Effects of substituents and solvents on the photochemical properties of zinc phthalocyanine complexes and their protonated derivatives

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Abstract

Zinc phthalocyanine derivatives containing various ring substituents and axial ligands were studied with respect to the effect of substituents on protonation. Aggregation resulted in failure of some of the ZnPc derivatives to protonate. In fact addition of protonating agents to aggregated ZnPc derivatives resulted in increase in aggregation followed by slow degradation. Axial ligands were lost on protonation. Photobleaching, fluorescence and singlet oxygen quantum yields of the protonated derivatives were compared with those of the unprotonated derivatives. In all cases protonation decreases the singlet oxygen and fluorescence quantum yields. However, photobleaching quantum yields decreased (i.e. stability increased) for the protonated derivatives except when axial ligands were present, where protonation resulted in decrease in stability.

1. Introduction

Phthalocyanines (Pc) contain an extended π conjugated system with unique electronic properties, resulting in a diverse number of applications ranging from industrial to biomedical [1]. Metalated azaporphyrins have four nitrogen atoms which exhibit basic properties and should be able to participate in acid–base interaction with acid media. Unprotonated Pcs are of D_{4h} symmetry. Monoprotonation of the external nitrogen atoms leads to lowering of symmetry for the mono-, di- and tri-protonated forms, resulting in splitting and a bathochromic shift of the Q band [2, 3, 4, 5, 6, 7, 8 and 9]. The tetra-protonated species then revert back to D_{4h} symmetry, but the Q band is still shifted to the red. The shift of the Q band to the red is desirable for applications of phthalocyanines as photosensitizers in photodynamic therapy (PDT).

It is widely believed that during PDT, the photosensitiser is excited to its triplet state, and then transfers the energy to ground-state triplet oxygen $O_2(^3\Sigma_g)$ forming the excited-state singlet oxygen, O_2 ($^1\Delta_g$), through the so called Type II mechanism. The O_2 ($^1\Delta_g$) species is believed to be the chief agent in PDT. Thus there has been a wide interest in the ability of Pc molecules to generate singlet oxygen. There have been only limited reports pertaining to photochemical and photophysical behaviour of protonated phthalocyanines [5]. A red shift in the fluorescence emission was observed upon protonation [5]. A large decrease in fluorescence, triplet state and singlet oxygen quantum yields and triplet state life times were observed following protonation of zinc tetra-*tert*-butyl phthalocyanine [5]. The decrease in the singlet oxygen quantum yield was explained in terms of the decrease in the energy of the triplet state to a value where energy transfer to ground state oxygen is no longer favourable.

In this work we report on the influence of ring substituents, axial ligands and solvents on the quantum yields of singlet oxygen (Φ_Δ), fluorescence (Φ_F) and photobleaching (Φ_p) for protonated and unprotonated zinc phthalocyanine derivatives shown in Fig.1. The paper reports for the first time the effects of solvents and axial ligands on Φ_Δ, Φ_F and Φ_p values of the protonated ZnPc derivatives. The effects of protonation on the photobleaching is also reported here for the first time.

ZnPc: $R_1 = R_2 = H$

ZnTNPc: $R_1 = H; R_2 = NO_2$

ZnTTBPPc: $R_1 = H; R_2 = $

ZnTAPc: $R_1 = H; R_2 = NH_2$

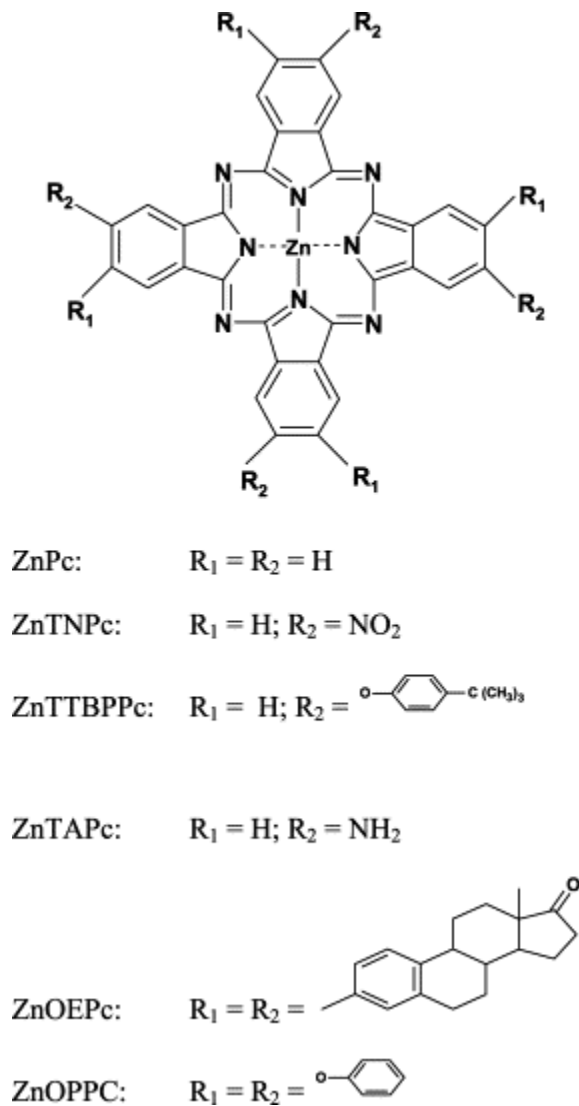ZnOEPc: $R_1 = R_2 = $

ZnOPPC: $R_1 = R_2 = $

Fig. 1. Molecular structure of the ZnPc derivatives.

2. Experimental
2.1. Materials

Zinc phthalocyanine (ZnPc) was purchased from Aldrich. (Piperidino)ZnPc, ((pip)ZnPc), (pyridino)ZnPc ((py)ZnPc) and cyanoZnPc ([(CN)ZnPc]⁻) were synthesized using established procedures for axially substituted metallophthalocyanines. For the (pip)ZnPc or (py)ZnPc complexes, ZnPc was refluxed, respectively, in piperidine or pyridine for 3 h. The solvent was then evaporated in air and the solid dried at

60 °C, and washed with hexanes. For [(CN)ZnPc]$^-$ preparation, 4.6×10^{-4} mol dm^{-3} of ZnPc was mixed with an excess of potassium cyanide and the mixture refluxed in dimethylformamide (DMF) for 3 h. The resulting solution was evaporated to dryness and the solid washed in water and recrystallized from absolute ethanol. The axially ligated ZnPc derivatives are known to be five-coordinate and are thus represented as (pip)ZnPc, (py)ZnPc and (CN)ZnPc [10]. Zinc octaphenoxyphthalocyanine (ZnOPPc) [11], zinc (octaestrone)phthalocyanine (ZnOEPc) [11], zinc tetranitro phthalocyanine (ZnTNPc) [12], zinc tetra(*tert*-butylphenoxy)phthalocyanine (ZnTTBPPc) [13] and zinc tetraamino phthalocyanine (ZnTAPc) [12] were synthesized and characterized following reported procedures.

Dimethylsulfoxide (DMSO, SAARCHEM) was dried on alumina before use and dimethylformamide (DMF, SAARCHEM) was freshly distilled. Trifluoroacetic acid (TFA, Fluka) and 1,3-diphenyl*iso*benzofuran (DPBF, Aldrich) were used as received.

2.2. Protonation

Protonation of the ring was performed by the addition of increasing concentrations of TFA to a fixed concentration of the ZnPc derivative, and observing the spectral changes that accompany the TFA addition. Protonation is achieved when the intensities of the red-shifted new bands reach their maxima. Only the mono-protonated and di-protonated forms of ZnPc (represented as [ZnPc·H]$^+$ and [ZnPc·H$_2$]$^{2+}$), respectively, were obtained using TFA. Concentrated (98%) sulfuric acid was used in order to obtain tri- and tetra-protonated derivatives of unsubstituted ZnPc. The substituted ZnPc derivatives degraded on addition of sulphuric acid.

2.3. Photochemical studies

Quantum yields of singlet oxygen (Φ_Δ) photogeneration were determined (error ±10%) using the relative method with unsubstituted zinc phthalocyanine (ZnPc) as reference. The experimental set-up has been described before [11, 14, 15, 16 and 17]. Briefly, a 2 ml DMSO solution of the mixture of the ZnPc standard or derivative (about 1×10^{-6} M) and DPBF (4.35×10^{-5} mol dm^3), was introduced to the cell and photolysed in the Q band region with 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 far infrared radiation. An interference filter (Intor, 670 nm with a bandwidth of 20 nm) was placed additionally in the light path before the sample.

Quantum yields of singlet oxygen were determined in air-saturated DMSO solutions. The following relationship which has been described before [11, 14, 15, 16 and 17] was employed (Eq. (1))

$$\Phi_\Delta = \Phi_\Delta^{Std} \cdot \frac{R I_{abs}^{Std}}{R^{Std} I_{abs}}$$

(1)

Where Φ_Δ^{Std} is the singlet oxygen quantum yield in the presence of unsubstituted ZnPc as a standard. For ZnPc standard, Φ_Δ^{Std} in DMF is 0.56 [18]. R and R^{Std} are the DPBF photobleaching rates in the presence of ZnPc derivatives under discussion in this work, and unsubstituted ZnPc standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the ZnPc derivatives and ZnPc standard, respectively. No significant changes in the absorbance of the ZnPc derivatives were observed during the singlet oxygen studies, showing that the phthalocyanine complexes do not react with singlet oxygen within the time scale of the DPBF reaction.

Photobleaching quantum yields Φ_p were determined using the usual Eq. (2) [15]

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

(2)

where C_t and C_0 in mol l^{-1} are Pc concentrations after and prior to irradiation, respectively. V is the reaction volume, S the irradiated area (1.4 cm^2) of the cell, t the irradiation time, N_A is the Avogadro's number and I_{abs} the overlap integral of the radiation source light intensity and the absorption of the Pc.

Fluorescence quantum yields (Φ_F) were calculated by a comparative method using zinc phthalocyanine as a standard ($\Phi_{F(ZnPc)}$=0.18) [19]. UV–visible spectra were recorded on a Cary 500 UV/visible/NIR or Cary 1E UV/Visible spectrophotometers.

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

Spectral changes for the protonation of MPc complexes have been reported [2] and as explained in the introduction, the spectra consists of shifting of the Q band to the red with successive protonation, Fig. 2. The Q band is split for the mono-, di- and tri-protonated derivatives due to loss of symmetry. The tetra-protonated species regains symmetry, hence the Q band spectra is not split. *Cis* di-protonation is of C_{2v} symmetry and is expected and to show a single Q band [20]. The fact that we see a split Q in Fig.2 for di-protonated species, suggests that *trans* (of D_{2h} symmetry) protonation occurs. The protonations occurred with isosbestic points as shown in Fig.2(b). Tri- and tetra-protonation could only be obtained for non-ring substituted ZnPc including axially ligated ((L)ZnPc) species using a strong acid such as sulphuric acid and

not when TFA was employed. Ring substituted ZnPc derivatives decomposed on addition of sulphuric acid.
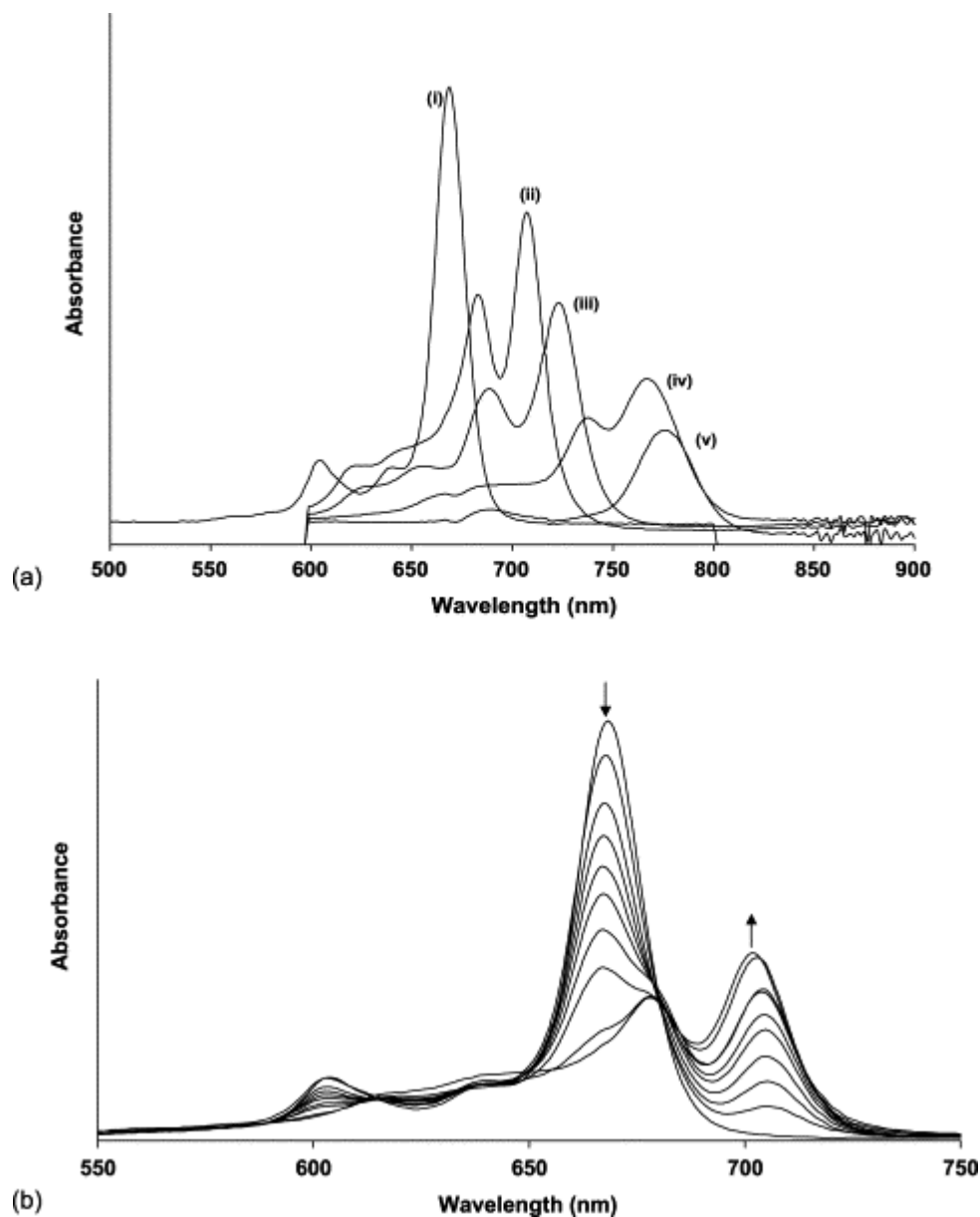

Fig. 2. (a) Absorption spectral changes observed on addition of sulfuric acid (98%) to ZnPc in DMF. Spectrum (i) is for ZnPc before addition of acid, (ii) first, (iii) second, (iv) third and (v) fourth protonations. Sulfuric acid CONCENTRATIONS=1.84, 7.36, 11.04, 12.88 mol dm^{-3}, for (ii), (iii), (iv) and (v), respectively. (b) Isosbestic spectral changes observed for the first protonation of ZnPc in DMF, using increasing concentrations of TFA. TFA concentrations increase as follows: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 5.2 and 7.0 mol dm^{-3}.

Formation constants for the first protonation (K_f) for the ZnPc derivatives in DMF ranged from 0.23 to 0.63, Table 1. These values are comparable to those reported in the literature for protonation of

phthalocyanines [4 and 5]. Protonation occurred more readily in the presence of electron donating peripheral substituents as expected, Fig. 3. Thus ZnTTBPPc (K_f=0.63) containing phenoxy ring substituted with $C(CH_3)_3$ groups was easier to protonate than unsubstituted ZnPc (K_f=0.23). It has also been reported that [20] annulation or extension of the π conjugated system tends to increase the basicity of the ring, hence enhance protonation. Thus on this basis alone ZnOPPc is more readily protonated than ZnPc. Considering only the low energy component of the split Q band, the magnitude of the shift of the Q band to the red compared with the corresponding unprotonated species was larger for the ZnPc species containing electron-donating substituents (ZnTTBPPc and ZnOPPc) than for unsubstituted ZnPc, which in turn had a larger shift than ZnTNPc containing electron-withdrawing substituents, Table 2. A larger red shift was observed for ZnTTBPPc than for ZnOPPc for the second protonation. Smaller red shifts have been reported for porphyrins substituted with electron withdrawing compared to electron donating substituents [21].

Table 1. Effect of solvent on the Q band maxima of protonation of ZnPc

Table 1
Effect of solvent on the Q band maxima of protonation of ZnPc

Solvent	Dipole moment, μ	Solvent Basicity, SB[a]	Q-band[b] λ_{max} (nm)	λ_{max}/nm, first proton[c]	λ_{max}/nm, second proton[c]	[TFA], first proton (M)[d]	K_f[e]
Chloroform	1.90	0.071	670	683, 708	690, 720	0.75	2.7
Benzonitrile	3.50	0.281	673	677, 703	683, 713	1.80	0.95
1,4-Dioxane	0.45	0.444	665	678, 703	683, 712	3.41	0.45
THF	1.69	0.591	666	677, 703	683, 712	5.11	0.32
DMF	3.79	0.613	668	678, 701	685, 713	6.71	0.23
DMSO	3.96	0.647	670	678, 703	685, 713	6.11	0.27
n-Butylamine	1.30	0.944	668	678, 703	684, 711	7.13	0.21
Triethylamine	0.72	0.885	664	–	–	–	–
Pyridine	2.21	0.581	673	–	–	–	–

[a] Values from Ref. [25].
[b] Q band maxima of the unprotonated species.
[c] Q band maxima of protonated species.
[d] Concentration of TFA required to complete first protonation.
[e] K_f, stability constants for the first protonation.
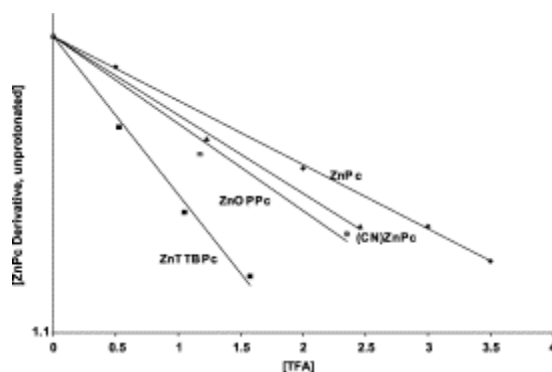

Fig. 3. Change in absorbance with concentration of TFA for selected ZnPc complexes in DMF.

Table 2
Q band shifts following protonation of ZnPc in DMF, using TFA

	$\lambda_{Q\ band}$ (nm)		
	Unprotonated (log ε in brackets)	First proton[a]	Second proton[a]
ZnTTBPPc	679 (5.02)	688, 717 (9, 38)	710, 744 (31,65)
ZnOPPc	677 (5.10)	688, 715 (11,38)	702, 732 (25,55)
ZnPc	666 (5.37)	678, 701 (10,33)	685, 713 (17,45)
ZnOEPc[b]	679 (5.44)	–	–
ZnTNPc	647, 683 (4.45, 4.67)	685, 712 (2, 29)[c]	–
ZnTAPc[b]	720 (3.02)	–	–
(py)ZnPc	669 (5.44)	680, 701 (11,32)	685, 713 (16,44)
(CN)ZnPc	672 (5.38)	679, 702 (7,30)	684, 714 (12,42)
(pip)ZnPc	670 (5.40)	678, 702 (8,32)	684, 714 (14,44)

[a] Numbers in brackets are the wavelength numbers by which the Q band of the protonated species has shifted compared to the neutral species.
[b] Aggregated in solution and did not protonate.
[c] Wavelength shifts based on the Q band associated with the monomeric peak at 683 nm.

Q band positions of protonated species vary as the protonating agent is changed as follows for first protonation of ZnPc: TFA (678,701)<H$_2$SO$_4$ (684,707)~ Lewis acid (AlCl$_3$) (685,708), suggesting that the Q band red-shifting is proportional to the strength of the acid, since this trend follows the order of the strength of the acid. AlCl$_3$ undergoes hydrolysis in solution forming a complex acid H$^+$−[AlCl$_4$]$^-$ [20]. It has been reported [6] that complexes are formed between the protonated species and the undissociated acid, this could result in the observed shift in the spectra with different acids.

ZnTNPc gave spectral changes shown in Fig. 4a on addition of TFA. Before addition of TFA, the complex shows aggregation as evidenced by the presence of a broad high-energy band at 647 nm in addition to the sharper band at 685 nm. The low energy band is associated with the monomeric species and the high-energy band with the aggregated species [10]. Analysis of the aggregated nature of the ZnTNPc complexes was reported before [22]. A dimeric constant of K_D (682 nm) was reported to be 2.60×10^5 M^{-1} [22]. The spectral changes observed on addition of acid to solutions of ZnTNPc consisted of a decrease in the monomer peak and an initial increase in the peak due to the aggregated (dimeric) species. The latter then began to decrease in intensity. These changes suggest that addition of protonating agents results in the shift of the monomer–dimer equilibrium towards the dimeric species, followed finally by protonation as shown in Fig. 4b. Only the first protonation could be achieved for this complex, and the protonation required a very large concentration of TFA. Spectral changes observed for ZnTAPc and ZnOEPc on addition of protonating agents were similar to those shown in Fig. 4a. However, protonation was not

achieved for these complexes even at very high TFA concentrations. Addition of large concentrations of TFA resulted in the degradation of both of these complexes (ZnTAPc and ZnOEPc). The aggregated nature of ZnTAPc [21], ZnTNPc [21] and ZnOEPc [11] complexes has been reported before. Aggregation in phthalocyanines occurs via intermolecular π–π interactions [23 and 24]. For this type of aggregates, the monomers are not chemically bonded but exist as loosely associated species. The presence of axial ligands prevents aggregation. Thus, the observation of increased aggregation on addition of acids to these complexes may suggest possible weak coordination of the solvent to the axial position, which may be lost on addition of acid enhancing aggregation. And the observation also suggests that the aggregated species is not readily protonated as judged by the lack of red shift for ZnTAPc and ZnOEPc, and by the large concentration of TFA which was required to complete the first protonation of ZnTNPc.
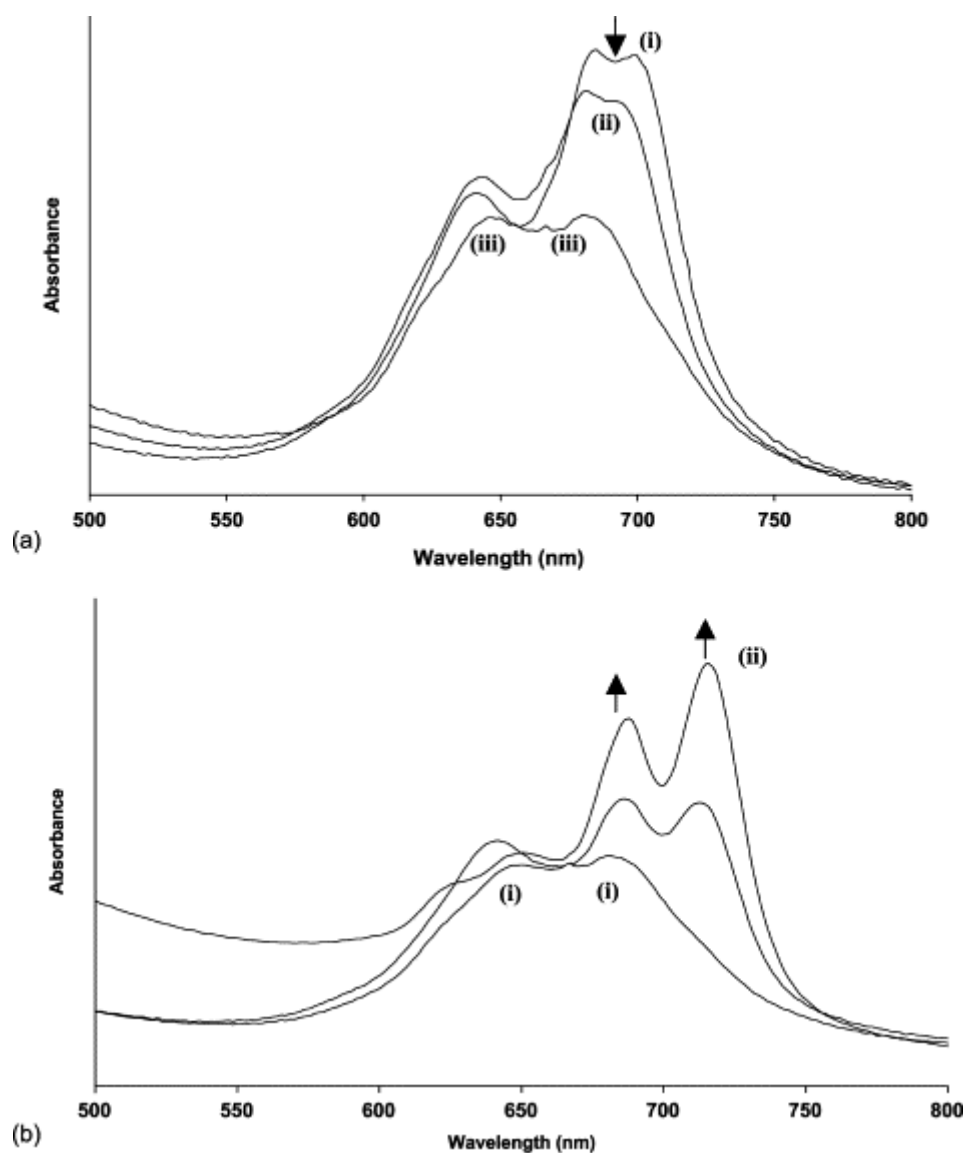

Fig. 4. (a) Spectral changes observed on addition of TFA to ZnTNPc (3.2×10^{-5} mol dm^{-3}) in DMF. (i) No TFA (ii) [TFA]=1.18 mol dm^{-3}, (iii) [TFA]=2.35 mol dm^{-3}. (b) Evolution of spectra due to protonation of

ZnTNPc. (i) the last spectrum (iii) in **Fig. 4(a)** and (ii) final spectrum obtained following addition of acid (1.2×10^1 mol dm^{-3} of TFA).

Fig. 5 shows that protonation of ZnPc containing axial ligands proceeds by the loss of the axial ligands as judged by the small blue shift of the Q band to that of non-ligated ZnPc, on addition of the acid. Also MPc complexes containing cyanide axial ligand are identified with a split B band. In Fig. 5, the B band collapses into one on protonation, hence confirming the loss of the axial ligand. However, as the observations below will demonstrate, axial ligands still have an effect on the protonation, suggesting that axial ligands are lost simultaneously with the protonation process. Immediately after addition of acid, peaks due to the protonated species were observed at the same time as the blue shift in the Q band. The axial ligands employed in this work are electron donating and all show easier protonation than ZnPc in DMF (which is presumably (DMF)ZnPc), see Fig. 3 for the [(CN)ZnPc]$^-$ derivative. The curves for (py)ZnPc and (pip)ZnPc were almost at the same position as for [(CN)ZnPc]$^-$. Thus this work also suggests that the basicity of the Pc ring is enhanced by the axially coordinated ligands.
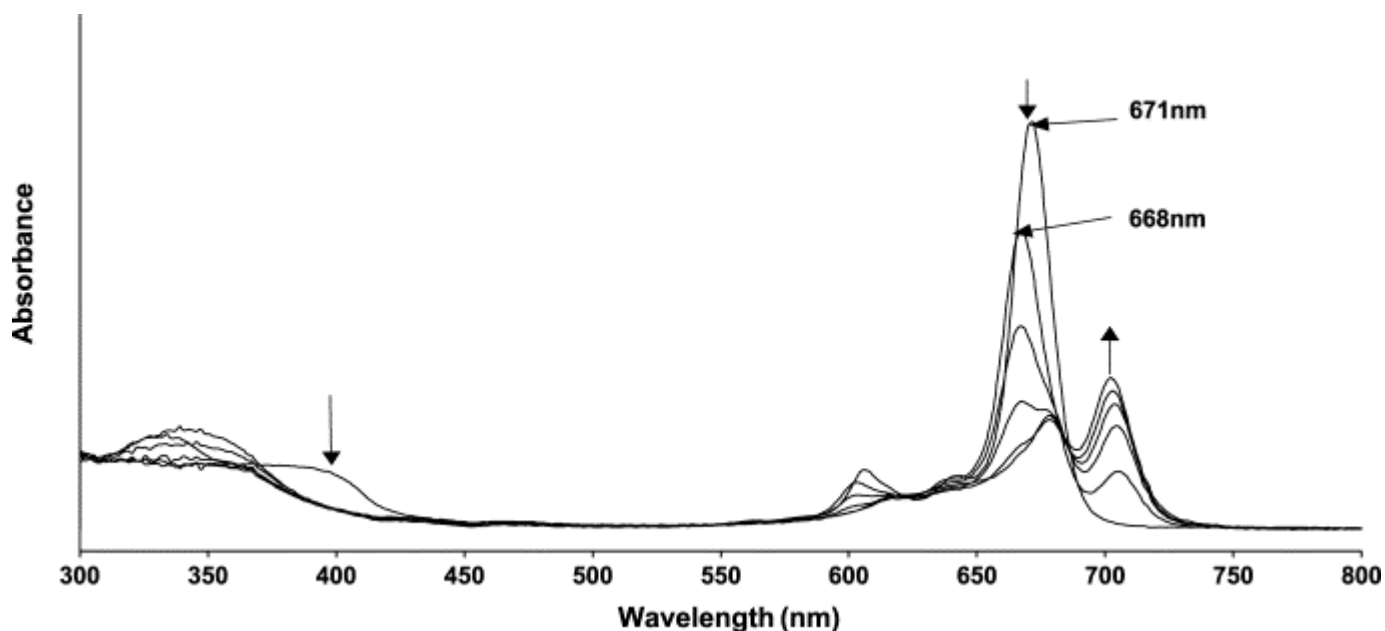

Fig. 5. Absorption spectral changes observed for the first protonation of (CN)ZnPc (4.26×10^{-6} mol dm^{-3}) in DMF, using TFA. [TFA]$=1.18-6.0 \times$mol dm^{-3}.

3.2. Solvent effects on protonation

Q-band positions of protonated derivatives of ZnPc species are almost the same, Table 1, irrespective of solvent type (except in the case of chloroform). The concentration of TFA needed to effect protonation increased linearly with solvent basicity [25] as shown in Fig. 6, hence confirming that the least basic solvents encourage protonation more than the more basic solvents. Chloroform being an acidic solvent,

may add to the acid strength of TFA, resulting in a larger red shift. This is in agreement with the argument presented above that extent of red-shifting is proportional to acid strength.
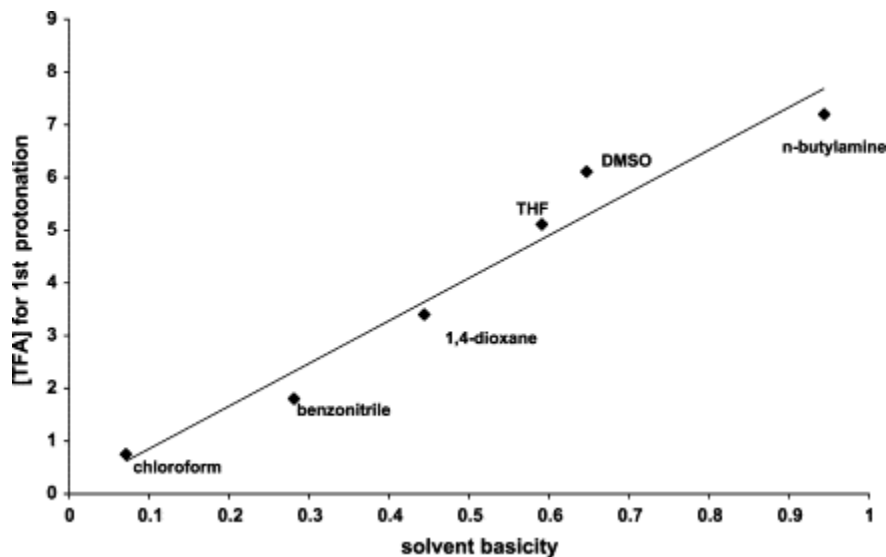

Fig. 6. Variation of solvent basicity with the concentration of TFA required to complete the first protonation of ZnPc.

There was no protonation when pyridine and triethylamine were used as solvents. Pyridine formed a white precipitate of pyridinium trifluoroacetate with TFA. Thus, TFA reacted with the solvent instead of the ring. Amines are basic; hence the formation of a quaternary salt on adding TFA to an amine solution is not unexpected. Protonation in the highly basic n-butylamine was accompanied by a great loss of heat and effervescence.

Two factors (basicity and coordinating strength of solvent) may be competing in determining the relative ease of protonation of the Pc ring. While solvent basicity impedes ring protonation, axial coordination of the solvent may aid it by increasing the basicity of the ring. However, Table 1 shows that DMSO, with a relatively high dipole moment of 3.96 hence more strongly coordinated to the central zinc ion, results in easier protonation of the ring (slightly higher K_f value) than for DMF with a lower dipole moment.

In spite of the higher basicity of n-butylamine compared to triethylamine, protonation was observed in the former instead of precipitation observed for the latter. This could be attributed to the higher polarity (coordinating strength) of n-butylamine, resulting its coordination to the central ZnPc metal. As observed above for the axially ligated ZnPc derivatives, the axial n-butylamine will be lost on protonation. Broadening of the Q band of the neutral species was observed on addition of TFA to solutions of ZnPc in n-butylamine, suggesting that the loss axial ligands is accompanied by aggregation.

Stepwise deprotonation of the protonated ZnPc derivaties was achieved on addition of hydrazine to the solution of the protonated species, as evidenced by reversal of spectral changes.

3.3. Singlet oxygen quantum yields

Table 3 shows singlet oxygen quantum yield (Φ_Δ) for the unprotonated and mono-protonated ZnPc complexes under discussion. Φ_Δ values for the unprotonated ZnPc derivatives are all higher than for the corresponding protonated derivatives as has been reported before for zinc tetra-*tert*-butyl phthalocyanine [5]. The neutral ZnPc derivatives studied have lower Φ_Δ values than ZnPc itself (Φ_Δ=0.56). This could be explained by the possible quenching of singlet oxygen by ligands or by aggregation effects in for example ZnTNPc. Aggregation lowers Φ_Δ values through dissipation of energy by the aggregates. The lowering of Φ_Δ values following protonation is attributed to the lowering of the triplet energy to the level where transfer of energy to ground state oxygen is no longer favourable, as suggested before [5].

Table 3. Photochemical data for neutral and protonated ZnPc derivatives

Complex	Φ_Δ	$10^5/\Phi_p$	Φ_F
ZnPc	0.56[a]	2.23	0.18[b]
[ZnPc.H]$^+$	0.39	0.23	0.12
ZnTTBPPc	0.42	9.41	0.13
[ZnTTBPPc·H]$^+$	0.12	2.33	0.076
ZnOPPc	0.53	12.1	0.17
[ZnOPPc·H]$^+$	0.26	2.62	0.042
(py)ZnPc	0.48	1.32	0.22
[(py)ZnPc·H]$^+$	0.41	2.09	0.19
(CN)ZnPc	0.51	0.12	0.14
[(CN)ZnPc·H]$^+$	0.37	1.38	0.11
(pip)ZnPc	0.31	0.14	0.16
[(pip)ZnPc·H]$^+$	0.25	1.63	0.18
ZnTNPc	0.24	–	0.12
[ZnTNPc·H]$^+$	0.11	–	–

Results refer to first protonation only. Solvent DMF.

For the ZnTAPc and ZnTOEPc, Φ_Δ for the protonated species were not obtained since these species did not protonate.

3.4. Photobleaching studies

Photobleaching results in a decrease in the intensity of the absorption peaks without formation of new peaks. The quantum yield of photobleaching (Φ_p) was found to decrease for ring substituted ZnPc derivatives and for unsubstituted ZnPc containing no axial ligands following protonation, Table 3. Phthalocyanine molecules in general photodegrade oxidatively via attack by singlet oxygen generated by them. As suggested earlier, protonation may quench the singlet oxygen, hence it is expected that Φ_p values

of protonated species would be generally lower than for corresponding unprotonated derivatives, and this is the case in Table 3 for non-axially ligated ZnPc derivatives. However, for the axially ligated ZnPc derivatives, protonation resulted in an increase in Φ_p value. Considering un-protonated derivatives, axial ligands impart some extra photostability on the Pc ring compared to ring substituted or unsubstituted derivatives containing no axial ligands, as judged by the low Φ_p for the former compared to the latter, Table 3. As earlier suggested, however, protonation leads to the loss of these axial ligands, which amounts to the removal of this extra photostability. As a result, the Φ_p values increase when the axially ligated ZnPc derivatives are protonated. It has been reported before that unprotonated ZnTNPc, undergoes phototransformation to the monomer, rather than photodegradation [22]. For the protonated $[ZnTNPc \cdot H]^+$ no spectral changes were observed on photolysis, showing that this complex is stable to photodegradation.

3.5. Fluorescence quantum yield

As observed before [5], the fluorescence quantum yield (Φ_f) is reduced on protonation. This was generally observed in Table 3. The excitation spectra (Fig. 7) was similar to the absorption spectra, consistent with the presence of a single species under the conditions used in this work. For ZnTNPc, Φ_F could not be obtained since dilute solution are required for fluorescence studies, and dilution of protonated $[ZnTNPc \cdot H]^+$ resulted in the deprotonation back to the neutral species, hence confirming the ease of reduction of this species.

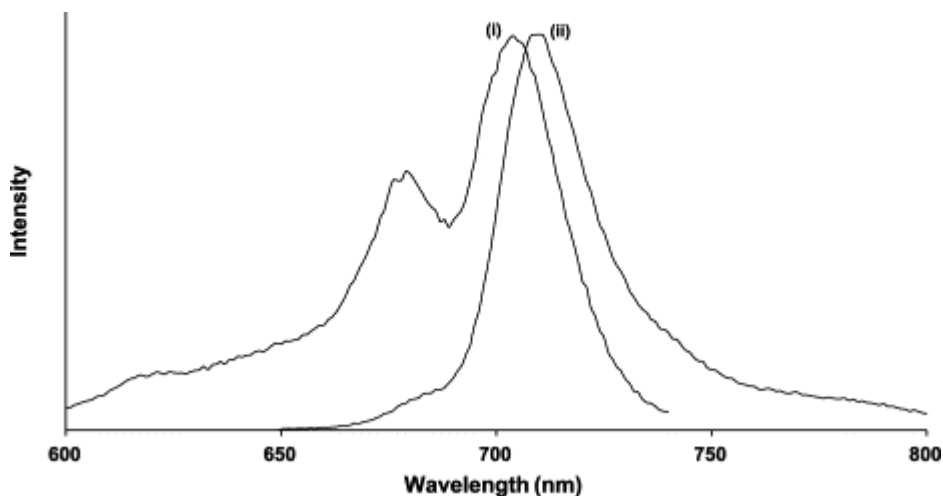Fig. 7. Fluorescence excitation (i) and emission (ii) spectra of (a) $[ZnPc \cdot H]^+$ in DMF. Excitation wavelength (λ_{Exc})=630 nm.

3.6. Conclusion

In conclusion we have shown in this work that protonation of ZnPc derivatives is dependent on the axial ligands and on the ring substituents. Ring substituted ZnPc complexes which were aggregated in solution

were not readily protonated. Addition of protonating agents resulted in enhanced aggregation. Axial ligands were lost on protonation. The ease of protonation decreased with the increase in the basicity of the solvent. In all cases protonation decreases the singlet oxygen and fluorescence quantum yields. However, photobleaching quantum yields decreased for the protonated derivatives except when axial ligands were present, where protonation resulted in decrease in stability.

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