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The preparation and photophysical measurements of perdeutero zinc phthalocyanine

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Abstract

The fully deuterated photosensitizer, zinc phthalocyanine-d_{16}, was synthesized and its excited singlet and triplet state photophysics determined. Surprisingly, no differences in the excited state kinetics or quantum yields were observed compared with the undeuterated material. Furthermore, deuteration of the axial pyridine ligand of the metallophthalocyanine produced no changes in its photophysical behaviour. These results are compared with recent work (A. Beeby, A.W. Parker, M.S.C. Simpson and D. Phillips, *J. Photochem. Photobiol. B: Biol., 16* (1992) 73–81) in which the photophysical properties of aluminium phthalocyanines were altered in deuterated solvents, and the effects of deuteration on the non-radiative relaxation processes of phthalocyanines were discussed. Implications for the use of such compounds in photodynamic therapy are also mentioned.

Keywords: Zinc phthalocyanine; Photophysics; Deuterium; Photodynamic therapy

1. Introduction

We have previously shown that the deuteration of axially bound water ligands of disulphonated aluminium phthalocyanine ($AlPcS_2$) increases the singlet and triplet quantum yields (Φ_F and Φ_T) and the fluorescence lifetime (τ_F) [1,2]. It was demonstrated that this effect was due to a significant reduction in the rate of $S_1 \rightarrow S_0$ internal conversion, and this implies that the vibrational modes of the axial ligands play an important role in the deactivation of the excited electronic states of the phthalocyanine via non-radiative pathways. Other workers have shown that deuteration of the methanol ligand bound to magnesium porphyrin increases the triplet lifetime by reducing the rate of $T_1 \rightarrow S_0$ intersystem crossing [3].

Isotopic substitution of deuterium for protium within a molecule is known to result in changes in the excited state photophysics and has been reported for a number of classes of compounds, including aromatic hydrocarbons [4–7], aliphatic carbonyls [6,7] and porphyrins [8–11]. In these studies, vibrational modes involving certain protons have been shown to be important in the relaxation process of the excited states. Thus changes in the vibrational frequencies of the C–H (C–D) bonds lead to a change in the vibrational overlap integral between the excited and ground states and therefore to changes in the rates of interconversion; this is particularly important for $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ conversions where the energy gaps are relatively large [6]. Experiments with selectively deuterated porphins have indicated that inner ring N–H groups contribute more to non-radiative deactivation pathways than outer ring C–H groups, and the outer ring C–H (β-positions) do not affect such deactivation pathways at all. Position-dependent deuterium effects on radiationless transitions have also been reported for anthracene, naphthalene and carbonyl compounds [4,5,12].

Phthalocyanines have shown promise as potential photosensitizing agents for the treatment of neoplastic disease via photodynamic therapy (PDT) [13,14], and the activity of these compounds is mediated by the triplet state. PDT efficacy depends on the formation of the cytotoxic species singlet oxygen ($O_2(^1\Delta_g)$), produced via a type II process of energy transfer from the excited triplet state of the dye to ground state molecular oxygen. The quantum yield of singlet oxygen production (Φ_Δ) is related to the triplet yield (Φ_T) by the equation

$$\Phi_\Delta = S_\Delta \Phi_T$$

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where S_Δ is the fraction of triplet state quenching by ground state oxygen that leads to the formation of singlet oxygen. Clearly, an increase in the triplet quantum yield for a particular phthalocyanine compound could conceivably lead to an enhanced PDT effect. This was demonstrated by Beeby et al. [1,2] for $AlPcS_2$ in aqueous solution, where alteration of the axial ligand of the metal–phthalocyanine complex from H_2O to D_2O enhanced the triplet quantum yield by 30%. Subsequent work has shown that Φ_Δ increases by a corresponding amount.

In this paper, we describe the synthesis and photophysical properties of perdeutero zinc phthalocyanine designed to investigate whether deuteration of the phthalocyanine ring affects the excited state dynamics.

2. Experimental details

2.1. Preparation of perdeutero zinc phthalocyanine (ZnPc-d_{16})

Perdeuterated zinc phthalocyanine was synthesized from phthalodinitrile-d_4, prepared by the method of von Hopff and Gallegra [15] starting from tetradeutero phthalic acid (MSD Isotopes, Quebec, Canada). The final phthalocyanine was produced by the reaction of phthalodinitrile-d_4 with zinc acetate in *N*,*N*-dimethylethanolamine at 135 °C. The purified product was obtained after washing with 4 M HCl (×2), H_2O (×2) and ethanol (×2); it was taken up in methanol and evaporated to dryness. Initial assessment of the nature of the material was performed using absorption spectroscopy (see Section 2.2): the product was dissolved in toluene/1% pyridine and identified by the single peak of the Q-band at approximately 670 nm.

The isotopic purity of the perdeuterated compound (molecular weight, 593) was determined using positive mode secondary ion mass spectroscopy (+SIMS); the compound was dissolved in a matrix of sulphuric acid; mass analysis: 593.5 ($[P]^{\cdot +}$), 609.3 ($[P+O]^{\cdot +}$), 625.2 ($[P+O_2]^{\cdot +}$) [16].

Zinc phthalocyanine was prepared using the above method starting from phthalonitrile (Aldrich) and was also purchased directly (Eastman Kodak, Rochester, New York). Mass spectral analysis of this compound (molecular weight, 577) dissolved in a matrix of phosphoric acid/sulphuric acid (2 : 1) is as follows: 578.2 ($[P+H]^{\cdot +}$), 594.2 ($[P+O+H]^{\cdot +}$) [16].

In the +SIM spectrum of ZnPc-d_{16} there was no evidence of undeuterated zinc phthalocyanine, and therefore it was assumed to be 100% isotopically pure.

2.2. Photophysical measurements

Stock solutions of ZnPc-d_{16} and ZnPc were prepared in pyridine or pyridine-d_5 at a concentration of approximately 10 mg ml^{-1} and further diluted in toluene. The working solutions were prepared in 1% v/v pyridine in toluene.

UV–visible absorption and corrected fluorescence emission spectra were obtained using Perkin Elmer Lambda 2 and Perkin Elmer LS5B machines respectively. The fluorescence quantum yields (Φ_F) were determined by the method of Rhys-Williams et al. [17] using chlorophyll *a* in ether ($\Phi_F = 0.32$) [18] and cresyl violet in methanol ($\Phi_F = 0.54$) [19] as standards.

Fluorescence lifetimes were recorded by the method of time-correlated single photon counting using the apparatus described elsewhere [20]. The experimental conditions were as described previously [1]. The decays were obtained with 10 000 counts or more in the peak channel and were fitted by iterative reconvolution and least-squares analysis; the goodness of fit was judged via reduced χ^2 values, the random distribution of residuals and the autocorrelation function of residuals.

Triplet state studies were carried out using the laser flash photolysis apparatus of the Engineering and Physical Sciences Research Council (EPSRC) Rutherford Appleton Laboratory. The experimental set-up and running conditions have been described previously [1]. Samples were thoroughly degassed by the freeze–pump–thaw technique using a high-vacuum line. Triplet quantum yields were determined via the comparative method [21] using zinc tetraphenyl porphyrin (ZnTPP) as standard ($\Phi_T = 0.83$, $\epsilon_T(470\ \text{nm}) = 74\,000\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$) [22]. Samples were excited at 355 nm using an excimer-pumped dye laser (pulse width, 10 ns) and were maintained in the range 0.05–0.5 mJ per pulse. Decay traces were obtained from the average of at least 64 shots. For the determination of the self-quenching rate constant of ZnPc-d_{16}, the sample was excited at 670 nm. Values for the triplet extinction coefficient were determined via the singlet depletion method [23] ($\epsilon_S = 1.8 \times 10^5\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$) [1] from the triplet-minus-singlet difference spectrum obtained using a time-gated optical multichannel analyser/spectrograph.

Singlet oxygen studies were carried out on air-equilibrated samples ($2 \times 10^{-6}\ \text{mol dm}^{-3}$) dissolved in toluene/1% pyridine. Samples were excited at 355 nm from an excimer-pumped dye laser system (pulse width, 10 ns) by pulses within the power range 0.05–0.5 mJ per pulse. The emitted singlet oxygen luminescence was detected at right angles to the excitation beam with a North Coast E0-817P Ge photodiode/amplifier combination. The sample was held in a 10 mm × 10 mm cuvette close to the Ge device and irradiated by the laser source via a 5 mm diameter liquid light guide. The singlet oxygen luminescence from the sample was selected by a 1270 nm silicon interference filter (bandpass, 30 nm) placed close to the detector.

Singlet oxygen quantum yields (Φ_Δ) were determined via comparison of the magnitude of the luminescence signal of the sample vs. that of zinc tetraphenyl porphyrin standard in toluene ($\Phi_\Delta = 0.73$) [24] by extrapolation of the decay curve back to $t = 0$ (the laser pulse).

Table 1
Photophysical parameters of ZnPc and ZnPc-d_{16} in toluene/1% pyridine (or 1% pyridine-d_5) and of ZnPc determined by other workers (see references for experimental conditions)

Pc species	Φ_F	τ_F (ns)	Φ_T	τ_T (μs)	$\Delta\epsilon_T$ (mol^{-1} dm^3 cm^{-1})	ϕ_Δ
ZnPc and ZnPc-d_{16} (this work)	0.34 ± 0.03	3.10 ± 0.01	0.58 ± 0.08	330 ± 30 [a]	36000 ± 6000	0.54 ± 0.05
ZnPc	0.30 [25]	3.90 [25]	0.65 [26]	300 [25]		0.40 [27]

[a] [phthalocyanine] = 3×10^{-6} mol dm^{-3}.

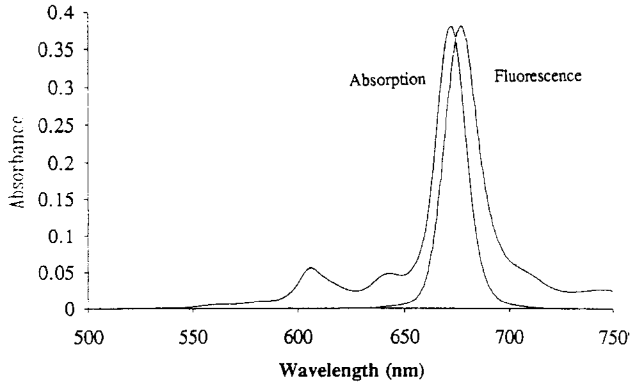

Fig. 1. Absorption and normalized fluorescence emission (uncorrected) spectra of ZnPc-d_{16} in toluene/1% pyridine-d_5.

3. Results

The photophysics of ZnPc and ZnPc-d_{16} were identical and are reported in Table 1. Furthermore, there was no difference n the photophysical behaviour on deuteration of the pyridine, which acts as an axial ligand. The photophysical parameters determined for the compounds in this work are summarized n Table 1 and are compared with values reported in the literature for other zinc phthalocyanines.

The absorption and fluorescence emission spectra of ZnPc and ZnPc-d_{16} in either toluene/1% pyridine or toluene/1% pyridine-d_5 were identical. As shown in Fig. 1 they display a Q-band absorption maximum at 671.5 nm and a fluorescence emission maximum at 676 nm. The ground state extinction coefficient for each species was calculated to be 1.8×10^5 mol^{-1} dm^3 cm^{-1}. Typical decays of the excited triplet state and emitted singlet oxygen luminescence of ZnPc-d_{16} in toluene/1% pyridine are shown in Figs. 2 and 3. The triplet state absorbances measured at $t = 0$ for the zinc phthalocyanine species were linear with respect to the laser power up to 0.3 mJ per pulse, as shown in Fig. 4. The data for ZnPc and ZnPc-d_{16} in the presence of either 1% pyridine-d_5 or 1% pyridine (data not shown) fitted the same curve, indicating identical triplet quantum yields for all the systems studied. Similarly, the variation in the singlet oxygen emission intensity with the laser power was identical for both compounds (data not shown). The lifetime of singlet oxygen (τ_Δ), calculated from the slope of the ln(signal) vs. time plot shown in the inset of Fig. 3, was determined to be 29 μs. This value is consistent with that reported in the literature for τ_Δ in toluene [28]. As can be seen in Fig. 3, the singlet oxygen decay consists of a spike around $t = 0$, originating from the tail of the phthalocyanine fluorescence extending out to 1270

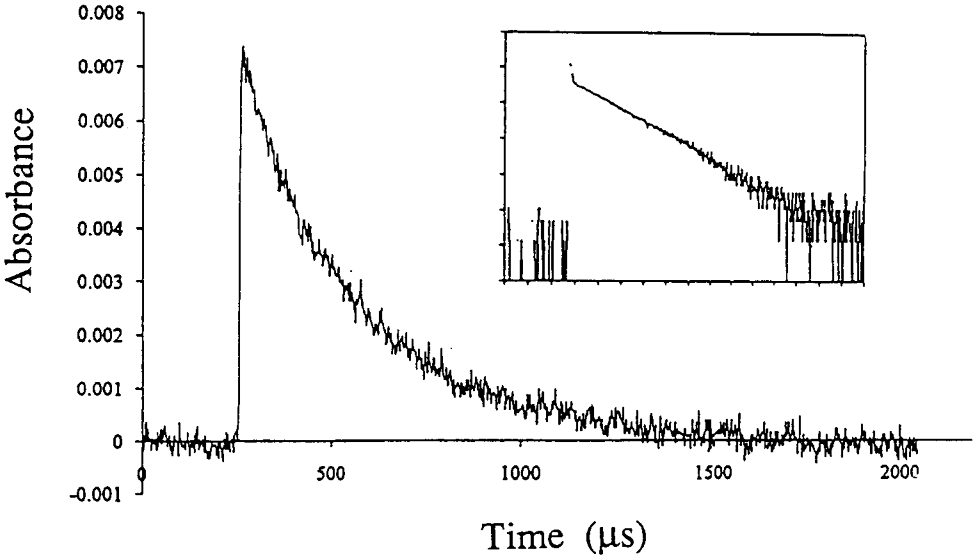

Fig. 2. Decay of the excited triplet state of ZnPc-d_{16} in toluene/1% pyridine-d_5. Inset shows log(absorbance) vs. time (s) plot used to determine the value of τ_T (330 μs); [ZnPc-d_{16}] = 3×10^{-6} mol dm^{-3}.

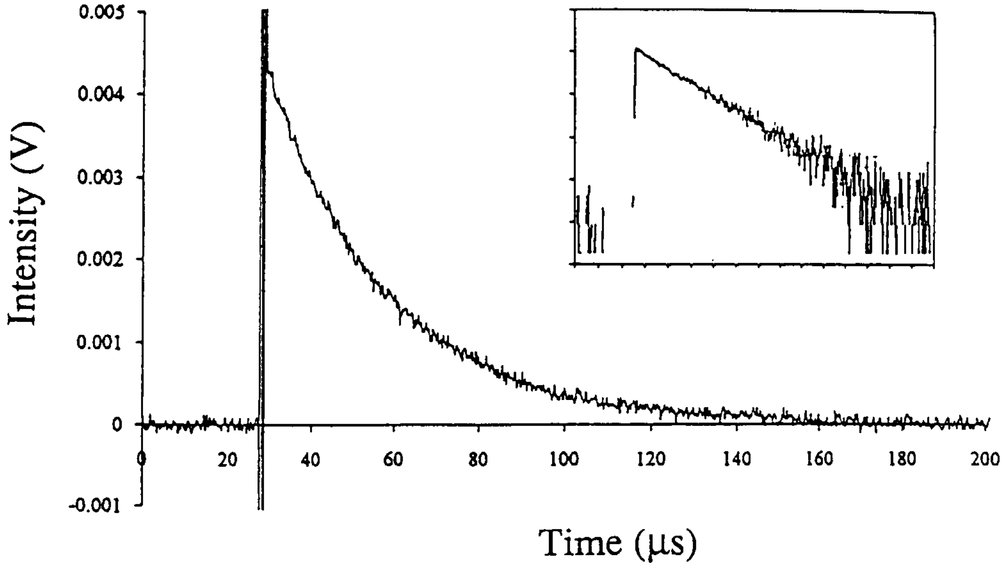

Fig. 3. Time-resolved luminescence decay (measured at 1270 nm) of singlet oxygen generated by 355 nm laser excitation (power, 0.2 mJ) of ZnPc-d_{16} in toluene/1% pyridine-d_5. Inset shows ln(luminescence intensity) vs. time (s) plot used to calculate the singlet oxygen lifetime in this solvent, $\tau_\Delta = 29$ μs.

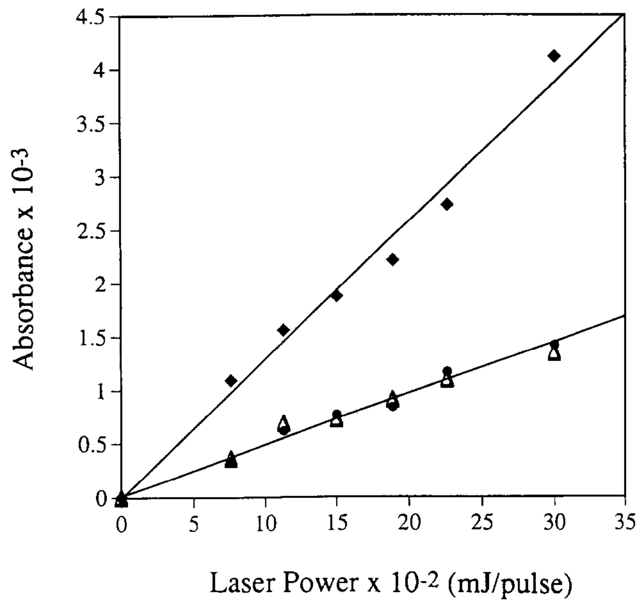

Fig. 4. Laser power vs. triplet absorbance at 490 nm (measured at t_0, the laser pulse) of ZnPc (●) and ZnPc-d_{16} (△) in toluene/1% pyridine-d_5, and ZnTPP (◆) in toluene standard. The data obtained for the phthalocyanine compounds in the presence of 1% non-deuterated pyridine are fitted to the same line of the graph.

nm, superimposed on an exponential decay arising from the singlet oxygen luminescence. The intensity of the singlet oxygen decay signal at $t = 0$ was determined by extrapolation of the decay curve.

From the photophysical parameters in Table 1, the rates of $S_1 \rightarrow S_0$ fluorescence (k_F), $S_1 \rightarrow S_0$ internal conversion (k_{IC}) and $S_1 \rightarrow T_1$ intersystem crossing (k_{ISC}) were calculated using the equations

$$k_F = \frac{\Phi_F}{\tau_F}$$

$$k_{ISC} = \frac{\Phi_T}{\tau_F}$$

$$k_{IC} = \frac{1 - (\Phi_F + \Phi_T)}{\tau_F}$$

and are $k_F = (1.1 \pm 0.1) \times 10^8$ s^{-1}, $k_{ISC} = (1.8 \pm 0.2) \times 10^8$ s^{-1} and $k_{IC} = (2.6 \pm 0.2) \times 10^7$ s^{-1}.

The quenching of the triplet state by oxygen proceeds with a bimolecular rate constant of $(1.1 \pm 0.1) \times 10^9$ mol^{-1} dm^3 s^{-1}, close to the diffusion- controlled limit and comparable with that observed for other phthalocyanines [29]. This was determined using a value of 1.8×10^{-3} mol dm^{-3} for the oxygen concentration in air-equilibrated toluene at 20 °C (assuming that the concentration of oxygen will be the same in toluene as in benzene [30]).

The observed triplet lifetimes for ZnPc-d_{16} and ZnPc varied with the sensitizer concentration, as measured by A_{670} (the peak of the Q-band), and fitted an equation of the form

$$\frac{1}{\tau_T} = k_R + k_Q[\mathrm{ZnPc}]$$

where k_R is the rate coefficient for the decay of the triplet state at zero sensitizer concentration, k_Q is the rate coefficient of the excited triplet state quenching by the ground state and [ZnPc] is the sensitizer concentration. A plot of the reciprocal triplet lifetime vs. concentration for ZnPc-d_{16} over the range 0–4 mM is shown in Fig. 5 from which the following values were determined: $k_Q = (3.6 \pm 0.2) \times 10^8$ mol^{-1} dm^3 s^{-1}; $k_R = 2700 \pm 150$ s^{-1}. The triplet lifetime of both ZnPc and ZnPc-d_{16} at zero concentration, i.e. where there is no

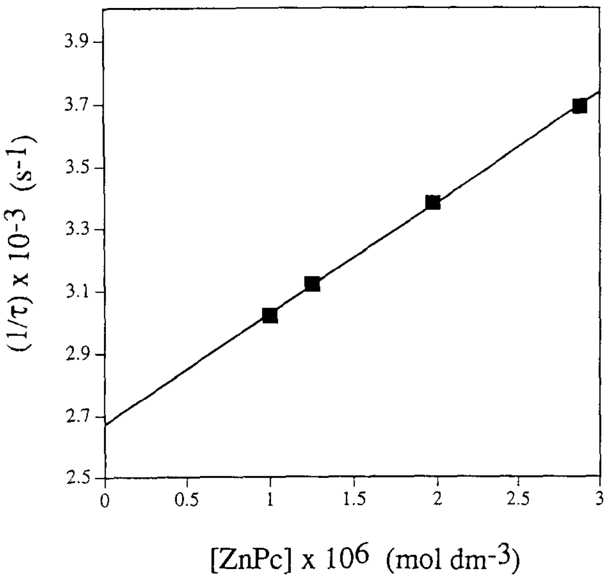

Fig. 5. A plot of the reciprocal triplet state lifetime vs. ZnPc-d_{16} concentration in toluene/1% pyridine-d_5. The laser excitation wavelength was 670 nm and the power was 0.2 mJ.

ground state self-quenching, was calculated to be 370±40 μs.

4. Discussion

When the zinc phthalocyanine ring was fully deuterated, we observed no changes in the absorption and emission spectra or in the fluorescence and triplet state quantum yields and lifetimes. Singlet oxygen is generated exclusively from the triplet state of these species and therefore the quantum yield of singlet oxygen production mirrors that of the triplet yield; it is unaltered by C–H macrocycle deuteration. The results of the present study were somewhat surprising when compared with the work reported by Gradyushko et al. [10] who studied zinc porphins similar in structure to zinc phthalocyanines. They showed that full deuteration of the zinc porphin macrocycle caused an increase in the phosphorescence lifetime in alcoholic solutions of 40%, and this was attributed to a reduction in the rate of $T_1 \rightarrow S_0$ intersystem crossing due to deuteration. Our studies show that both $S_1 \rightarrow S_0$ and $S_1 \rightarrow T_1$ non-radiative pathways are unaffected by full peripheral deuteration. Furthermore, because the triplet lifetime does not change on deuteration, we can conclude that the rate of the $T_1 \rightarrow S_0$ non-radiative process is not dependent on the vibrational modes of the peripheral C–H bonds.

In previous experiments with $AlPcS_2$ [1,2], the quantum yields of internal conversion ($S_1 \rightarrow S_0$) were found to be significant in aqueous solution and decreased from 0.43 to 0.26 on changing the solvent from H_2O to D_2O. In methanol solutions, the internal conversion yield was reduced to 0.08–0.11. Studies on methanol solutions of disulphonated aluminium phthalocyanine have shown that there is no change in the rate of the $S_1 \rightarrow S_0$ internal conversion process, although, on deuteration of the methanol ligand, a decrease in the rate of the $T_1 \rightarrow S_0$ intersystem crossing process is observed [31]. In this work, we determined that, for ZnPc or ZnPc-d_{16} in toluene/1% pyridine (d_0 or d_5), the internal conversion yield ($1-(\Phi_F+\Phi_T)$) is 0.08±0.11.

The present results suggest that the C–H vibrational modes of zinc phthalocyanine are unimportant in the non-radiative deactivation mechanisms of the excited singlet or triplet states. This is surprising since anharmonic C–H stretching vibrations have been cited as having a major role in non-radiative deactivations in a variety of aromatic hydrocarbons and porphyrins [3–11].

No differences were observed on changing the axial ligand of ZnPc or ZnPc-d_{16} from pyridine to pyridine-d_5. This work shows that there is no effect from the ligand on the rate coefficients of $S_1 \rightarrow T_1$ intersystem crossing and $S_1 \rightarrow S_0$ internal conversion. A similar effect was observed when studying $AlPcS_2$ in methanol [1,2], in which the solvent environment, and thus probably the axial ligand, was altered from methanol to methanol-d_1 or methanol-d_4. However, these studies showed an effect of increasing ligand deuteration on the triplet lifetime which correlated with the proximity of the deuterium to the oxygen–metal ligand bond. However, unlike $AlPcS_2$, the zinc phthalocyanines do not show a decrease in the rate of $T_1 \rightarrow S_0$ intersystem crossing. This indicates that the $T_1 \rightarrow S_0$ non-radiative pathway is unaffected by deuteration of the axial pyridine ligand. It is conceivable, therefore, that pyridine ligand deuteration for the zinc phthalocyanine species is too far removed from the nitrogen–metal ligand bond to have any effect on the photophysics of the molecule. In addition, the pyridine ligand for zinc complexes is probably not as tightly bound as either water or methanol ligands for aluminium complexes; this could be an important factor in the influence of the ligand on the photophysics of the parent molecule. However, it has been reported that the excited state properties of zinc porphyrin complexes are affected when the axial methanol or ethanol ligands are deuterated [10]. Also Gradyushko et al. [3] have shown that the phosphorescence lifetime of magnesium tetraphenyl porphyrin in toluene is increased when the axial ligand is altered from methanol to either methanol-d_1 or methanol-d_4. This clearly shows that certain axial ligands that may be considered as weak binders to a complex can influence the excited state dynamics.

From the work carried out in this study and from other results obtained by us, it can be seen that the effects of deuteration on the photophysics of phthalocyanine species may be very specific. It is probable that the nature of the solvent environment and the axial ligand solvating the central metal ion have no effect on internal conversion but influence intersystem crossing. Further studies are under way with a range of phthalocyanines and solvent systems to elucidate these initial findings.

5. Conclusions

Full deuteration of ZnPc produced no change in the excited singlet or triplet state photophysics. It can therefore be concluded that deuteration of the phthalocyanine ring is not an effective method for enhancing the PDT efficiency of a phthalocyanine sensitizer, since there was no enhancement of the triplet or singlet oxygen quantum yields.

Similarly, the deuteration of the axial ligand of ZnPc did not alter the photophysical properties. It is conceivable that the effect of deuteration on the non-radiative relaxation processes of excited state phthalocyanines is dependent on the ligand, solvent and metal phthalocyanine. Work is under way to study the photophysics of a fully deuterated, water-soluble phthalocyanine and phthalocyanines with specifically deuterated axial ligands.

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