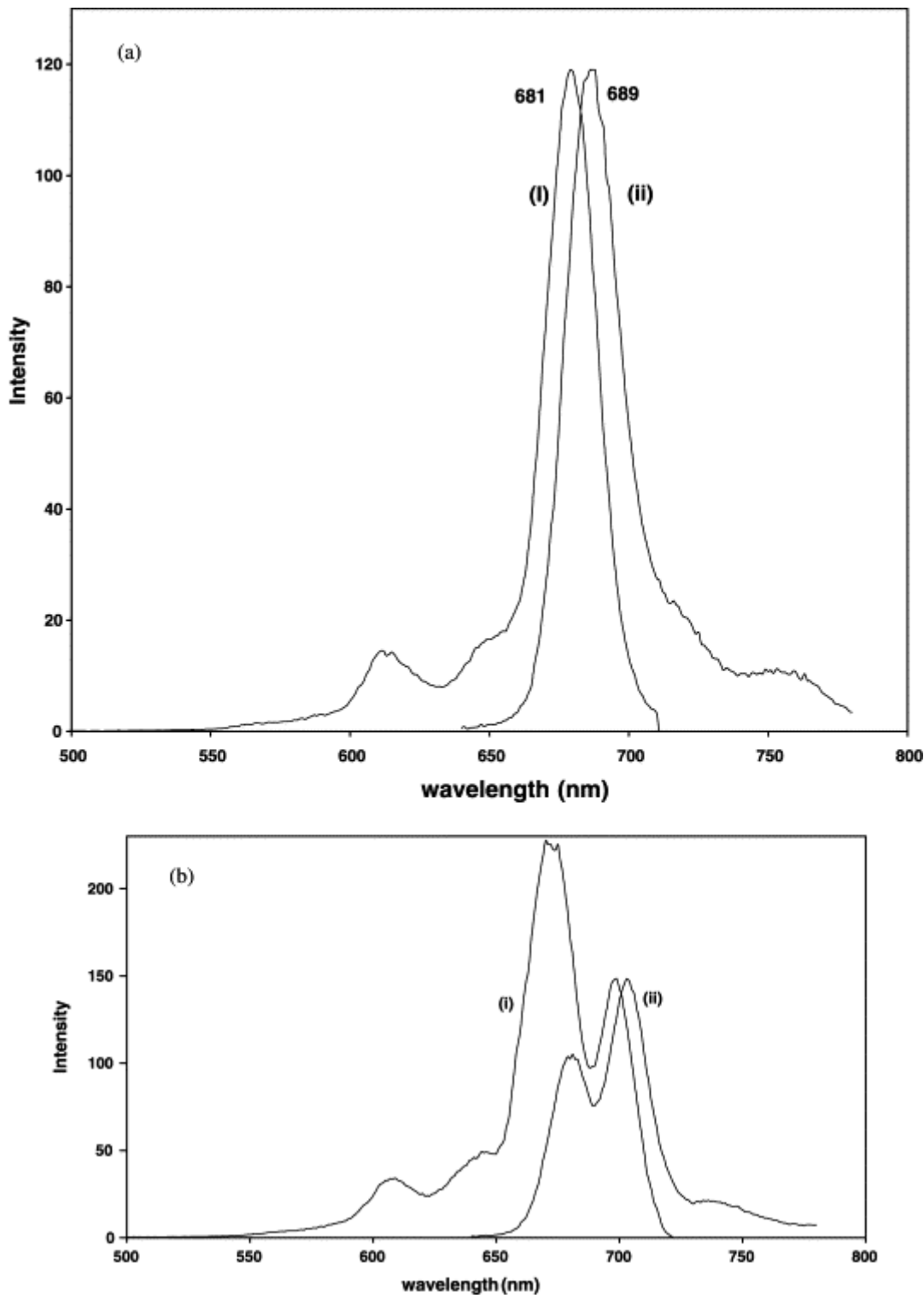
Fig. 5. Fluorescence excitation (i) and emission (ii) spectra of (a) ZnOEPc in DMSO and (b) ZnOPPc in THF. Excitation wavelength ($\lambda_{Exc}$)=630 nm.

Table 5. Fluorescence data for ZnPc derivatives in various solvents

| | Solvent | Emission wavelength, $\lambda_{Em}$ (nm) | Stokes shift, $\Delta\lambda_{stokes}$ (nm) | $\Phi_F (\pm 0.03)$ |
|---|---|---|---|---|
| ZnPc | DMSO | 679 | 7 | 0.2 |
| | DMF | 675 | 5 | 0.17 |
| | THF | 672 | 5 | 0.23 |
| | Pyridine | 681 | 7 | 0.2 |
| | n-Butylamine | 674 | 5 | 0.12 |
| | Benzonitrile | 681 | 7 | 0.13 |
| | Benzene | 676 | 4 | 0.06 |
| | Toluene | 676 | 4 | 0.07 |
| ZnOEPc | DMSO | 689 | 8 | 0.15 |
| | DMF | 684 | 4 | 0.19 |
| | THF | 682 | 5 | 0.13 |
| | Pyridine | 692 | 8 | 0.21 |
| | n-Butylamine | 687 | 6 | 0.15 |
| | Benzonitrile | 691 | 8 | 0.16 |
| | Benzene | 687 | 5 | 0.2 |
| | Toluene | 687 | 6 | 0.17 |
| ZnOPPc | DMSO | 687 | 8 | 0.21 |
| | DMF | 684 | 7 | 0.17 |
| | THF | 686, 704 | 6,14 | 0.31 |
| | Pyridine | 689[a] | 8 | 0.23 |
| | n-Butylamine | 683 | 5 | 0.12 |
| | Benzonitrile | 688[a] | 8 | 0.26 |
| | Benzene | 686, 704 | 6, 14 | 0.21 |
| | Toluene | 684, 703 | 4, 13 | 0.1 |
| (py)ZnPc | DMSO | 679 | 7 | 0.19 |
| | DMF | 676 | 7 | 0.22 |
| | Benzene | 676 | 4 | 0.16 |
| | Toluene | 677 | 5 | 0.08 |

Table 5 shows that the highest fluorescence quantum yield ($\Phi_F$) value was observed in THF solutions (except for ZnOEPc) followed in general by pyridine. The high $\Phi_F$ values in THF could reflect (i) the slow degradation of MPc species in this solvent following excitation as mentioned above, and/or (ii) low quenching abilities of THF for the excited singlet states. Toluene consistently showed low $\Phi_F$ values for all the complexes. Toluene has a low viscosity of 0.61 cp [40] compared to 1.1, 1.24 and 0.974 cp for DMSO, benzonitrile and pyridine, respectively. A decrease in viscosity of the solvent increases the possibility of deactivation of the excited state by external conversion. Comparing the same solvent (e.g. pyridine, DMF or DMSO), there is very little variation in the value of $\Phi_F$ for the different ZnPc complexes, showing that the nature of the peripheral substituents does not affect fluorescence very much.

In conclusion, this work has presented a comprehensive investigation of the effects of solvents on the singlet oxygen, fluorescence and photobleaching quantum yields. THF has proved to be a solvent which

behaves quite differently from the rest of the solvents. For example higher $\Phi_F$ values were obtained in this solvent for ZnPc and ZnOPPc and also phototransformation rather than photobleaching was observed for ZnOPPc in this solvent. It was also observed that the largest red shift of the Q band was observed in aromatic solvents, the highest shift being observed for 1-chloronaphthalene. Split Q band in the emission and excitation spectra of ZnOPPc was observed in some solvents and this is explained in terms of the lowering of symmetry following excitation.

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