A photophysical study of protonated (tetra-*tert*-butyl-phthalocyaninato)zinc

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A comprehensive photophysical study of protonated species of (tetra-*tert*-butylphthalocyaninato)zinc ($^{t}Bu_4ZnPcH_n^{n+}$, $n = 0–4$) is reported. Singlet and triplet state properties have been measured and discussed with reference to the effects of protonation which occur at the azomethine bridging nitrogens of the phthalocyanine macrocycle. Fluorescence anisotropy studies are included. The effect of protonation upon singlet oxygen generation has also been studied and discussed.

Introduction

The photophysical behaviour of metallophthalocyanines has been the subject of intensive study over the past decade, partly due to their potential applications in the area of photomedicine and photodynamic therapy, PDT. It is generally accepted that the excited triplet state of the phthalocyanine transfers energy to molecular oxygen, producing singlet oxygen, O_2 ($^1\Delta_g$), and/or enters into electron transfer reactions to produce cytotoxic radical species. In order to understand these processes it is necessary to fully characterise the excited singlet and triplet states of the dyes.

A common means of purifying phthalocyanines, as described by Linstead, involves the dissolution of the dye in concentrated acid followed by re-precipitation upon dilution with water. During the course of our studies of the substituted phthalocyanine dyes we have noted that the dyes are readily protonated in acid media, and that the absorption spectra change accordingly. However, there have been very few previous studies of the spectroscopic behaviour of the protonated species. UV–Vis spectroscopy has been used to monitor the degree of protonation of phthalocyanines by Gaspard[1] and Iodko[2] and their co-workers who observed the species PcH_n^{n+}, for $n = 0–4$, and the effect of mono-protonation upon the triplet state of (phthalocyaninato)aluminium was reported by Lang *et al.*[3] Despite these cursory studies there have been no comprehensive studies of the protonated phthalocyanines (Pcs). Studies carried out on the properties of aluminium Pcs in solutions of pH 1–12 have been carried out, although no direct evidence of protonation was reported. Two groups have reported the appearance of new bands at *ca.* 710 nm in the absorption spectra of concentrated solutions of sulfonated Pcs as well as red-shifted emission spectra. Some of the observed spectral features have been explained in terms of re-absorption of fluorescence,[4] but our new findings suggest that a more complete explanation may include the presence of protonated species.[5]

In the study described below we have examined the properties of (tetra-*tert*-butylphthalocyaninato)zinc, $^{t}Bu_4ZnPc$, in acidic media and have observed the species $^{t}Bu_4ZnPcH_n^{n+}$, for $n = 0–4$. The material used here is prepared by the condensation of 4-*tert*-butylphthalonitrile, and although some workers claim the preparation of single isomers of this compound[6] the substitution pattern(s) for the compound used here is not known.

Table 1 Absorption maxima of $^{t}Bu_4ZnPcH_n^{n+}$ ($n = 0–4$) in EtOH

n	$[H^+]$/mol dm^{-3}	B_1/B_2 Envelope maxima/nm	Q Band maxima/nm
0	~0	349	674
1	2.9×10^{-2}	331, 361	686, 712
2	1.76	335, 392	695, 729
3	75% H_2SO_4 : EtOH	307, 417	750, 778
4	100% H_2SO_4	443	807

Results

Singlet state properties

The addition of sulfuric acid to ethanolic solutions of $^{t}Bu_4ZnPc$ gave rise to five distinct species that could be detected by UV–Vis absorption spectroscopy (Fig. 1). Isosbestic points were observed for each of the conversions (except $n = 3$ or 4), indicating sequential protonation without the presence of side reactions such as dimerisation, aggregation or decomposition. By comparison with published results[2] these were assigned to protonated forms of the phthalocyanine, $^{t}Bu_4ZnPcH_n^{n+}$, where $n = 0–4$, and represent the stepwise addition of hydrogen ions to the azomethine bridges of the macrocycle. Mono, di and tri ($n = 1–3$) protonated species demonstrated a splitting of both the B_1/B_2 envelope and the Q band, whilst the spectrum of tetra-protonated phthalocyanine resembles that of the parent phthalocyanine, but red shifted with $\lambda_{max} = 807$ nm (Table 1). The integrated area of all the spectra, $\int I \cdot d\bar{v}$, from 550–850 nm of PcH_n^{n+} remained constant.

The extinction coefficients, ε_{max}, for each of the protonated species were determined and are listed in Table 2. From the data obtained at low acid concentrations the pK_a values were determined from the absorption spectra of solutions containing a range of acid concentrations using eqn. (1), where $pK_a = -\log$

$$A = (\varepsilon_{Pc} - \varepsilon_{PcH^+}) \frac{C_T}{1 + K[H^+]} + (\varepsilon_{PcH^+})C_T \qquad (1)$$

($1/K$), ε_{Pc} and ε_{PcH^+} are the extinction coefficients of $^{t}Bu_4ZnPcH_{n-1}^{(n-1)+}$ and $^{t}Bu_4ZnPcH_n^{n+}$ respectively, C_T is the total concentration of phthalocyanine and $[H^+]$ is the concentration of hydrogen ions in mol dm^{-3}. At low concentrations it is assumed that $[H^+] = [H_2SO_4]$. The calculated pK_a values of the species $^{t}Bu_4ZnPcH^+$ and $^{t}Bu_4ZnPcH_2^{2+}$ are included in Table 2.

Table 2 Absorbance and fluorescence data for PcH_n^{n+} ($n = 0–4$) in EtOH

| n	λ_{max}/nm (UV–Vis)	pK_a	ε_{max}/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm (Emission)	Φ_F
0	674	—	$1.6 \pm 0.1 \times 10^5$	682	0.26 ± 0.02
1	712	2.9 ± 0.3	$8.7 \pm 0.2 \times 10^4$	717	0.12 ± 0.01
2	729	0.18 ± 0.05	$1.1 \pm 0.1 \times 10^5$	735	0.07 ± 0.01
3	778	—	$6.8 \pm 0.4 \times 10^4$	788	0.03 ± 0.005
4	807	—	$1.8 \times 0.1 \times 10^5$	820	0.01 ± 0.005

Table 3 Fluorescence lifetimes of PcH_n^{n+} ($n = 0–4$) in EtOH

n	τ_1/ns (Amplitude, yield)	τ_2/ns (Amplitude, yield)	τ_3/ns (Amplitude, yield)	χ^2	DW
0	3.4 (100, 100)	—	—	1.36	1.85
1	2.8 (97.1, 98.9)	1.1 (2.9, 1.1)	—	1.16	1.99
2	1.8 (85.9, 92.6)	0.9 (14.1, 7.5)	—	1.36	1.91
3	1.3 (97.0, 94.4)	2.5 (3.0, 5.6)	—	1.34	1.98
4	0.9 (99.3, 96.7)	2.2 (0.5, 1.2)	7.7 (0.2, 2.2)	1.4	1.89

Much higher concentrations of sulfuric acid were required to generate the tri- and tetra-protonated species ($n = 3$ and 4), and under these conditions this approximation becomes inappropriate. Instead it would be necessary to consider the Hammett acidity functions, for which no values for H_2SO_4 in ethanol have been published to date.

Protonation of the phthalocyanine ring resulted in a red shift in the fluorescence emission of the dyes, accompanied by a large decrease in the fluorescence quantum yield. The fluorescence emission spectra are shown in Fig. 1 and the fluorescence quantum yields summarised in Table 2. The fluorescence excitation spectra closely resemble the absorption spectra, confirming the existence of a single species under the conditions used.

The fluorescence lifetimes of the protonated species ^tBuZn-PcH_n^{n+} ($n = 0–4$) are listed in Table 3. The parent phthalocyanine decays by simple first order kinetics. Decays from the acidified solutions could not be adequately described by single exponential functions, but did yield excellent fits to a double-exponential function $[I(t) = A_1 \exp(^{-t}/\tau_1) + A_2 \exp(^{-t}/\tau_2)]$. These were characterised by a dominant component which accounted for >90% of the emission, and it is these values which represent the measured fluorescence lifetime τ_F of each protonated species and are used in subsequent calculations. The secondary, minor components are attributed to the presence of other protonated species in the samples. There is a general trend showing a decrease in the fluorescence lifetime with increased protonation of the phthalocyanine rings.
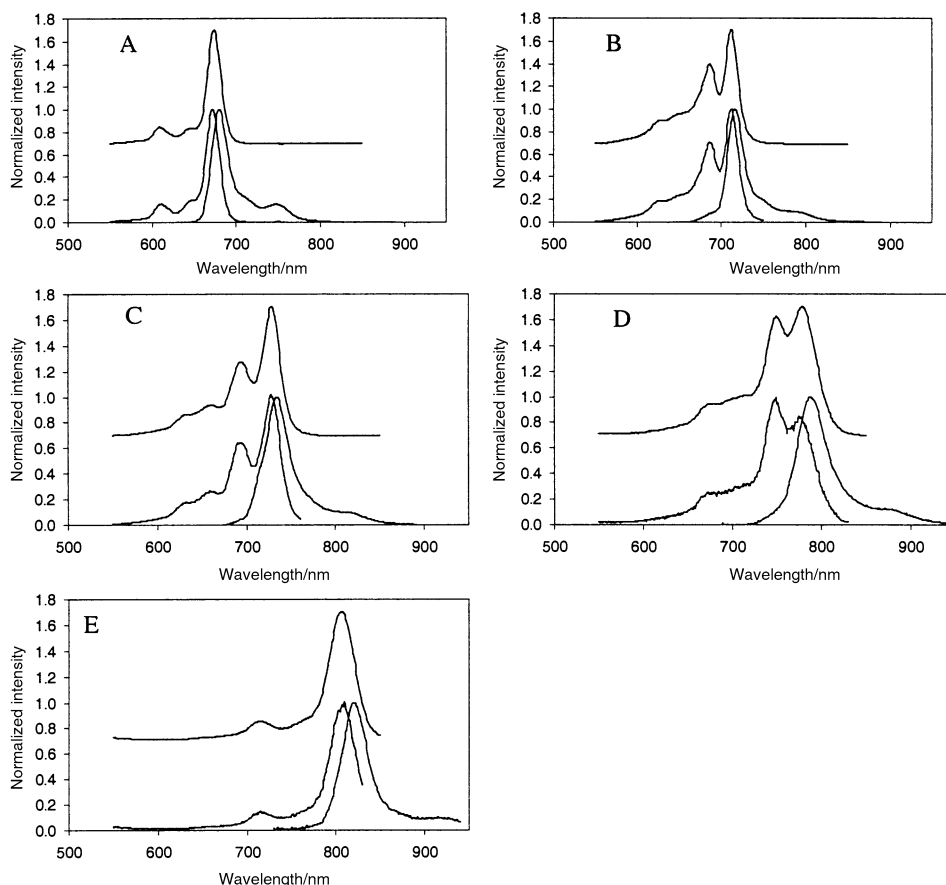
Fig. 1 Normalised fluorescence emission and fluorescence excitation spectra of PcH_n^{n+} in EtOH. Offset: normalised absorption spectra. A) $n = 0$ (emission: $\lambda_{ex} = 615$nm; excitation: $\lambda_{em} = 760$ nm); B) $n = 1$ (emission: $\lambda_{ex} = 625$ nm; excitation: $\lambda_{em} = 770$ nm); C) $n = 2$ (emission $\lambda_{ex} = 635$ nm; excitation: $\lambda_{em} = 770$ nm); D) $n = 3$ (emission: $\lambda_{ex} = 680$ nm; excitation: $\lambda_{em} = 840$ nm); E) $n = 4$ (emission $\lambda_{ex} = 715$ nm; excitation: $\lambda_{em} = 840$ nm).

Table 4 Triplet state data for PcH$_n^{n+}$ (n = 0–4) in EtOH

n	τ_T/µs	λ_{max}/nm	Φ_T	Φ_Δ
0	200 ± 20	490 ± 10	0.58 ± 0.05	0.54 ± 0.03
1	40 ± 4	500 ± 10	0.44 ± 0.04	0.075 ± 0.005
2	35 ± 4	500 ± 10	0.40 ± 0.04	<0.075
3	31 ± 3	540 ± 20	0.22 ± 0.03	—
4	13 ± 1	560 ± 20	0.18 ± 0.03	—

Triplet state measurements

Triplet state species were studied by laser flash photolysis. The $^3\pi\pi^*$ excited states of species n = 0–2 were populated using the 3rd harmonic from the Nd:YAG laser, 355 nm. Tri- and tetra-protonated species were excited using the output from a dye laser at 680 and 700 nm respectively. Protonation induced a shift in the triplet–triplet absorption spectrum, a reduction in the triplet quantum yield (Φ_T) and a significant decrease in the excited state lifetime (τ_T). These results, summarised in Table 4, are consistent with those observed by Lang *et al.*[3] for sulfonated chloro(phthalocyaninato)aluminium in which a decrease of τ_T from 290 to 90 µs was observed upon protonation of one bridging nitrogen.

The triplet–triplet extinction coefficients for all of the triplet states were determined to be 36000 ± 6000 dm^3 mol^{-1} cm^{-1} at λ_{max} (500 nm). This value is consistent with that of the parent phthalocyanine at 490 nm and was used in subsequent calculations of Φ_T. Conversion of the parent phthalocyanine (n = 0) into ^{t}Bu$_4$ZnPcH$^+$ induced a 10 nm red-shift in the transient spectrum, and a decrease in the triplet quantum yield from 0.54 to 0.44. The lifetime τ_T fell from 200 µs ([H$^+$] ~ 0 mol dm^{-3}) to 40 µs ([H$^+$] = 3 × 10^{-2} mol dm^{-3}). At intermediate acid concentrations, when a mixture of Pc and PcH$^+$ co-existed in solution [assuming[7a] eqn. (2)], the observed triplet decay

$$^3Pc^* + H^+ \xrightleftharpoons{\text{Fast}} {}^3PcH^{+*} \qquad (2)$$

remained monoexponential, depicting an average value of both component lifetimes.
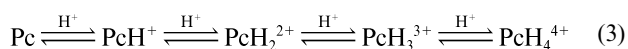
Singlet oxygen formation

The quantum yields of singlet oxygen formation are given in Table 4. PcH$^+$ and PcH$_2^{2+}$ displayed a large decrease in $^1O_2$ production. In addition, although phosphorescence from the parent phthalocyanine could be observed[8] at 1090 nm, no triplet state emission from PcH$^+$ could be observed over the wavelength range 1000–1300 nm.

Discussion

Singlet state properties

Low pH induced a concomitant shift in absorption and fluorescence spectra, consistent with a series of protonation equilibria[2] [eqn. (3)].

$$Pc \xrightleftharpoons{H^+} PcH^+ \xrightleftharpoons{H^+} PcH_2^{2+} \xrightleftharpoons{H^+} PcH_3^{3+} \xrightleftharpoons{H^+} PcH_4^{4+} \quad (3)$$

The origin of red shifts in the spectra may be rationalised using the same theoretical framework[9] invoked to explain the effect of peripheral substituents on the wavelength of monomer absorption. Addition of a hydrogen ion onto peripheral ring nitrogens stabilises the LUMO by withdrawing electrons from α-positions of the phenyl ring towards the nitrogen atoms. Excitation into the first excited singlet state involves transfer of electron density from inner ring carbon atoms to nitrogen atoms. This is facilitated by the electron attracting action of hydrogen substituents, leading to a reduction of the HOMO–LUMO energy gap.

Recent work has studied the effect of protonation on the photophysics of disulfonated (phthalocyaninato)aluminium (AlPcS$_2$), a compound which has seen considerable interest for its applications within PDT.[10] The observations reported in this paper are distinct from those presented there—a red-shifted absorption was observed which was attributed to protonation of the axially ligating water molecules, resulting in two distinct dimers, one at pH 2.5, the other at pH 7.5. ^{t}Bu$_4$ZnPc studied here has no axial ligands, and so this different behaviour is not unexpected. Similar shifts to those reported here have been observed in the absorption spectra of protonated Schiff base metalloporphyrins[11] and attributed to a resonance effect of the withdrawing groups rather than delocalisation of the positive charge onto the ring. This is not surprising since in these molecules the positive charge is located on an imine moiety of the ring and, hence, is somewhat removed from conjugation of the ring.[12] Large changes in the B$_1$/B$_2$ envelope were also observed on protonation (Table 1). These are analogous to those induced by amino substituents on metallophthalocyanine[13] in which a band was observed at 450 nm due to splitting of the B$_1$/B$_2$ envelope.

The theory of Morley *et al.*[9] predicts very small shifts of the B$_1$/B$_2$ envelope upon peripheral substitution, thus it would appear that development of this theorem is required to cover all ligand binding cases. Splitting of the B$_1$/B$_2$ envelope and Q band may be attributed to removal of the degeneracy of transitions polarised along the x and y directions. Binding of hydrogen to the phthalocyanine ligand lowered the symmetry of the complex from D_{4h} to D_{2h} so that x and y transitions are no longer equivalent. This is corroborated by fluorescence anisotropy measurements. At hydrogen ion concentrations of 3 × 10^{-2} mol dm^{-3} a similar spectrum to that measured for ^{t}Bu$_4$H$_2$Pc (a D_{2h} complex) was obtained. A negative anisotropy was observed at wavelengths below 690 nm, corresponding to excitation into a higher energy level than the emitting state. Using the Perrin equation [eqn. (4)], and the measured r_{av} of

$$r_f = 0.2(3\cos^2\theta_a - 1) \qquad (4)$$

−0.2, the angle between transition dipole moments of absorbing and emitting states may be calculated to be 90° (λ_{ex} = 605 nm). At wavelengths >605 nm, state mixing caused the measured value for r_{av} to be higher (less negative) than its true value. An angle of 90° is consistent with removal of x and y degeneracy. At wavelengths above 690 nm a large positive anisotropy was measured (0.3 at 700 nm), *i.e.* excitation at this wavelength produced the emitting state directly. Effects on the viscosity of the solution due to the addition of acid (0.03 mol dm^{-3}) are negligible. With no added acid, the anisotropy had an average value of 0.075 although fluctuations with λ_{ex} were observed, consistent with observations for a fluorophore of D_{4h} symmetry.

Triplet state properties

A reduction in photoactivity of ^{t}Bu$_4$ZnPc was observed as the concentration of hydrogen ions increased. Table 5 shows radiative and non-radiative rate constants calculated using measured quantum yield and lifetime data. Simple relations used in calculations are shown in the table.

As protonation of the ring increased, the rate of radiative deactivation of S$_1$, k_F^o, decreased, whilst that of internal conversion, k_{ic}, increased. The rate of intersystem crossing remained constant at 1.8 ± 0.25 × 10^8 s^{-1}. These trends are easily explained in terms of fundamental photophysical behaviour and are directly related to changes in ΔE (S$_1 \longleftarrow$ S$_0$ energy gap) upon protonation.

Despite an increase in the intrinsic lifetime, τ_0 ($\tau_0 = 1/k_F^o$), the measured lifetime of fluorescence decreased from 3 to 0.88 ns upon complete protonation (Table 3). This was due to a concur-

Table 5 Rate constants of radiative and non-radiative deactivation pathways of PcH_n^{n+} ($n = 0–4$) in EtOH

n	$k_F^\circ/s^{-1} = \Phi_F/\tau_F$	$k_{isc}/s^{-1} = \Phi_T/\tau_F$	$\Phi_{ic} = 1 - (\Phi_F + \Phi_T)$	$k_{ic}/s^{-1} = \Phi_{ic}/\tau_F$
0	$7.2 \pm 0.9 \times 10^7$	$1.6 \pm 0.2 \times 10^8$	0.16 ± 0.05	$4.4 \pm 1.4 \times 10^7$
1	$4.3 \pm 0.6 \times 10^7$	$1.6 \pm 0.2 \times 10^8$	0.44 ± 0.04	$1.6 \pm 0.2 \times 10^8$
2	$3.9 \pm 0.7 \times 10^7$	$2.2 \pm 0.3 \times 10^8$	0.53 ± 0.04	$2.9 \pm 0.4 \times 10^8$
3	$2.3 \pm 0.4 \times 10^7$	$1.7 \pm 0.3 \times 10^8$	0.75 ± 0.03	$5.8 \pm 0.6 \times 10^8$
4	$1.14 \pm 0.6 \times 10^7$	$2.0 \pm 0.4 \times 10^8$	0.81 ± 0.03	$9.2 \pm 1 \times 10^8$
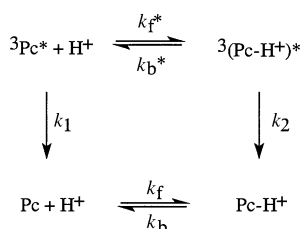
Fig. 2 Triplet state equilibria of PcH^+.

rent increase in internal conversion pathways. Non-radiative transitions increase as the energy gap between states decreases according to the 'energy gap law'.[14] Rate constant k_{ic} values are in good agreement with this 'energy gap law' and with previously published data that has been related to the energy of the singlet state.[7b,15]

Equilibria contributing to excited triplet state dynamics are presented in Fig. 2. Constants k_1 and k_2 represent the triplet decay rate of unprotonated and monoprotonated phthalocyanine species, whilst, k_f, k_b and k_f^*, k_b^* are the rates of H^+ binding/dissociation in the ground and excited states respectively.

Experimentally, the triplet state decay profile could be adequately described by single exponential functions. This suggests that fast exchange between $^3Pc^*$ and $^3PcH^{+*}$ occurred within the lifetime of the excited state such that k_f^* and k_b^* are faster than k_1 and k_2 consistent with theory.[7a] The equilibrium constant, K^*, is represented by eqn. (5).

$$K^* = \frac{k_f^*}{k_b^*} = \frac{[^3PcH^*]}{[^3Pc^*][H^+]} \quad (5)$$

The experimentally observed decay may be represented by the sum of two first order decays, $-d[^3Pc^* + {}^3PcH^{+*}]/dt = k_1[^3Pc^*] + k_2[^3PcH^{+*}]$. Substituting for $[^3PcH^{+*}]$ gives eqn. (6).

$$-(1 + K^*[H^+])\frac{d[^3Pc^*]}{dt} = (k_1 + k_2K^*[H^+])[^3Pc^*] \quad (6)$$

However, $-d[^3Pc^*]/dt = k_{obs}[^3Pc^*]$, thus the observed rate of decay k_{obs} is a first order process that may be expressed by eqn. (7).

$$k_{obs} = \frac{k_1 + K^*[H^+]k_2}{1 + K^*[H^+]} \quad (7)$$

At high $[H^+]$, $K^*[H^+] >> 1$, therefore $k_{obs} \sim k_2$—the rate of decay of $^3PcH^{+*}$, whilst at low $[H^+]$, $1 >> K^*[H^+]$ hence $k_{obs} \sim k_1$—the rate of decay of $^3Pc^*$. At intermediate $[H^+]$ an average value was observed which depended on the relative contribution of k_1 and k_2.

Singlet oxygen formation

A large decrease in the yield of singlet oxygen formation was observed upon protonation. Such a large reduction was inconsistent with the measured decrease in Φ_T and τ_T. This may be explained by a lowering of the triplet energy to a value where

energy transfer to ground state oxygen is no longer favourable. Lang et al.[3] have reported a substantial reduction in the rate of quenching, k_Q, by O_2 of the triplet state of protonated chloro-(phthalocyaninato)aluminium ($k_Q = 6.6 \times 10^7$ dm^3 mol^{-1} s^{-1}) relative to that of unprotonated phthalocyanine ($k_Q = 1.6 \times 10^9$ dm^3 mol^{-1} s^{-1}). It has been shown,[7c,16] that k_Q may be correlated with the energy gap between triplet state species participating in energy transfer and formation of singlet oxygen. It may be inferred that, since the energy required to promote ground state molecular oxygen to its singlet state will remain constant, the energy of $^3Pc^*$ must have decreased. It was not possible to corroborate this experimentally since phosphorescence of PcH^+ could not be detected. However, it has been shown that k_{isc}, and therefore ΔE ($S_1 \rightarrow T_1$), remained constant upon protonation, thus E_T of PcH^+ may be estimated to be ~8400 cm^{-1} (cf. 9090 cm^{-1} for $^tBu_4ZnPc$), $E_\Delta = 7882$ cm^{-1}.

Experimental

(Tetra-tert-butylphthalocyaninato)zinc was purchased from Aldrich and used as received. Identical results were obtained using (tetra-tert-butylphthalocyaninato)zinc from condensation of the corresponding phthalonitrile and subsequent metallation using standard methodology[17] followed by chromatographic purification. Solutions were prepared in absolute ethanol (Haymann Ltd) and stored in the dark. Solutions were acidified by the addition of concentrated sulfuric acid (Fisons AnalaR). Samples prepared for fluorescence spectroscopy were prepared such that the maximum absorption was <0.1 across the range 200–800 nm, whilst for triplet state and singlet oxygen measurements samples were prepared with a maximum absorbance of 0.2.

Absorption spectra were recorded on an ATI-Unicam UV-2 spectrophotometer. Samples were held in quartz cuvettes with a 1 cm pathlength and were recorded using a reference cell containing pure solvent. Fluorescence excitation spectra were recorded using a Spex FluoroMax spectrofluorimeter using 1 nm band pass for both excitation and emission monochromators. Emission spectra were obtained on a home built NIR fluorimeter. The chopped excitation source was obtained from a 150 W xenon lamp (Bentham IL6 Illluminator) and focused onto the slits of the excitation monochromator (Bentham TM 300V). The fluorescence emission was collected at 90° to the excitation beam and passed through an emission monochromator (Triax 390, Jobin Yvon) and onto a silicon diode detector. The signal was passed through a lock-in amplifier (Stanford SR510) and transferred to a PC. Quantum yields were recorded using a diode array spectrophotometer. The samples were excited using the output of a 5 mW HeNe laser (Melles Griot) and the emission collected at 90° and dispersed using a spectrograph (Bentham TM-300V monochromator) and the light intensity measured using a diode array (EG&G 1453a). Data acquisition times of 10 s were used for all emission spectra and the spectra were spectrally corrected for the response of the detection optics using a curve generated using a standard tungsten lamp. Quantum yields were recorded relative to chlorophyll a in ether ($\Phi_f = 0.34$)[18] (Sigma), and (phthalocyaninato)zinc in 1% pyridine–toluene ($\Phi_f = 0.30$)[8] using the method of Williams et al.[19] Data were recorded in aerated media, although no differences in values were observed upon degassing using a freeze–pump–thaw protocol.

Fluorescence lifetimes were recorded using the method of time-correlated single photon counting using equipment that has been described elsewhere.[20] Samples were excited at 610 nm and the emission selected according to the species under study. Lifetimes were found to be constant within experimental error whether obtained in aerated or degassed solution.

The triplet state studies were carried out using laser flash photolysis. The samples were excited at 355 nm using the 3rd harmonic of a Q-switched Nd : YAG laser, (Spectra Physics GCR 150-10); for longer wavelength excitation the 2nd harmonic of a Q-switched Nd : YAG laser was used to pump a dye laser (Lambda Physik, FL2002) which used DCM in DMSO as the gain medium. A 10 Hz train of pulses of light was delivered to the sample chamber *via* a liquid light guide ($\Phi = 8$ mm) with typical pulse energies of 0.05–0.5 mJ per pulse at the sample. The samples were held in a 1×1 cm cuvette and were degassed by a freeze–pump–thaw procedure. Transient species were probed at 90° using the output of a CW tungsten lamp, and the probe wavelength was selected using a monochromator (Bentham TM-300V) and the intensity detected by a photomultiplier (Hamamatsu R928) and recorded using a digital oscilloscope (Tektronix TDS320). The transients obtained from 10–65 laser shots were averaged and transferred to a PC where they were converted to absorbance values and the decays were analysed using a non-linear least squares procedure in a spreadsheet (Excel).

Triplet quantum yields were recorded using the relative method.[21] The triplet quantum yield, Φ_T was determined according to eqn. (8), where Φ represents the triplet quantum

$$\Phi_T = \Phi_{std} \times \frac{A_x}{\varepsilon_x} \times \frac{\varepsilon_{std}}{A_{std}} \tag{8}$$

yield, A is the absorbance of the transient species shortly after the laser pulse and ε is the molar extinction coefficient of the triplet state at the probe wavelength. The subscripts x and std refer to the unknown and standard respectively. Methylene blue in ethanol ($\Phi_T = 0.52$, $\varepsilon_T = 14400$ dm^3 mol^{-1} cm^{-1} at 420 nm) and benzophenone ($\Phi_T = 1.00$, $\varepsilon_T = 6250$ dm^3 mol^{-1} cm^{-1} at 525 nm) were used as standards.[17]

Triplet extinction coefficients of the phthalocyanines were determined by the singlet depletion method using a range of probe wavelengths, and the transient absorption spectra were recorded by probing the transient absorption over the range 350–750 nm in 5 nm increments. Triplet lifetimes were determined by fitting the observed decay of the transient absorption transient using a spreadsheet package (Excel).

Singlet oxygen yields were determined using the time-resolved luminescence measurements. Aerated samples were irradiated at 355 nm with pulse energies in the range 0.05–1.00 mJ per pulse. The luminescence was collected at 90° and passed through a narrow band-pass interference filter (1270 nm, Infra-red Engineering) before detection by a liquid nitrogen cooled germanium photodiode (North coast EO-817P). The signal was recorded and averaged over 2–32 shots using a digital oscilloscope (Tektronix TDS320) before transfer to a PC for analysis (Excel).

Where errors are presented in tabulated data, the reported value is the mean of at least ten data followed by the standard deviation.

Conclusions

This work has demonstrated the effects of protonation upon the photophysical behaviour of a simple phthalocyanine. Using UV–Vis spectroscopy we have shown that this Pc undergoes sequential protonation on the bridging azomethine nitrogen atoms. Protonation has been shown to reduce the energy of the excited states and to reduce their lifetimes. Although PcH$^+$ and PcH$_2{}^{2+}$ have been shown to produce singlet oxygen ($^1O_2$) the higher protonated species PcH$_3{}^{3+}$ and PcH$_4{}^{4+}$ do not, probably as a result of the triplet state energy being inadequate to sensitise the oxygen.

This is the first comprehensive study of the effects of Pc macrocycle protonation to date, and we are now turning our attention to other more substituted phthalocyanines that are used in PDT applications.

Acknowledgements

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