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Journal of Photochemistry and Photobiology A: Chemistry 188 (2007) 200–206

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photophysical and photochemical properties of zinc and aluminum phthalocyanines in the presence of magnetic fluid

Mopelola Idowu, Tebello Nyokong *

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

Received 31 August 2006; received in revised form 10 October 2006; accepted 7 December 2006
Available online 14 December 2006

Abstract

The effect of magnetic fluid (MF) on the photophysical and photochemical parameters of zinc and aluminum phthalocyanines are reported. The complexes studied are zinc (II) phthalocyanine (ZnPc), chloroaluminum phthalocyanine ((Cl)AlPc) and tetrasulfonated aluminum phthalocyanine ((Cl)AlTSPc). The parameters are studied in dimethylsulfoxide (DMSO) for all complexes and also in aqueous media for (Cl)AlTSPc. The triplet lifetimes for (Cl)AlTSPc and ZnPc decreased while the triplet quantum yields increased in the presence of MF. For (Cl)AlPc, the triplet lifetimes were found to increase with decrease in laser energy while there was photoreduction to the Pc^{-3} species. Singlet oxygen and photodegradation quantum yields decreased in the presence of MF, suggesting quenching.

Keywords: Magnetic fluid; Zinc phthalocyanine; Aluminum phthalocyanine; Triplet quantum yields; Triplet lifetime; Fluorescence; Photodegradation

1. Introduction

Metallophthalocyanine (MPc) derivatives have attracted attention due to their diverse electronic, optical and structural properties, which has resulted in their applications in fields such as photosensitization [1], nonlinear optics [2], catalysis [3], liquid crystals [4] and sensing [5]. Cancer remains a major burden to human health. Chemotherapy, radiotherapy, photodynamic therapy (PDT) and hyperthermia (HPT) have been used independently but each does not completely eradicate the malignant tissues.

PDT modality combines the selectivity of fibre optic directed light with the cell destruction properties of singlet oxygen. MPc complexes are promising as photosensitizers for PDT, due to their intense absorption in the red region of visible light. Incorporation of non-transition metals such as zinc and aluminum in the centre of the Pc ring results in complexes with high triplet state quantum yields and long triplet lifetimes, which are required for efficient photosensitization. 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 [6].

Hyperthermia (HPT) is a type of treatment in which body tissue is exposed to high temperatures to damage and kill cancer cells or to make cancer cells more sensitive to the effects of radiation and certain anticancer drugs [7]. Malignant cells are more sensitive to heat than normal cells and raising of temperature is a way to selectively destroy cancer cells. HPT has given impressive results such as shrinkage of tumours and eradication of up to about 15% of tumour but in most cases the tumour re-grows.

Recent advances in treatment of tumours is towards the synthesis of bi-functional agents that allows the combined action of PDT and HPT. This is expected to result in tumour damaging based on both heat (in HPT) and light photosensitization (in PDT) [8]. HPT also increases the cellular uptake of oxygen since the heating up of the cell causes dilation which allows free flow of oxygenated blood to the cells [9]. This is essential for PDT where ground state oxygen is needed to produce cytotoxic derivatives of oxygen [6]. The preferential uptake of phthalocyanines in tumours may help to localize the magnetic fluid in tumours for HPT.

ZnPc and AlPc derivatives have potential for use as photosensitizers in PDT. While iron oxides (magnetic fluid, MF) used in HPT are in clinical trials for treatment of tumours [10]. It has recently been reported that MF does not change absorption or

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[*] Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

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doi:10.1016/j.jphotochem.2006.12.013

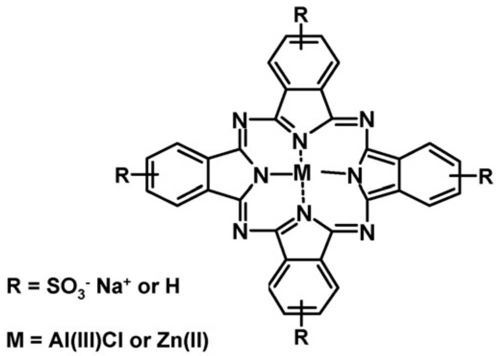

Fig. 1. Molecular structure of (Cl)AlPc and ZnPc complexes.

fluorescence spectral properties of ZnPc [8] in ethanol. Since solvents affect the photophysical and photochemical properties of MPc complexes [11], we study these properties for ZnPc and AlPc complexes in DMSO in this work. For PDT applications, it is important to study the behaviour of complexes in aqueous media, thus we present the study of the photophysical behaviour of (Cl)AlTSPc in water (PBS pH 7.4) and in the presence or absence of MF. In addition we study the photostability of MPcs during photosensitized reactions as well as their ability to generate the singlet oxygen. Hence in this work, we study the effect of MF on singlet oxygen quantum yield, photostability, triplet life time and yield, and fluorescence quantum yield of (Cl)AlPc, ZnPc and aluminum sulfophthalocyanine ((Cl)AlTSPc) complexes (Fig. 1) in DMSO. For the latter complex, the studies are also performed in aqueous solutions.

2. Experimental

2.1. Materials

Zinc (ZnPc) and chloroaluminum (ClAlPc) phthalocyanines were synthesized, purified and characterized using literature methods [12,13]. Chloroaluminum ((Cl)AlTSPc) and zinc (ZnTSPc) tetrasulfophthalocyanines were synthesized, purified and characterized according to the method of Weber and Busch [14]. $ZnPcS_{mix}$ containing a mixture of sulfonated derivatives was synthesized using fuming sulphuric acid (30% SO_3) in accordance with literature [15].

$FeCl_2$, $FeCl_3$, triethylamine ($(C_2H_5)_3N$), $Fe(NO_3)_3$ and anthracene-9,10-bis-methylmalonate (ADMA, acid form), 3-diphenylisobenzofuran (DPBF) were obtained from Aldrich. Dimethylsulfoxide (DMSO, SAARCHEM) was dried before use. For aqueous solutions, ultra pure water was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA). Phosphate-buffered saline (PBS) solution (0.01 M, pH 7.4) was prepared using appropriate amounts of Na_2HPO_4, KH_2PO_4 and chloride salts, dissolved in ultra pure water.

2.2. Synthesis of magnetic fluid

Synthesis of magnetic fluid based on spinel ferrites was obtained by co-precipitation of Fe^{2+} and Fe^{3+} ions in alkaline medium as has been reported before [8,16]. Briefly a mixture of 6 ml concentrated nitric acid, 250 ml of aqueous solution of $FeCl_2$ (0.005 mol l^{-1}) and 250 ml of aqueous solution of $FeCl_3$ (0.010 mol l^{-1}) was heated to 95 °C, under vigorous stirring (2700 rpm). An aqueous solution of sodium hydroxide (120 ml, 1 mol l^{-1}) was then quickly added to the stirring solution until pH 12 was reached. Following which the product was left overnight on a magnet to effect the magnetic ordering of the Fe ions. Further passivation was carried out by the enrichment of the Fe^{3+} with 10 ml of hot ferric nitrate $Fe(NO_3)_3$ (5.05 g, 0.5 mol l^{-1}) under stirring for 3 min. The synthesis was concluded with the peptization of the nanoparticle by addition of aqueous triethylamine ($(C_2H_5)_3N$, 0.1 mol l^{-1}). This step helps in the control of surface density while reducing the ionic strength of the aqueous medium. The formed MF (30 mg) was combined with 5 mg of each of the MPc complexes in Fig. 1 under vigorous stirring at 2700 rpm for 4 h to give the bifunctional agent for HPT and PDT.

2.3. Equipment

Fluorescence excitation and emission spectra, were recorded on a Varian Eclipse spectrofluorimeter. UV–vis spectra were recorded on a Varian 500 UV–vis/NIR spectrophotometer. Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye (Pyridine 1 dye in methanol). Single pulse energy ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360). The triplet life times were determined by exponential fitting of the kinetic curves using the program OriginPro 7.5. Photo-irradiations for photodegradation or singlet oxygen determination were performed using a General electric Quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and water were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 20 nm) was additionally placed in the light path before the sample. Light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 3.09×10^{16} photons s^{-1} for photobleaching and to be 1.26×10^{16} photons s^{-1} for singlet oxygen studies. Solutions for triplet yield and life time determinations were deaerated in nitrogen before laser irradiations.

Transmission electron microscope (TEM) pictures of MF and MF in the presence of MPc were obtained using a JEOL JEM 1210 transmission electron microscope at 100 kV accelerating voltage.

2.4. Photophysical and photochemical studies

Fluorescence quantum yields (Φ_F) were determined by comparative method [17] (Eq. (1)),

$$\Phi_F = \Phi_F(\mathrm{Std}) \frac{F A_{\mathrm{Std}} \eta^2}{F_{\mathrm{Std}} A \eta_{\mathrm{Std}}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence curves of the MPc derivatives and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, respectively, and η and η_{Std} are the refractive indices of solvents used for the sample, respectively. ZnPc in DMSO was used as a standard, $\Phi_{\mathrm{F}} = 0.18$ [18]. At least three independent experiments were performed for the quantum yield determinations. Both the sample and the standard were excited at the same relevant wavelength.

Triplet quantum yields were determined using a comparative method based on triplet decay, using Eq. (2):

$$\Phi_{\mathrm{T}}^{\mathrm{Sample}} = \Phi_{\mathrm{T}}^{\mathrm{Std}} \frac{\Delta A^{\mathrm{Sample}} \varepsilon^{\mathrm{Std}}}{\Delta A^{\mathrm{Std}} \varepsilon^{\mathrm{Sample}}} \tag{2}$$

where $\Delta A^{\mathrm{Sample}}$ and ΔA^{Std} are the changes in the triplet state absorbance of the MPc derivative and the standard, respectively. $\varepsilon^{\mathrm{Sample}}$ and $\varepsilon^{\mathrm{Std}}$ are the triplet state extinction coefficients for the MPc derivative and standard, respectively. $\Phi_{\mathrm{T}}^{\mathrm{Std}}$ is the triplet state quantum yield for the standards (ZnPc in DMSO, $\Phi_{\mathrm{T}}^{\mathrm{Std}} = 0.65$ [19]; and ZnTSPc in aqueous solution, $\Phi_{\mathrm{T}}^{\mathrm{Std}} = 0.56$ [20]).

Photodegradation (Φ_{d}) quantum yield determinations were carried out using the experimental set-up described above and described in detail before [11]. Typically, a 2 ml portion of the respective MPc solution (absorbance ~1.0) was irradiated in the Q band region with the photo-irradiation set-up described above. The values of photobleaching quantum yields (Φ_{d}) were determined using Eq. (3),

$$\Phi_{\mathrm{d}} = \frac{(C_0 - C_t) V N_{\mathrm{A}}}{I_{\mathrm{abs}} S t} \tag{3}$$

where C_t and C_0 are the MPc concentration after and prior to irradiation, respectively. S is the irradiation area of the cell, t the irradiation time, N_{A} the Avagadro‘s number and I_{abs} is the overlap integral of the radiation light source intensity.

Eq. (4) [21,22] was employed for calculating singlet oxygen quantum yields:

$$\Phi_{\Delta} = \Phi_{\Delta}^{\mathrm{Std}} \frac{W I_{\mathrm{abs}}^{\mathrm{Std}}}{W^{\mathrm{Std}} I_{\mathrm{abs}}} \tag{4}$$

where $\Phi_{\Delta}^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard (ZnPc in DMSO ($\Phi_{\Delta}^{\mathrm{ZnPc}}$ 0.67) [21] and (ZnPcSmix, $\Phi_{\Delta}^{\mathrm{Std}} = 0.45$ in aqueous solution) [23]. W and W^{std} are the singlet oxygen quencher photobleaching rates in the presence of the MPc derivatives and standards respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the MPc derivatives and standards, respectively. The experiments for Φ_{Δ} determinations were similar to those described above for photobleaching except singlet oxygen quenchers (ADMA in aqueous solutions and DPBF in DMSO) were added. The absorbance was 0.2 at the irradiation wavelength. To avoid chain reactions, the concentration of DPBF was kept at $\sim 3 \times 10^{-5}$ mol l^{-1}, while that of ADMA was kept at $\sim 6 \times 10^{-5}$ mol l^{-1}.

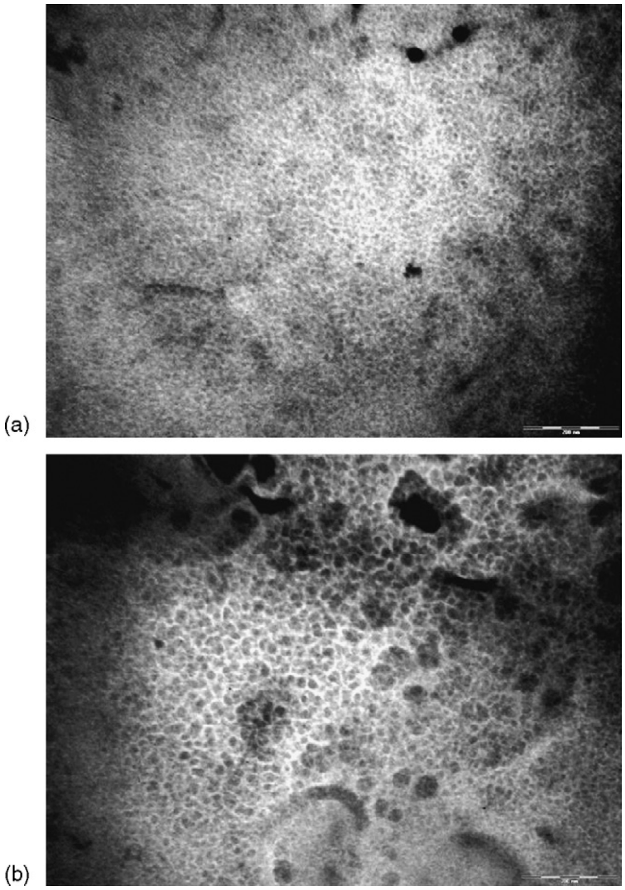

Fig. 2. Scanning electron microscopes of (a) MF alone and (b) MF plus (Cl)APc. Magnification = 100,000. Burnt in scale bar = 200 nm.

3. Results and discussion

3.1. Photophysical studies

Fig. 2 shows the transmission electron microscopy (TEM) pictures of MF and MF in the presence of (Cl)AlPc. There was a slight change in the morphology of MF and MF in the presence of (Cl)AlPc showing slight aggregation, probably due to the less hydrophilic phthalocyanine molecules adsorbed onto it, though the crystallinity of the nanoparticles was maintained. Fig. 3 shows that the Q band maxima of MPc derivatives did not shift in the presence of MF, showing that MF does not affect the absorbance properties of MPc derivatives, hence can be used in conjunction with them for medical applications. In aqueous media (PBS, pH 7.4), there was also no shift in the Q band on addition of MF, only an increase in background. It is also important to note that the spectrum of (Cl)AlTSPc in aqueous media shows some aggregation in PBS pH 7.4 as judged by the presence non-vibronic bands (between 600 and 650 nm) to the high energy side of the Q band. These bands are typical of aggregation in MPc complexes. The presence of MF did not affect aggregation in water. For all complexes in DMSO, no aggregation was obtained for concentrations less than 1×10^{-5} M in the presence or absence of MF. The lack of shift in the Q band maxima was also observed for fluorescence spectra in DMSO (Fig. 4) as has

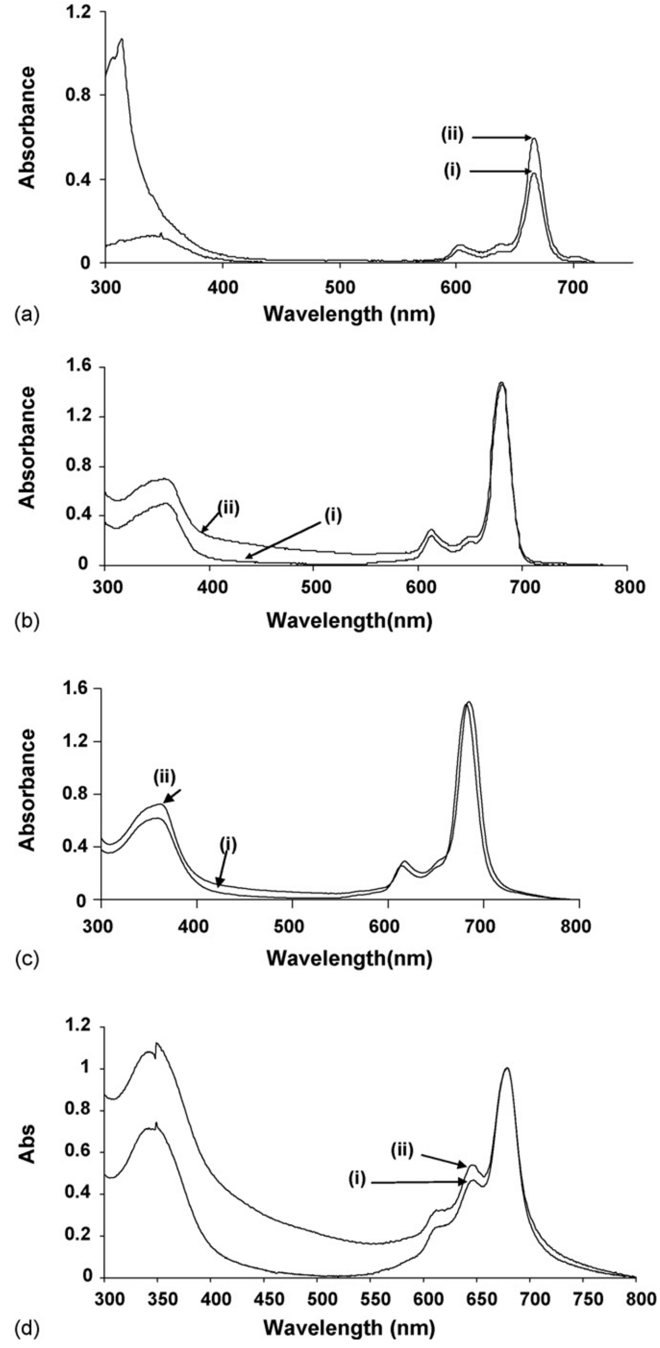

Fig. 3. Spectral behaviour of (a) ZnPc, (b) (Cl)AlPc and (c) (Cl)AlTSPc (i) alone and (ii) in the presence of MF. Solvent DMSO (for a, b and c). (d) AlTSPc in aqueous medium (i) alone and (ii) in the presence of MF.

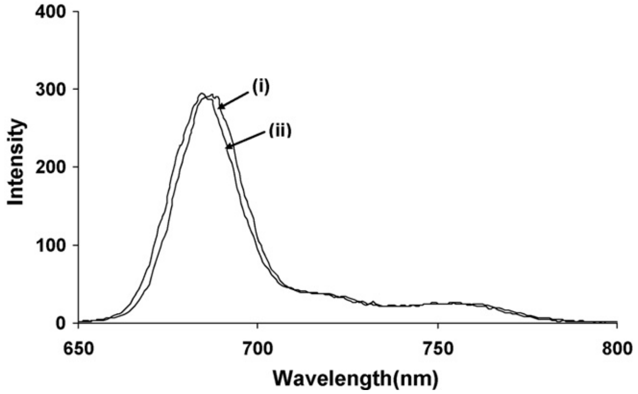

Fig. 4. Fluorescence emission of (Cl)AlPc in the presence (i) and absence (ii) of MF.

been reported before [8] for ZnPc in ethanol. No change in fluorescence spectra was observed for (Cl)AlTSPc in aqueous media and in the presence of MF. On addition of MF to ZnPc in DMSO there was a slight decrease in the quantum yield of fluorescence (Φ_F) and the values are typical of MPc complexes. In DMSO and in the absence of MF, Φ_F values for (Cl)AlPc and (Cl)AlTSPc, were much higher than for ZnPc (Table 1). The higher value of Φ_F for the AlPc complexes in the absence of MF compared to the ZnPc complexes could be due to the heavy atom effect of Zn, which encourages intersystem crossing to the triplet state. On addition of MF, the Φ_F values for all complexes decreased due to the heavy atom effect and the paramagnetic nature of the MF. However, due to the dissipation of the excited singlet state by aggregation, Φ_F values for (Cl)AlTSPc in aqueous medium was found to be lower than in DMSO and decreased in the presence of MF as was the case for all complexes in DMSO.

Fig. 5 shows the triplet decay curves for (Cl)AlPc alone and in the presence of MF in DMSO. The curves are similar. Plots of ln A versus time (inset) are linear, showing a first order dependence of the triplet state. This was also observed for (Cl)AlTSPc

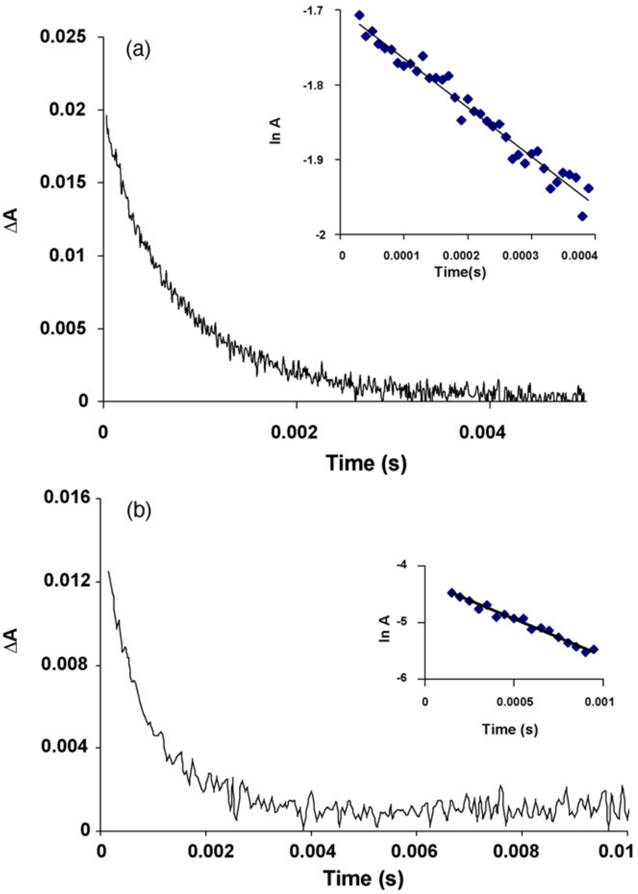

Fig. 5. Triplet decay curves of (Cl)AlPc (a) and (Cl)AlPc in the presence of MF (b). Solvent = DMSO.

Table 1
Photophysical and photochemical results obtained for complexes at laser energy 3.5 mJ

Solvent	Complexes	Φ_T	τ_T (μs)	Φ_Δ	Φ_F	$10^5/\Phi_d$	S_Δ
DMSO	ZnPc	0.65 [19]	350	0.67 [21]	0.18 [17]	4.53	1.03
	ZnPc-MF	0.70	310	0.50	0.16	4.02	0.71
	AlPc	0.20	720	0.29	0.34	0.12	1.45
	AlPc-MF	0.28	750	0.24	0.27	0.14	0.86
	AlTSPc	0.38	1335	0.38	0.30	0.32	1.00
	AlTSPc-MF	0.41	1295	0.28	0.15	0.29	0.68
PBS 7.4	AlTSPc	0.36	560 [26]	0.34	0.13	0.24	0.94
	AlTSPc-MF	0.38	500	0.32	0.10	0.11	0.84

Reference in brackets for literature values.

in aqueous media (PBS pH 7.4). This confirms that the decay is monoexponential and that only the observed decay is due to the depopulation of the triplet state and not quenching by triplet state quenchers such as oxygen. A bioexponential behaviour was reported for ZnPc in the presence of MF in ethanol [8], instead of a monoexponential one observed in this work. This confirms that solvents do affect the photophysical behaviour of the complexes. The presence of oxygen in the solvent may also affect the triplet decay behaviour. As will be discussed below, much lower triplet lifetimes were observed in ethanol compared to the values reported here. The curves in Fig. 5 were employed in calculating triplet life times (τ_T) and quantum yields (Φ_T) of the complexes in the presence and absence of MF. The Φ_T values for AlPc complexes are lower than for ZnPc (Table 1) as expected since Zn is heavier than AlPc. On addition of MF, Φ_T values increased for all complexes (Table 1) as expected by the heavy atom effect and the presence of paramagnetic species. The increase in Φ_T is only marginal for (Cl)AlTSPc in aqueous media (Table 1).

The τ_T values for (Cl)AlTSPc in DMSO were found to be much higher than for ZnPc and (Cl)AlPc (Table 1). In general AlPc derivatives show longer lifetimes than the corresponding ZnPc derivatives [24]. In water the triplet lifetimes for (Cl)AlTSPc are still higher than for ZnPc in DMSO. These values are usually lower in water due to quenching and aggregation. The triplet lifetimes observed for ZnPc in ethanol [8] were much lower than reported in this work in DMSO. It is important to note that τ_T values are affected by oxygen so it is essential to remove oxygen efficiently in order to obtain good results. This was done in this work as explained in the experimental section. τ_T values generally (except for (Cl)AlPc) decreased in the presence of MF as expected by the heavy atom effect. The decrease was observed both in water and DMSO for (Cl)AlTSPc. The lack of decrease in τ_T for ClAlPc might be due to the phototransformation behaviour discussed below. The laser energy was kept the same for studies in the presence and absence of MF, hence the lack of decrease in τ_T values is not due to the changes in laser energy.

It was observed that during laser irradiation to determine τ_T and Φ_T values, the spectra for both (Cl)AlPc and (Cl)AlTSPc in DMSO changed as shown in Fig. 6. No transformation of (Cl)AlTSPc was observed in aqueous media. The spectral changes observed in Fig. 6, showed a decrease in the Q band and an increase in the absorption near 580 nm. However, on exposure of the solution to air, the Q band increased in intensity and the band around 580 nm decreased suggesting that this band is due to a reduction product of the AlPc complexes. Only ring reduction is expected in AlPc complexes. The first ring reduction in MPc complexes is characterized by a decrease in the Q band and the formation of weak bands between 500 and 600 nm [25]. Thus during laser irradiation, the AlPc derivatives were partly transformed to an anion (Pc^{-3}). This type of transformation has been observed before during photodegradation of pyridinoporphyrazines [22] using visible light. The suggested mechanism for the formation of Pc^{-3} in the presence of H donors is shown by Eqs. (5) and (7):

$$\mathrm{AlPc} + h\nu \rightarrow {}^{3}\mathrm{AlPc}^{*} \qquad (5)$$

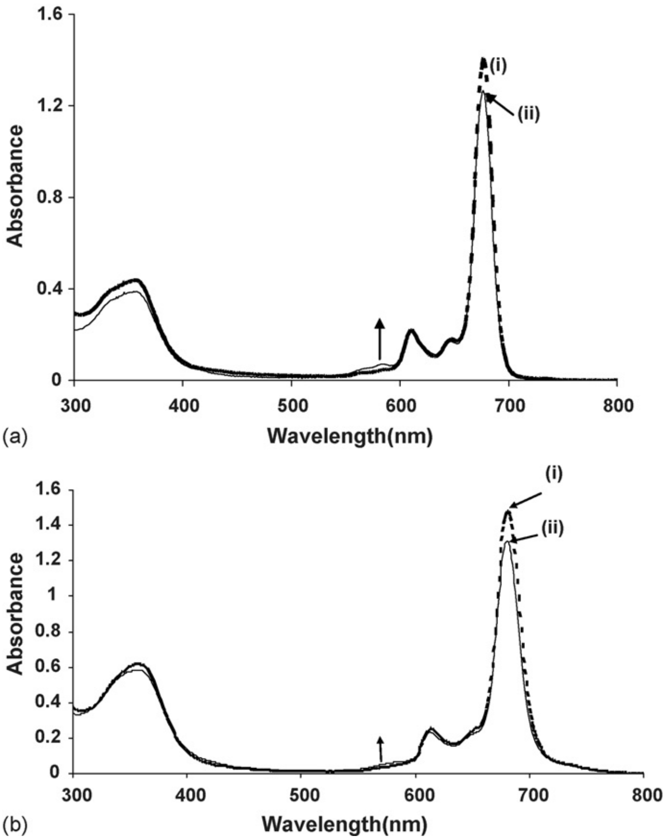

Fig. 6. Spectral change observed on exposure of (a) (Cl)AlPc and (b) (Cl)AlTSPc to laser irradiation at 7 mJ. (i) Before and (ii) after laser irradiation in DMSO.

Table 2
Effects of laser energy on absorbance, triplet lifetime and quantum yield for (Cl)AlPc in DMSO

Laser energy (mJ)	τ_T (μs)	Φ_T	Change in Q band absorbance
3.5	720	0.20	0.08
5.3	620	0.29	0.12
6.7	510	0.30	0.12
7.0	510	0.31	0.13

$$^3\text{AlPc}^* + \text{S–H} \rightarrow \text{AlPc}^{\bullet-} + \text{S–H}^{\bullet+} \quad (6)$$

$$\text{AlPc}^{\bullet-} + \text{O}_2 \rightarrow \text{AlPc} + \text{O}_2^{\bullet-} \quad (7)$$

The presence of radicals such as $O_2^{\bullet-}$ and $\text{AlPc}^{\bullet-}$ suggest the possible involvement of type I (radical) mechanism in addition to the more common type II (singlet oxygen) mechanism when (Cl)AlPc is employed as a photosensitiser.

For ZnPc there were no spectral changes on exposure to laser light. This is most probably due to the fact that AlPc containing a trivalent central metal is more easily reduced than ZnPc. However, there were no significant spectral changes on exposure of the AlPc complexes to unfiltered white light or white light filtered to remove UV light (used for photobleaching and singlet oxygen quantum yield determinations). The laser light has a much larger intensity than the white light. We investigated the effect of laser energy on the phototransformation of AlPc derivatives to the Pc^{-3} species. Phototransformation increased with laser energy as judged by the decrease in the Q band absorption (Table 2). Thus the formation of the Pc^{-3} increased with increase in laser energy. Whereas, the triplet lifetimes increased (and Φ_T decreased) with decrease in laser energy (Table 2). Thus the increase in Pc^{-3} was directly related to the decrease in triplet lifetime as laser energy increased. The presence of paramagnetic species such as Pc^{-3} is expected to result in the decrease in triplet lifetime, but an increase in triplet yield [24], as shown in Table 2.

On addition of MF, the phototransformation of AlPc derivatives decreased. For example the Q band decreased by 11% in the absence of MF for (Cl)AlPc, but only by 3% in its presence. For (Cl)AlTSPc there was no decrease of the Q band on laser irradiation in the presence of MF. These observations suggest that the MF results in the recovery of the Q band absorption by oxidizing the Pc^{-3} back to the Pc^{-2} as shown by Eq. (8):

$$\text{AlPc}^{-3} + \text{Fe}^{3+} \rightarrow \text{AlPc}^{-2} + \text{Fe}^{2+} \quad (8)$$

Thus in the presence of MF, the effects of Pc^{-3} on the photophysical properties will be minimal.

The increase (rather than decrease) in triplet life time for (Cl)AlPc in the presence of MF could be a result of the phototransformation of (Cl)AlPc discussed above. The phototransformation was more pronounced for (Cl)AlPc than AlTSPc.

3.2. Photochemical studies

No phototransformation of AlPc derivatives was observed during singlet oxygen studies as shown by Fig. 7. There was no decrease in the Q band or formation of new bands. The singlet oxygen quantum yields (Φ_Δ) for all three complexes decreased in the presence of MF, suggesting quenching of singlet oxygen by MF (Table 1). For (Cl)AlTSPc, a decrease in Φ_Δ was also observed in aqueous media (Table 1). The S_Δ (Φ_Δ/Φ_T) values are close to unity before addition of MF (except for (Cl)AlPc) implying efficient quenching of the triplet states by O_2 ($^3\Sigma_g$). Following addition of MF the values deviated from unity showing a less efficient quenching by oxygen (Table 1). Again deviations observed for (Cl)AlPc could be related to the phototransformation by laser light.

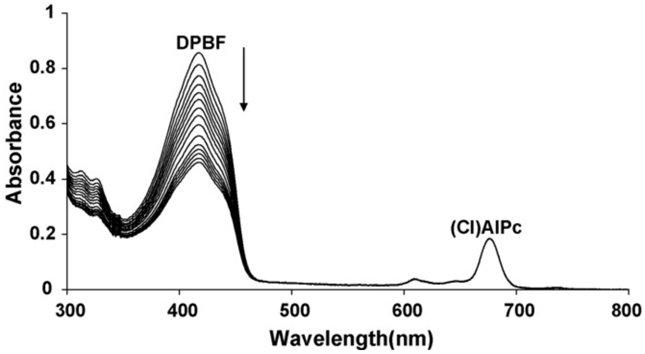

Fig. 7. Spectral changes observed during Q band irradiation of (Cl)AlPc in the presence of MF and DPBF.

Photodegradation quantum yields (Φ_d) for the complexes are shown in Table 1. No phototransformation of the MPc complexes was observed during the photodegradation studies as judged by the lack of formation of new absorption bands as the Q band decreased in intensity. Table 1 shows that the AlPc derivatives were more stable than ZnPc, in DMSO, and (Cl)AlTSPc in aqueous media was also more stable than ZnPc in DMSO. Also for ZnPc (in DMSO) and (Cl)AlTSPc (in both DMSO and PBS pH 7.4), there was a clear decrease in the Φ_d values in the presence of MF. Again a deviation from the trend is observed (Cl)AlPc. It is believed that photodegradation is a singet oxygen mediated process, hence its efficiency should depend on the value of Φ_Δ. Thus since Φ_Δ decreases in the presence of MF, Φ_d should decrease also.

4. Conclusions

We have shown in this work that absorption, fluorescence and excitation spectra of ZnPc, (Cl)AlTSPc and (Cl)AlPc are not changed by the presence of MF, suggesting that the latter can be used in conjunction with these MPc complexes in combined HPT/PDT modality. The triplet lifetimes for ZnPc and (Cl)AlTSPc decreased while triplet quantum yields increased in the presence of MF due to the heavy atom effect and the paramagnetism of MF. Fluorescence quantum yields also decreased for all complexes in the presence of MF due to the heavy atom effect. Singlet oxygen and photodegradation quantum yields decreased in the presence of MF due to quenching of singlet oxygen by MF. The changes in the quantum yields and lifetimes in the presence of MF are not too drastic allowing for the possible use of these complexes in combination for PDT/HPT, particularly for the water soluble (Cl)AlTSPc.

Acknowledgements

This work was supported by Rhodes University and by the National Research Foundation (NRF, GUN 2053657) of South Africa.

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