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Synthesis and physicochemical behaviour of aluminium trikis and tetrakis (diaquaplatinum) octacarboxyphthalocynine

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ABSTRACT

The combination of chemotherapy and photodynamic therapy was investigated by the synthesis and characterisation of phthalocyanine conjugates with Pt complexes. The complexes synthesized are: hydroxoaluminum trikis(diaquaplatinum) octacarboxyphthalocyanine (OHAlOCPc(Pt)$_3$) and hydroxoaluminum tetrakis(diaquaplatinum) octacarboxyphthalocyanine (OHAlOCPc(Pt)$_4$). The platinated phthalocyanine complexes gave long triplet lifetimes of 577 and 526 μs for OHAlOCPc(Pt)$_3$ and OHAlOCPc(Pt)$_4$, respectively. The triplet quantum yields were found to be 0.45 for OHAlOCPc(Pt)$_3$ and 0.57 OHAlOCPc(Pt)$_4$ while the singlet oxygen quantum yields were found to be 0.38 and 0.48, respectively.

1. Introduction

Recent advances in treatment of tumors have led towards the use of bi-functional agents that allow the combined action of two methods of cancer treatment. Thus there has been interest in synthesizing covalent conjugates of photosensitizers for photodynamic therapy (PDT) of cancer such as phthalocyanines and porphyrins with cytotoxic Pt(II) complexes used in chemotherapy [1–5]. Such conjugates are expected to have high selectivity for tumor cells, allowing for a reduction in doses of platinum drugs, hence reducing their side effects.

Phthalocyanine (Pc) derivatives have gained importance in a number of fields including in their use as photosensitizers [6–10]. The effectiveness of Pc derivatives as PDT agents is due to their high absorption in the phototherapeutic window (600–800 nm) coupled with a long triplet lifetime to generate cytotoxic singlet oxygen ($^1O_2$) [6]. Singlet oxygen is extremely reactive and it destroys biomolecules. High singlet oxygen quantum yields depend on high triplet state quantum yields and lifetimes. Diamagnetic central metals are known to enhance these parameters [6].

Platinum complexes have been used in chemotherapy due to their potency. The most used platinum complex is cis-diamine-dichloro platinum (cisplatin), which is, however associated with many harmful side effects such as: allergy, neurotoxicity and many others [11]. The problem is the poor selectivity associated with cisplatin. The general formula of the first generation platinum complexes used as anti cancer agents is L_2PtX_2, where L is a non-leaving group such as an amine or thiol [11]. X represents good leaving groups such as the halides and carboxylates. The good leaving groups are replaced by water within the cells and leaving the platinum complex to bind irreversibly to biomolecules (DNA and enzymes).

Covalent conjugates of phthalocyanines with platinum complexes have been reported [2–5], but all reported phthalocyanine complexes within the conjugates contained electroactive central metals such as Ru, Co and Fe which are not appropriate for PDT. This study reports on the conjugates of aluminum phthalocyanines with diaquaplatinum. The complex synthesized is hydroxoaluminum trikis(diaquaplatinum) octacarboxyphthalocyanine (abbreviated as OHAlOCPc(Pt)$_3$, Scheme 1) and its behaviour compared to that of hydroxoaluminum tetrakis(diaquaplatinum) octacarboxyphthalocyanine (abbreviated as OHAlOCPc(Pt)$_4$). The latter contains four diaquaplatinum groups, Scheme 1. OHAlOCPc(Pt)$_3$ contains three diaquaplatinum groups leaving two COONa groups which then impart some limited

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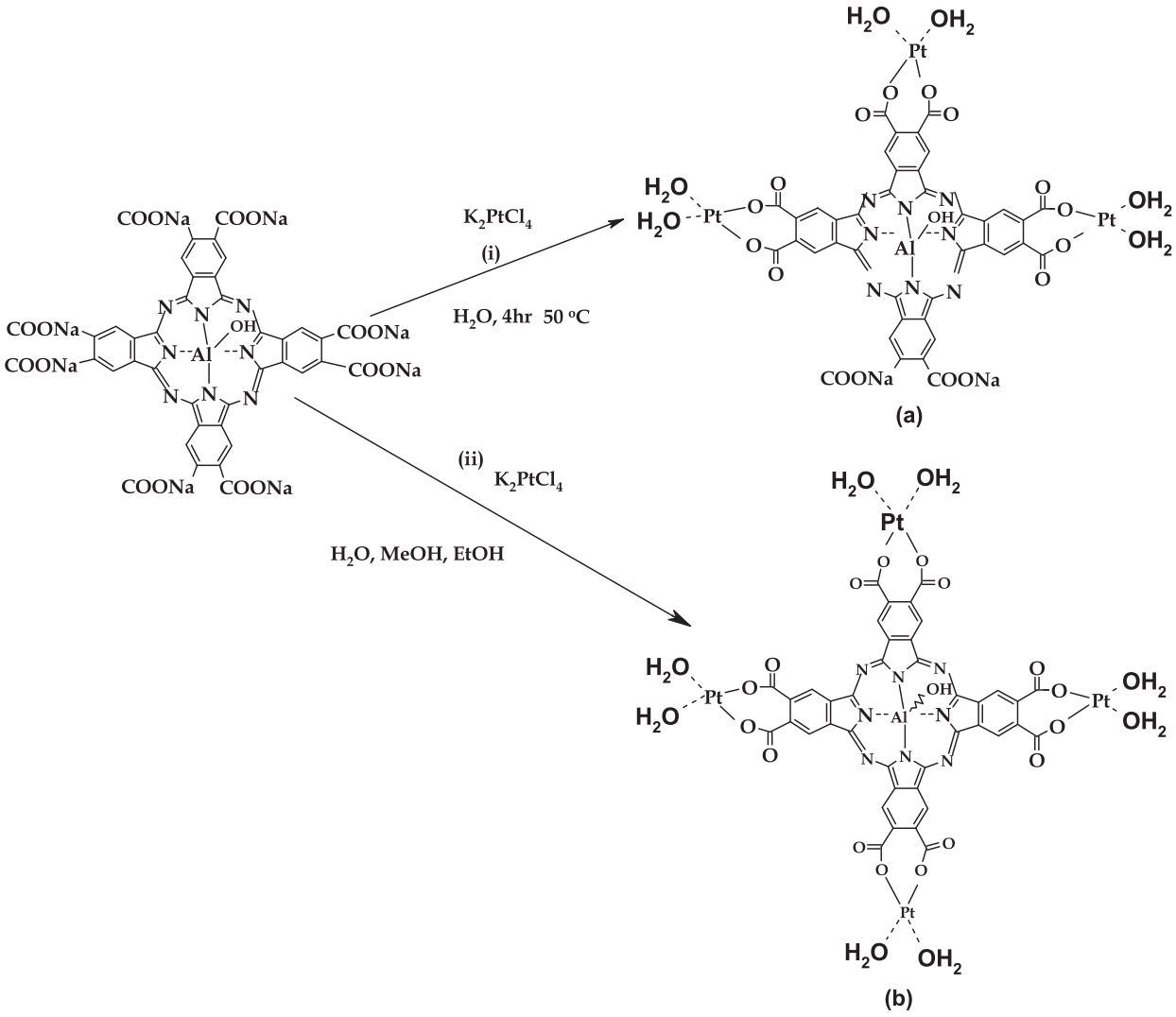

Scheme 1. Synthesis of hydroxoaluminum trikis(diaquaplatinum) octacarboxyphthalocyanine (OHAlOCPc(Pt)$_3$) (a) and hydroxoaluminum tetrakis(diaquaplatinum) octacarboxyphthalocyanine (OHAlOCPc(Pt)$_4$) (b) Ratio of Pc:Pt (i) (1:1.35); (ii) step 1 (1:4.5); step 2 (1:2.8).

solubility of the conjugate in water. The complexes containing four diaquaplatinum groups [2–5] are insoluble in water, water solubility is essential for delivery in PDT.

2. Experimental

2.1. Materials

1,8-Diazobicyclic[5.4.0] undec-7-ene (DBU), oleic acid and platinum acetylacetonoate (Pt(acac)$_2$) were from Fluka. Pyromellic anhydride, diphenyl ether, oleylamine, 1,2- hexadecanediol, 1,3-diphenlyisobenzofuran (DPBF), anthracene-9,10–bis-methylmalonate (ADMA), zinc phthalocyanine (ZnPc) and potassium hexachloroplatinate were from Aldrich. Methanol (MeOH), dimethylsulfoxide (DMSO), aluminium chloride, ethanol (EtOH) and sodium hydroxide were purchased from Saarchem. Hydroxo Al octacarboxy phthalocyanine (OHAlOCPc) and its sodium salt were synthesized according to literature methods [12]. AlPcS$_{Mix}$ (containing a mixture of sulfonated derivatives), used as a standard for the determination of singlet oxygen quantum yields in water, was synthesized according to literature methods [13]. Potassium tetrachloroplatinate was synthesized from potassium hexachloroplatinate according to literature methods [3].

2.2. Equipment

The ultra violet –visible (UV–Vis) spectra were recorded on a Shimadzu UV 2550 UV–Vis/NIR spectrophotometer. IR spectra (KBr pellets) were recorded on a on a Perkin–Elmer Spectrum 100 ATR FT-IR spectrometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectroflourimeter. Elemental analyses were carried out on a Vario EL III MicroCube CHNS Analyzer. Mass spectral data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF Mass spectrometer. Transmission electron microscope (TEM) images were recorded using JEOL JEM 1210 at 100 kV accelerating voltage. Energy dispersive spectroscopy (EDS) was done on a INCA PENTA FET coupled to the VAGA TESCAM using 20 kV accelerating voltage.

Fluorescence lifetimes and time resolved spectroscopy (TRES) were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 200, Picoquant GmbH) with a diode laser (LDH-P-670 with PDL 800-B, Picoquant GmbH, 670 nm, 20 MHz repetition rate, 44 ps pulse width). Fluorescence was detected under the magic angle with a peltier cooled photomultiplier tube (PMT) (PMA-C 192-N-M, Picoquant) and integrated electronics (PicoHarp 300E, Picoquant GmbH). A monochromator with a spectral width of about 8 nm was used to select the required emission

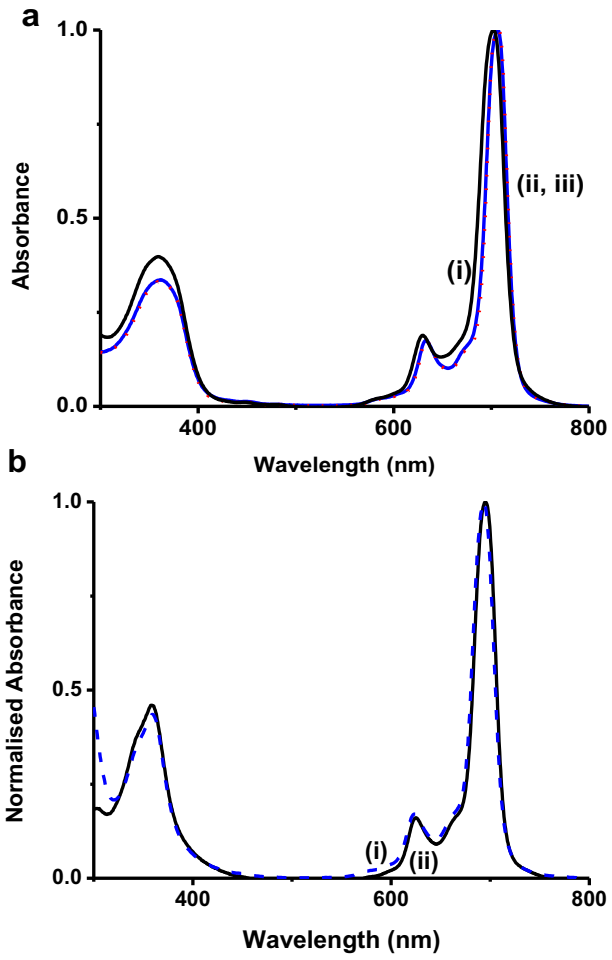

Fig. 1. Comparative UV–visible spectrum for (a) OHAlOCPc (i) and OHAlOCPc(Pt)$_3$ (ii) and OHAlOCPc(Pt)$_4$ (iii) in DMSO and (b) OHAlOCPc (i) and OHAlOCPc(Pt)$_3$ (ii) in water. Concentration $\sim 1 \times 10^{-5}$ M.

wavelength band. The response function of the system, which was measured with a scattering Ludox solution (DuPont), had a full width at half-maximum (FWHM) of 300 ps. All luminescence decay curves were measured at the maximum of the emission peak and lifetimes were obtained by deconvolution of the decay curves using the FluoFit Software program (PicoQuant GmbH, Germany). The support plane approach [14] was used to estimate the errors of the decay times.

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Discover equipped with a Lynx eye detector, using Cu-Kα radiation (1.5405 Å, nickel filter). Data were collected in the range from $2\theta = 5^\circ$–100°, scanning at 1° min^{-1} with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a silicon wafer slide. The X-ray diffraction data were treated using Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern.

A laser flash photolysis system was used to determine the triplet quantum yields and lifetimes. The excitation pulses were produced by a Quanta-Ray Nd:YAG laser (1.5 J/9 ns), pumping a Lambda Physik FL 3002 dye laser (Pyridin 1 in methanol). The analysing beam source was from a Thermo Oriel xenon arc lamp and a photomultiplier tube was used as a detector. The signals were recorded with a two channel 300 MHz digital oscilloscope (Tektronix TDS 3032C).

Photo-irradiations for singlet oxygen studies were done using 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 infrared radiations, respectively. An interference filter (Intor, 700 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter. A light intensity of 2.15×10^{16} photons s^{-1} cm^{-2} was employed for singlet oxygen quantum yield determinations.

2.3. Synthesis

2.3.1. Aluminium trikis (diaquaplatinum) octacarboxy phthalocyanine (OHAlOCPc(Pt)$_3$)

Aqueous solutions of the sodium salt of OHAlOCPc [4] (0.051 g, 0.055 mmol) and potassium tetrachloro platinate (0.076 g, 0.19 mmol) were mixed together and then stirred for 4 h at 50 °C, following literature methods [3]. The solution was allowed to form a precipitate over 2 days. The precipitate was then filtered and washed with water, ethanol, acetone and ether.

Yield 0.067 g (93%) Yield IR (KBr, cm^{-1}): 3436 (OH), 2915 (C–H), 1712 (C=O), 1699 (COOPt), 1437, 1347 (Al–N), 996 (C–O), 737 (Na–O), UV–Vis (DMSO): λ_{max} (log ε): 362 (4.86), 705 (5.25) nm), UV–Vis (Water): λ_{max} log ε: 322 (4.51), 695 (5.53) nm. Calcd. for $Na_2C_{40}H_{21}N_8O_{23}AlPt_3$ C, 29.29; N, 6.83; H 1.29. Found C, 29.60; N, 7.52; H, 2.08.

2.3.2. Aluminium tetrakis (diaquaplatinum) octacarboxy phthalocyanine (OHAlOCPc(Pt)$_4$)

According to reference [3] a mixture of mono-, di- and trisubstituted complexes occurs, when a ratio of 1: 7 (Pc to $K_2[PtCl_4]$) is employed, hence the platination is done in two steps [3].

Step 1

Aqueous solutions of the sodium salt of OHAlOCPc (0.052 g, 0.049 mmol) were dissolved in deionised water (12 mL) and then methanol (100 mL) was added. A solution of $K_2[PtCl_4]$ (0.085, 0.20 mmol) was prepared in 50% ethanol (200 mL). The two

Table 1
Photophysical and photochemical parameters of OHAlOCPc and its platinated derivatives.

Sample	Solvent	λ_{abs} (nm)	λ_{emm} (nm)	Φ_Δ	Φ_F	τ_F (ns)[a] ± 0.01	τ_0 (ns)	Φ_T	τ_T (μs)	Ref[b]
AlOCPc	DMSO	704	711	0.15	0.23	5.26 (100%)	35.1	0.20	756	TW
	Water	696	706	0.12	0.27	4.45 (100%)	16.5	0.32	450	[29]
OHAlOCPc(Pt)$_3$	DMSO	706	711	0.38	0.15	5.46 (100%)	36.4	0.45	577	TW
	Water	694	704	0.25	0.06	4.09 (100%)	68.2	0.36	36	TW
OHAlOCPc(Pt)$_4$	DMSO	706	711	0.48	0.05	5.34 (92.41%) 1.51 (7.59%)	100.8[c]	0.57	526	TW

[a] Abundances in brackets.
[b] TW = this work.
[c] Average lifetime employed.

solutions were quickly mixed and were stirred at room temperature for 3 h. The solution was then left to stand for 48 h, and the precipitate filtered off. The precipitate (which is the intermediate) was washed with water and allowed to dry. (Yield: 0. 071 g).

Step 2

The dry precipitate from step 1 (0.071 g) was dissolved in deionised water (20 mL) and methanol (80 mL). A solution of $K_2[PtCl_4]$ (0.083 g, 0.20 mmol) was prepared in 50% ethanol (200 mL). The two solutions were mixed and stirred for 3 h, and left to stand for 48 h. The solution was filtered and the precipitate washed with water, ethanol, acetone and ether. The product was dried in a vacuum to yield an intense greenish black solid.

Yield 0.0783 g (88%). IR (KBr, cm^{-1}): 3524 (OH), 2922 (C–H), 1715 (C=O), 1689 (COOPt), 1437, 1347 (Al–N), 996 (C–O), 737 (Na–O), UV–Vis (DMSO):λ_{max} (log ε): 362 (3.44), 706 (4.88) nm. Calcd. for $C_{40}H_{25}N_8O_{25}AlPt_4$ C, 26.35; N, 6.14; H 1.27. Found C, 26.28; N, 5.99; H, 1.98.

2.3.3. Synthesis of Pt nanoparticles

The platinum nanoparticles were synthesized following a modified method from reference [15].

$Pt(acac)_2$ (0.21 g, 0.54 mmol, acac = acetylacetonate), 1,2-hexadecanediol (0.54 g, 2.08 mmol) and diphenyl ether (25 mL) were added into a three neck flask. Under a nitrogen atmosphere, the mixture was heated under reflux for 10 min. Oleic acid (167 μL) and oleylammine (170 μL) were added as stabilizers and the mixture was refluxed for 20 min. The reaction was then cooled to room temperature. Ethanol (60 mL) was added to the solution and the black precipitate collected by centrifugation. The product was washed with ethanol and then further dispersed in hexane (60 mL) containing stabilizers: oleic acid (167 μL) and oleylammine (170 μL). The hexane was removed by centrifugation and the remaining solid was washed with water (2 × 50 mL) and ethanol (2 × 50 mL), and dried under vacuum for 1 week.

2.4. Photophysical and photochemical parameters

Fluorescence quantum yields (Φ_F) were determined by comparative method obtained from literature [16] (Equation (1)),

$$\Phi_F = \Phi_{F(std)} \frac{F.A_{std}n^2}{F_{std}.An^2_{std}} \quad (1)$$

where F and F_{std} are areas under the fluorescence curves of the synthesised OHAlOCPc, $OHAlOCPc(Pt)_3$ or $OHAlOCPc(Pt)_4$ derivatives and ZnPc standard, respectively. A and A_{std} are the absorbance for OHAlOCPc, $OHAlOCPc(Pt)_3$ or $OHAlOCPc(Pt)_4$ derivatives and the standard, respectively, while η and η_{std} are the reflective indices for solvents used for the sample and standard, respectively. The standard was ZnPc in DMSO ($\Phi_{F(std)} = 0.20$ [17]). The experiments were done in duplicates for fluorescence quantum yield determinations. The sample and standard were excited at 616 nm for AlOCPc and at 626 nm for the $OHAlOCPc(Pt)_3$ or $OHAlOCPc(Pt)_4$ derivatives.

The triplet quantum yields (Φ_T) were determined using a comparative method which is based on the decay of the triplet state using equation (2)

$$\Phi_T^{Sample} = \Phi_T^{Std} \frac{\Delta A_T^{Sample} \varepsilon_T^{std}}{\Delta A_T^{Std} \varepsilon_T^{Sample}} \quad (2)$$

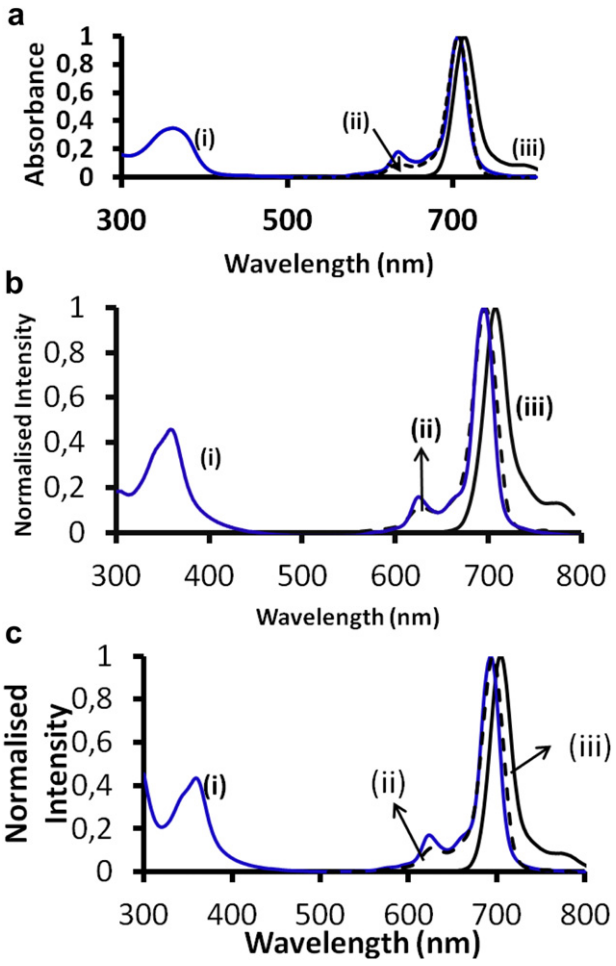

Fig. 2. Absorption (i), excitation (ii) and emission (iii) spectra of (a) $OHAlOCPc(Pt)_4$ in DMSO, (b) OHAlOCPc in water and (c) $OHAlOCPc(Pt)_3$ in water.

where ΔA_T^{Sample} and ΔA_T^{std} are the triplet state absorbance of the sample and the standard, respectively. ε_T^{Sample} and ε_T^{Std} are the triplet state extinction coefficients of the standard and sample, respectively. Φ_T^{Std} is the triplet state quantum yield for the ZnPc standard ($\Phi_T^{Std} = 0.65$ in DMSO [18]).

The singlet oxygen quantum yield (Φ_Δ) determinations were carried out using an experimental setup that is described in

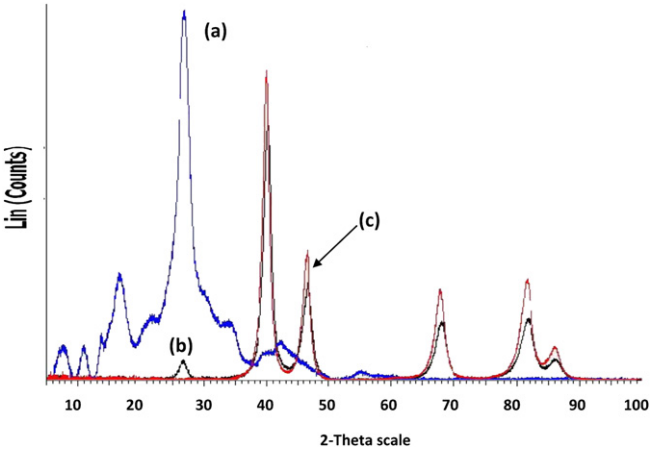

Fig. 3. Comparative XRD spectrum for OHAlOCPc (a) and $OHAlOCPc(Pt)_3$ (b) and Pt nanoparticles (c).

detail elsewhere [19]. In this work Φ_Δ values were determined using DPBF or ADMA as singlet oxygen quenchers in DMSO and water, respectively, and ZnPc (or $AlPcS_{Mix}$) as a standard, equation (3):

$$\Phi_\Delta = \Phi_\Delta^{Std}\frac{W_{DPBF}\ I_{abs}^{Std}}{W_{DPBF}^{Std}\ I_{abs}} \quad (3)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc, ($\Phi_\Delta^{Std} = 0.67$ [12] in DMSO or $AlPcS_{Mix}$ ($\Phi_\Delta^{Std} = 0.34$) in water [20] and W_{DPBF} and W_{DPBF}^{Std} are the DPBF photobleaching rates in the presence of the MPc derivatives under investigation and the standards (ZnPc or $AlPcS_{Mix}$) respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the MPc complexes and the standards respectively. The initial DPBF (or ADMA) concentration used was kept the same for both the MPc complexes and ZnPc (or $AlPcS_{Mix}$). The molar extinction coefficient for DPBF at $\lambda = 417$ nm has been reported to be: $\varepsilon = 23000\ dm^3mol^{-1}\ cm^{-1}$ (DMSO) [21]. The molar extinction coefficient for ADMA at $\lambda = 380$ nm has been reported to be: log $(\varepsilon) = 4.1\ dm^3\ mol^{-1}\ cm^{-1}$ (in water [22]).

3. Results and discussion

3.1. Synthesis and spectroscopic characterisation

$OHAlOCPc(Pt)_3$ was synthesized in a manner that was slightly different to that reported in the literature for $FeOCPc(Pt)_4$ derivatives [4,5]. The synthesis of $OHAlOCPc(Pt)_3$ was carried out in water only, without an organic solvent (methanol) as used in the literature [5]. Reports suggests that the formation of the Pt-O covalent bond retards solubility in water. The last two remaining COONa in $OHAlOCPc(Pt)_3$ allows the complex to be sparingly soluble in the water. Elemental analysis confirmed the formation of the $OHAlOCPc(Pt)_3$ and $OHAlOCPc(Pt)_4$ complexes, with percent age carbon differing by less than 1%. The observed percentages are within acceptable values for phthalocyanine complexes, due to the known difficulties in the combustion of these molecules [23]. Molecular ion peaks were however not observed in the mass spectra of the two complexes in both the negative and positive modes. However the elemetal analysis clearly confirmed the purity of the complexes.

Fig. 1a shows the UV–Vis spectra of $OHAlOCPc(Pt)_3$, $OHAlOCPc(Pt)_4$ and OHAlOCPc in DMSO. The spectrum of $OHAlOCPc(Pt)_4$ is similar to that of $OHAlOCPc(Pt)_3$ with the Q band maxima at the same wavelength, Table 1. There is a slight red shift in the Q band of diaquaplatinum complexes compared to OHAlOCPc in DMSO. In water, there is a slight blue shift in the Q band of $OHAlOCPc(Pt)_3$ compared to OHAlOCPc (Fig. 1b and Table 1). But essentially there is no significant change in the electronic spectra on platination.

Fig. 2 shows the fluorescence spectra of the complexes in DMSO and water (where appropriate). In DMSO, the absorption and fluorescence excitation spectra of the complexes are similar and are mirror images of their respective emission spectra, confirming no change in symmetry upon excitation, Fig. 2a (using $OHAlOCPc(Pt)_4$ as an example). Fluorescence studies were also performed in water, Fig. 2b (for OHAlOCPc) and Fig. 2c (for $OHAlOCPc(Pt)_3$). The absorption and fluorescence excitation spectra of the complexes are similar and are mirror images of their respective emission spectra, again confirming no change in symmetry on excitation and lack of aggregation.

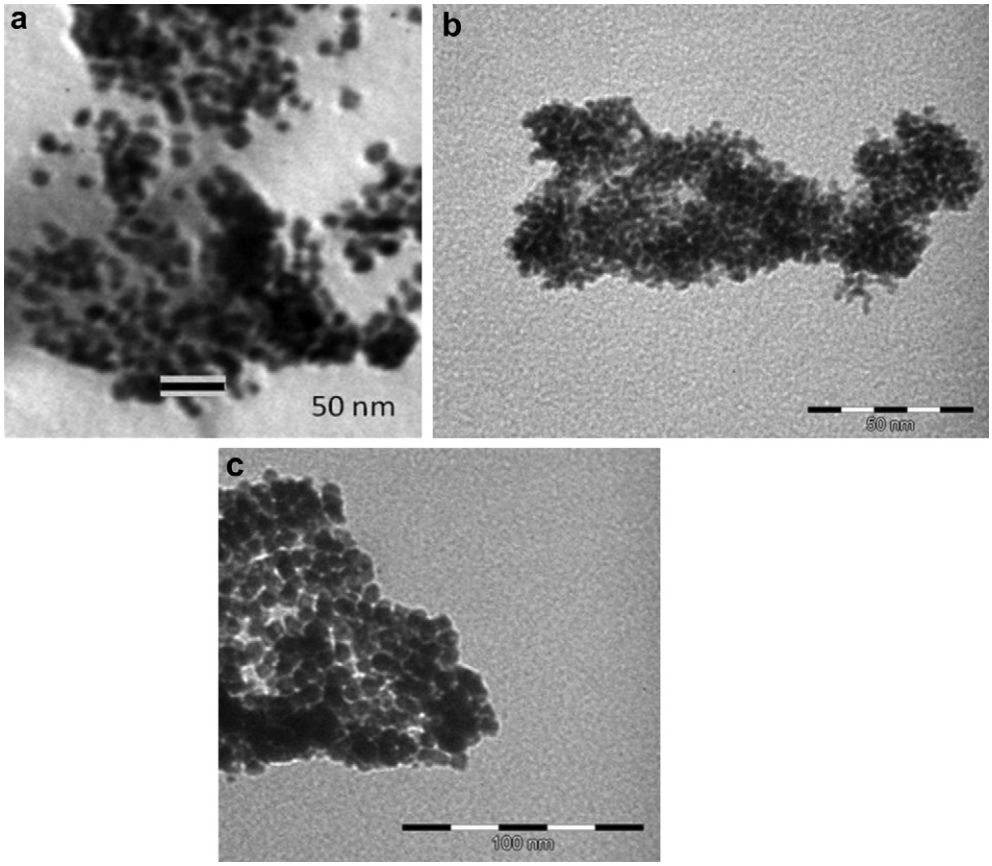

Fig. 4. TEM images of platinum nanoparticles (a), $OHAlOCPc(Pt)_3$ (b) and $OHAlOCPc(Pt)_4$ (c).

The corresponding $RuOCPcPt_4$ complexes are known to form aggregated particles [5]. This was found to be the case in this work as will be shown below using TEM images. XRD (Fig. 3) was employed to confirm the formation of nanoparticles for $OHAlOCPc(Pt)_3$ or $OHAlOCPc(Pt)_4$ complexes Fig. 3, where the diffractograms revealed new peaks due to the platinum. The OHAlOCPc had one peak at $2\theta = 26^\circ$ which is characteristic of Pcs [24,25]. The XRD spectrum (Fig. 3a) shows that OHAlOCPc has both amorphous and crystalline properties as judged by the broad base and sharp peaks. It has been reported before that MPcs are amorphous [26]. Comparison with The International Centre for Diffraction Data (ICDD) database revealed that the $OHAlOCPc(Pt)_3$ or $OHAlOCPc(Pt)_4$ complexes have patterns that fit Pt peak positions. This was also shown by the XRD of the Pt nanoparticles in Fig. 3c that were synthesized for comparison. The peaks around $2\theta = 35^\circ - 50^\circ$ belong to platinum with a 99.9% match. A similar XRD pattern has been observed for the corresponding $FeOCPc(Pt)_4$ with very broad Pc XRD peak being obtained [4]. Pt peaks were observed at $2\theta = 40$, 47, 69, 82 and 86° and corresponded to literature values. However, the peak at 67° was not observed in the literature [4]. The small peak observed at 26° is due to OHAlOCPc, Fig. 3b.

The size of the Pt conjugate (deemed to be nanoparticles by the appearance of broad peaks corresponding to Pt) was determined using XRD and the Debye-Scherrer [27] equation (4):

$$d(\mathring{A}) = \frac{k\lambda}{\beta Cos\,\theta} \tag{4}$$

where k is an empirical constant equal to 0.9, λ is the wavelength of the X-ray source, (1.5405 Å), β is the full width at half maximum of the diffraction peak, and θ is the angular position of the peak. The size of particles of $OHAlOCPc(Pt)_3$ was found to be 7.9 nm and 5.8 nm for $OHAlOCPc(Pt)_4$, confirming aggregation of platinated phthalocyanine complexes as observed before [5]. The size of Pt nanoparticles used for comparison in this work was found to be 3.4 nm.

TEM pictures of the Pt nanoparticles in methanol and the conjugates showed aggregation, Fig. 4. The EDS results, Fig. 5, gave the expected ratio of the metals in the aggregated particles (Al:Pt) of 1 (±0.12):3.2 (±0.16) for $OHAlOCPc(Pt)_3$ and 1 (±0.13): 4.2 (±0.22) for $OHAlOCPc(Pt)_4$. Thus the EDS proved the formation of $OHAlOCPc(Pt)_4$ and $OHAlOCPc(Pt)_3$ beyond a reasonable doubt.

3.2. Photophysical and photochemical parameters

The fluorescence quantum yields (Φ_F) for both complexes are listed in Table 1. $OHAlOCPc(Pt)_3$ and $OHAlOCPc(Pt)_4$ had Φ_F values that were lower than that of OHAlOCPc. This was expected due to the fact that the presence of the platinum in $OHAlOCPc(Pt)_3$ or $OHAlOCPc(Pt)_4$ encourages intersystem crossing, lowering the fluorescence quantum yield. The Φ_F values in water are much lower than in DMSO for $OHAlOCPc(Pt)_3$ but not for OHAlOCPc.

The fluorescence lifetimes were recorded using the TCSPC method, Fig. 6. A mono-exponential decay (Table 1) was observed for OHAlOCPc, indicating that there is only one species in the solution. The lifetimes were within the range reported for phthalocyanines [28]. $OHAlOCPc(Pt)_3$ showed a mono-exponential decay with one lifetime in both DMSO and water. $OHAlOCPc(Pt)_4$ gave a bi-exponential decay.

The presence of two lifetimes in phthalocyanines in the presence of Au nanoparticles has been explained in terms of quenched and unquenched fluorescence lifetime depending on orientation of Pc molecules [29]. A similar explanation is proposed for the observation of two lifetimes for $OHAlOCPc(Pt)_4$. The longer (unquenched) lifetime may be attributed to phthalocyanines/Pt conjugates in which the Pcs are oriented in a way that the fluorescence lifetime is not quenched and is indeed enhanced compared to OHAlOCPc alone. The shorter fluorescence lifetime which is of low abundance may attributed to the quenched fluorescence lifetime due to possible interaction between the Pc molecules.

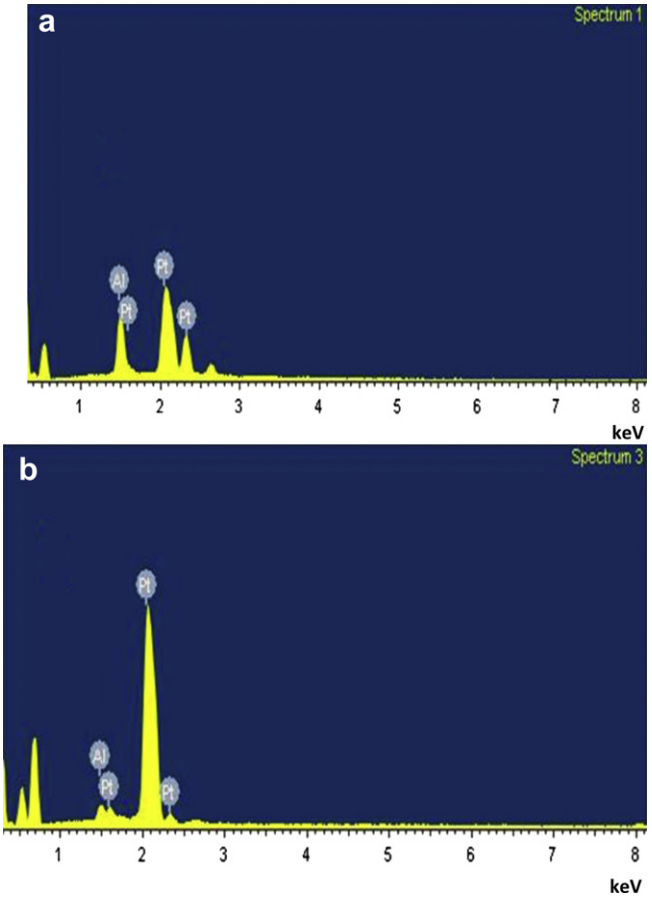

Fig. 5. EDS data for $OHAlOCPc(Pt)_3$ (a) and $OHAlOCPc(Pt)_4$ (b).

Time resolved emission spectra (TRES) were carried out in DMSO Fig. 7. This method confirmed two emitting species for $OHAlOCPc(Pt)_4$ with emission wavelengths at 711 and 709 nm, the former is at the same wavelength as observed $OHAlOCPc(Pt)_4$, Table 1 and is due to unquenched fluorescence, presumably the 709 nm peak is due to the quenched fluorescence.

Fluorescence radiative lifetimes (τ_0) are directly connected to absorption coefficients and excited state lifetimes and hence were estimated from the measurement of fluorescence quantum yield (Φ_F) and lifetime (τ_F) using Equation (5) [30]

$$\tau_0 = \tau_F/\Phi_F \tag{5}$$

The τ_0 valuesobtained for various phthalocyanines have been reported to be much larger than measured values, often observed in the ms range [31], hence the larger τ_0 values compared to τ_F in Table 1 are not surprising.

Metallic particles can increase or decrease the radiative decay rates of fluorophores, depending on orientations between the metal particles and the molecule [32–35]. Generally, the radiative decay rates are increased resulting in short lifetimes. The fact that we observe longer fluorescence lifetimes (τ_0 values, Table 1) for $OHAlOCPc(Pt)_3$ and $OHAlOCPc(Pt)_4$ compared to OHAlOCPc alone, suggests a decrease in radiative decay rates, most likely due to orientation of the Pc molecules.

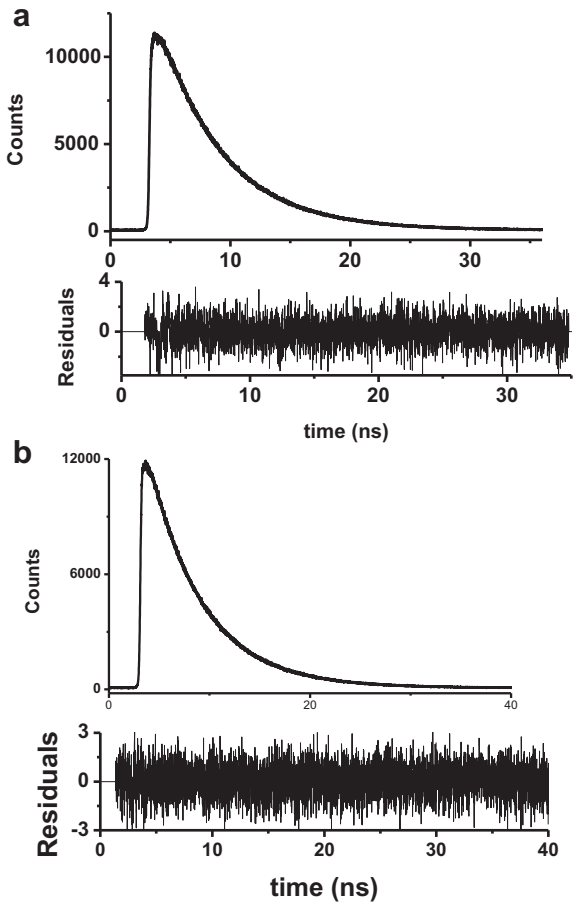

Fig. 6. Comparative fluorescence decay curves for AlOCPc (a) and OHAlOCPc$(Pt)_3$ (b) in DMSO.

The number of the absorbing molecules that undergoes intersystem crossing (isc) to the triplet state is a measure of the triplet state quantum yield. Representative transient differential spectrum and triplet decay curve for OHAlOCPc$(Pt)_3$ in DMSO are shown in Fig. 8. The transient spectra obtained show the same features as the absorption spectra. The result revealed that the conjugates (OHAlOCPc$(Pt)_4$ and OHAlOCPc$(Pt)_3$) had higher triplet quantum yields

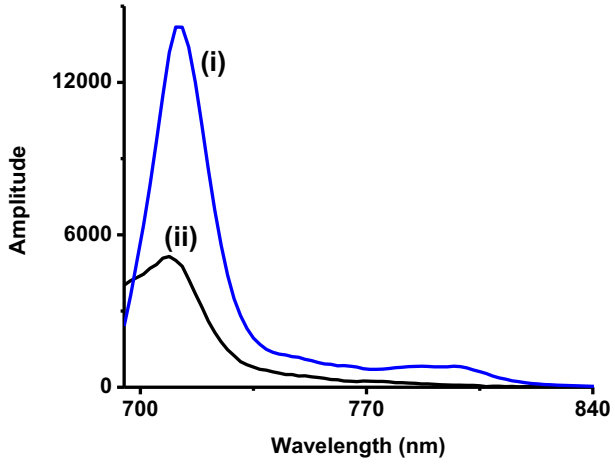

Fig. 7. Typical TRES spectrum for OHAlOCPc$(Pt)_4$ showing deconvuluted emissions peaks in DMSO. (i) unquenched and (ii) quenched fluorescence.

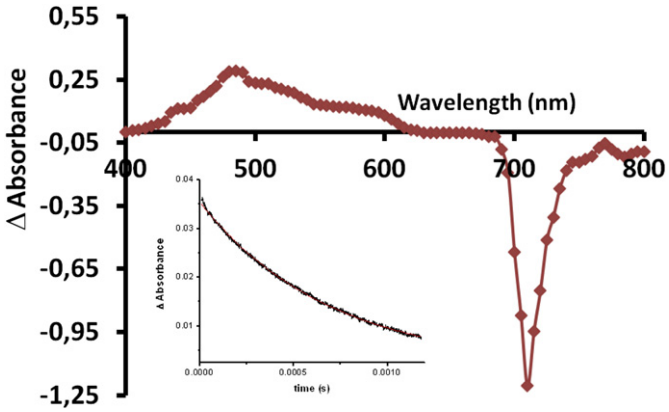

Fig. 8. A transient differential spectrum and inset: triplet decay curve of OHAlOCPc$(Pt)_3$ DMSO. (excitation wavelength = 692 nm in DMSO).

compared to the precursor (OHAlOCPc). This is expected due to the heavy atom effect exerted by Pt. Thus upon the addition of the platinum to the phthalocyanine, its efficiency as a photosensitiser is increased. There is a large decrease in triplet lifetimes on conjugation. Aluminium phthalocyanine derivatives are known to posses long lifetimes [36], hence the values obtained in Table 1. The triplet lifetimes decrease with the increase in the number of platinum groups in Table 1. When the solvent was changed from DMSO to water for OHAlOCPc$(Pt)_3$ there was a decrease in the triplet state quantum yields and triplet lifetimes. This is due to the known [17] quenching of the triplet state of phthalocyanines by water.

The singlet oxygen quantum yields were also determined in DMSO and in water. Corresponding to the increase in triplet yields, there is an increase in singlet oxygen quantum yields for the platinated complexes compared to OHAlOCPc. In water the singlet oxygen quantum yield was lower than that obtained in DMSO for OHAlOCPc$(Pt)_3$. Excited-state molecules can relax through a number of different pathways including two competing processes, intersystem crossing and photoinduced electron transfer (PET). The extent of PET processes is greater in the more polar solvent [37]. Thus, in comparison to singlet oxygen quantum yields measured in other solvents, the values obtained in water often are smaller.

4. Conclusions

Hydroxo aluminium octacarboxy (OHAlOCPc), hydroxoaluminium octacarboxy tris (diaquapalatinum) (OHAlOCPc$(Pt)_3$) and hydroxoaluminum tetrakis (diaquaplatinum) octacarboxyphthalocyanine (OHAlOCPc$(Pt)_4$) complexes were synthesised and their photophysical parameters were evaluated. It was shown that the conjugates were better photosensitisers compared to OHAlOCPc alone, due to their larger triplet state and singlet oxygen quantum yields. The improved singlet oxygen quantum yield values show that platination improves the efficiency of Pc complexes as photosensitizers. The platinated Pc complexes may have potential to be used for both photodynamic therapy (using Pcs) and chemotherapy (using coordinated Pt complexes).

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