

# Spectroscopic and photophysical behaviour of novel cadmium phthalocyanine derivatives tetra-substituted at the alpha and beta positions

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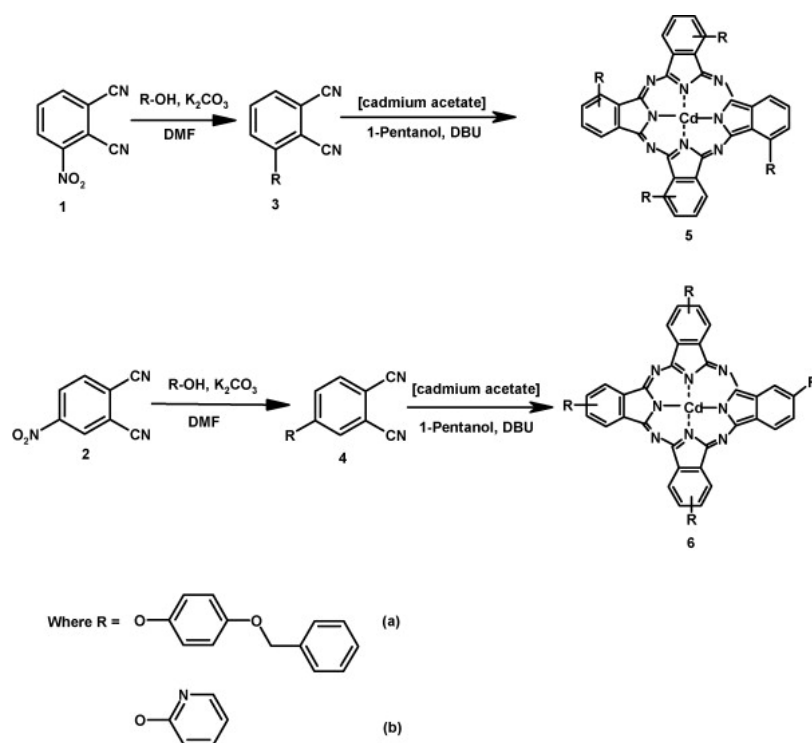
## Abstract

The syntheses of three cadmium phthalocyanine derivatives tetrakis{1,(4)-(4-benzyloxy)phenoxyphthalocyaninato} (5a), tetrakis{1,(4)-(2-pyridyloxy)phthalocyaninato} (5b) and tetrakis{2,(3)-(4-benzyloxy)phenoxyphthalocyaninato} (6a) are reported here for the first time. Spectroscopic and photophysical properties have also been determined and the results are discussed here paying particular attention to the influence of various organic solvents in relation to the position and type of substitution. Singlet oxygen quantum yields ( $\Phi_{\Delta}$ ) and photodegradation quantum yields ( $\Phi_{Pd}$ ) have also been discussed. The triplet quantum yields have been determined and ranged from  $\Phi_T = 0.36$  to 0.85, where the peripherally ( $\beta$ ) substituted derivatives generally give higher values than those substituted at the non-peripheral ( $\alpha$ ) positions. The triplet lifetimes ranged from  $\tau_T = 5$  to 40  $\mu$ s. In all cases (except toluene, due to the lack of data), the highest singlet oxygen quantum yields obtained were for the pyridyloxy-substituted derivatives 5b ( $\Phi_{\Delta} = 0.60$  in DMF) and 6b ( $\Phi_{\Delta} = 0.74$  in DMSO).

## 1. Introduction

Over the last century metallophthalocyanines have become the focal point of extensive research. This is due to the versatility of these complexes for a wide range of applications in fields such as non-linear optics [1], [2] and [3], chemical sensors [4], semiconductors [5], liquid crystals [6], [7] and [8] and catalysis [9]. The periphery of these macrocycles can be diversified by substituting with various substituent groups, which allow for enhanced solubility in most organic solvents and an alteration of the electronic properties of the Pc ring [10]. The presence of numerous positional isomers in tetra-substituted derivatives has been shown to account for their greater solubility versus their octa-substituted counterparts [11]. Further structural modification by a change in the central metal atom in addition to different substitution patterns and type of substituents can vary the excited state properties of the resultant MPc complexes. A study of the resultant effects thus provides for an interesting study, particularly in terms of the stability of the ground and excited state molecules. Research focused on tetra-substituted cadmium phthalocyanine derivatives in particular is relatively undeveloped at this stage. To our

knowledge of  $\alpha$  and  $\beta$ -substituted (4-benzyloxy)phenoxy cadmium phthalocyanines, such as those presented in this work, have not been reported. We have previously reported on the synthesis of  $\beta$ -substituted pyridyloxy derivatives (6b) [12], and in this work explore the properties of the  $\alpha$ -derivative. Our aim is therefore to develop novel cadmium phthalocyanines that may find use in industrial reactions as photocatalysts [13], [14] and [15]. The photochemistry and photophysics of cadmium phthalocyanines have not been fully explored. Since cadmium falls in the same group as zinc, it may also be useful to explore the properties of similarly substituted cadmium phthalocyanines to establish trends or differences pertaining to  $d^{10}$  metal substituted phthalocyanines, i.e. for comparative purposes and for the purpose of developing new materials for photocatalysis. The pyridyloxy substitution allows for a possibility of forming water-soluble derivatives by quaternization [16] and [17]. Herein we report on the synthesis, spectroscopic and photophysical properties of cadmium phthalocyanines tetra-substituted either at the  $\alpha$  or  $\beta$  positions with (benzyloxy)phenoxy and pyridyloxy substituent groups. The complexes are: tetrakis{1,(4)-(4-benzyloxy)phenoxyphthalocyaninato} cadmium (5a), tetrakis{1,(4)-(2-pyridyloxy)phthalocyaninato} cadmium (5b) and tetrakis{2,(3)-(4-benzyloxy)phenoxyphthalocyaninato} cadmium (6a), Scheme 1. The synthesis of the tetrakis{2,(3)-(2-pyridyloxy)phthalocyaninato} cadmium (6b) has been reported before [12].



Scheme 1. Syntheses of complexes 5a, 5b, 6a and 6b.

## 2. Experimental

### 2.1. Materials

Acetone, chloroform ( $\text{CHCl}_3$ ), dichloromethane (DCM), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol (EtOH), methanol (MeOH), 1-pentanol, tetrahydrofuran (THF), toluene were dried prior to use. Cadmium acetate dihydrate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), deuterated chloroform ( $\text{CDCl}_3$ ), deuterated dimethyl sulfoxide ( $\text{DMSO-d}_6$ ), 4-(benzyloxy)phenol, 2-hydroxypyridine, potassium carbonate ( $\text{K}_2\text{CO}_3$ ), diphenylisobenzofuran (DPBF), potassium bromide (KBr) and sodium borohydride ( $\text{NaBH}_4$ ) were purchased from Aldrich. Bromine ( $\text{Br}_2$ ) was purchased from Merck. Column chromatography was performed on silica gel 60 (Merck, 0.04–0.063 mm); 3-nitrophthalonitrile (1) and 4-nitrophthalonitrile (2) were synthesized and purified according to reported methods [18] and [19].

### 2.2. Equipment

FT-IR spectra (KBr pellets) were recorded on a PerkinElmer spectrum 2000 FT-IR spectrometer. UV–Vis (ultraviolet–visible) spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer and fluorescence emission and excitation spectra on Varian Eclipse spectrofluorimeter.  $^1\text{H}$  NMR spectra were obtained, in deuterated solvents, using a Bruker EMX 400 MHz NMR spectrometer and a Bruker AVANCE II 600 MHz spectrometer. MALDI-TOF mass spectra were recorded using an Applied Biosystems Voyager-DE STR at the University of Stellenbosch in Cape Town, with 2,5-dihydroxy benzoic acid as matrix.

Photo-irradiations 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, 670 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 MAX 5100 (Molelectron Detector Inc.) power meter.

Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Nd:YAG laser (Quanta-Ray, 1.5 J/90 ns) pumping a dye laser (Lambda Physic FL 3002, Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp (Thermo Oriel 66902), and a photomultiplier tube (Kratos Lis Projekte MLIS-X3) was used as the detector. Signals were recorded with a two-channel digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser

pulses. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

### 2.3. Syntheses and characterization

3-[(4-Benzyloxy)phenoxy]phthalonitrile (3a), 3-(2-pyridyloxy)phthalonitrile (3b) and 4-[(4-benzyloxy)phenoxy]phthalonitrile (4a) were prepared and purified according to reported methods [20] and [21]. Syntheses of 4b and 6b have been reported before [12].

#### 2.3.1. Tetrakis{1,(4)-(4-benzyloxy)phenoxyphthalocyaninato}cadmium(II)—5a

Under an inert atmosphere ( $N_2$ ), compound 3a (0.625 g, 1.82 mmol) was dissolved in dry 1-pentanol ( $\sim 2$  ml). To the solution cadmium acetate dihydrate (0.121 g, 0.454 mmol) and DBU (0.243 ml, 1.63 mmol) were added and the mixture heated under reflux to 160 °C for 16 h. The dark-green product was poured into MeOH and the resultant precipitate filtered, washed several times with MeOH and dried. The crude product was then purified by column chromatography, eluting with THF. Following evaporation of the solvent, the product was purified further by Soxhlet extraction first with acetone and finally with EtOH. Yield: 35%. UV-Vis (DMSO)  $\lambda_{max}$  nm (log  $\epsilon$ ): 327 (4.81), 397 (4.60), 632 (4.50), 702 (5.32). IR [(KBr)  $\nu_{max}/cm^{-1}$ ]: 2954 ( $\nu_{C-H}$ ), 1199 ( $\nu_{C-O-C}$ ).  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta/ppm$ : 9.73–9.03 (4H, m, Pc-H), 8.66–8.22 (4H, m, Pc'-H), 8.24–7.68 (28H, m, Pc'-H, Phenyl-H), 7.70–7.30 (12H, m, Phenyl-H), 5.64–5.39 (8H, m,  $CH_2$ ). MALDI-TOF MS  $m/z$ : calc. 1417.8 amu. Found 1419.12 amu  $[M+H]^+$ .

#### 2.3.2. Tetrakis{1,(4)-(2-pyridyloxy)phthalocyaninato}cadmium(II)—5b

A similar synthetic procedure to that for 5a was followed employing the following reagent quantities: 3b (0.396 g, 1.82 mmol), cadmium acetate dihydrate (0.121 g, 0.456 mmol), 1-pentanol ( $\sim 3$  ml), DBU (0.243 ml, 1.63 mmol).

However in terms of purification: The crude product was purified by column chromatography, eluting with  $CHCl_3/MeOH$  (10:1). Soxhlet extraction first with acetone and then with EtOH gave the desired compound 5b. Yield: 19%. UV-Vis (DMSO)  $\lambda_{max}$  nm (log  $\epsilon$ ): 323 (4.40), 389 (4.16), 620 (3.99), 684 (4.80). IR [(KBr)  $\nu_{max}/cm^{-1}$ ]: 1620 ( $\nu_{C-C}$ ), 1110 ( $\nu_{C-O-C}$ ).  $^1H$  NMR (600 MHz, DMSO- $d_6$ )  $\delta/ppm$ : 8.82–6.15 (m, 28H). MALDI-TOF MS  $m/z$ : calc. 997.27 amu. Found 997.84 amu  $[M+H]^+$ .

### 2.3.3. Tetrakis{2,(3)-(4-benzyloxy)phenoxyphthalocyaninato}cadmium(II)—6a

Synthesis and purification were as outlined for 5a using the following reagents and quantities: 4a (0.625 g, 1.82 mmol), cadmium acetate dihydrate (0.120 g, 0.452 mmol), 1-pentanol ( $\sim$  2 ml), DBU (0.243 ml, 1.63 mmol). Yield: 23%. UV–Vis (DMSO)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ): 341 (4.12), 631 (3.89), 656 (3.90), 688 (4.13). IR [(KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ ]: 2848 ( $\nu_{\text{C-H}}$ ), 1216 ( $\nu_{\text{C-O-C}}$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 7.83–7.16 (m, 56H). MALDI-TOF MS  $m/z$ : calc. 1417.8 amu. Found 1418.24 amu  $[\text{M}]^+$ .

## 2.4. Photochemical parameters

### 2.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield values ( $\Phi_{\Delta}$ ) values were determined in air using the relative method with DPBF acting as a singlet oxygen chemical quencher in DMSO, using Eq. (1):

(1)

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

where  $\Phi_{\Delta}^{\text{Std}}$  is the singlet oxygen quantum yield for the standard ZnPc ( $\Phi_{\Delta}^{\text{Std}} = 0.56$  in DMF [22], 0.67 in DMSO [23], 0.53 in THF [24] and 0.58 in toluene [25]).  $R$  and  $R^{\text{Std}}$  are the DPBF photobleaching rates in the presence of the respective MPc and standard respectively;  $I_{\text{abs}}$  and  $I_{\text{abs}}^{\text{Std}}$  are the rates of light absorption by the MPc and standard respectively. The light intensity used for  $\Phi_{\Delta}$  determinations was found to be  $2.97 \times 10^{16}$  photons  $\text{s}^{-1} \text{cm}^{-2}$ ; and the error in the determination was  $\sim 10\%$  (from several  $\Phi_{\Delta}$  values). Chain reactions induced by DPBF in the presence of singlet oxygen often occur [22], therefore the concentration of DPBF was lowered to  $\sim 3 \times 10^{-5}$  mol  $\text{dm}^{-3}$  for all solutions. DPBF degradation was monitored at 417 nm.

The fraction of the excited triplet state quenched by ground state molecular oxygen  $S_{\Delta}$  was calculated using Eq. (2):

(2)

$$S_{\Delta} = \frac{\Phi_{\Delta}}{\Phi_{\text{T}}}$$

where  $\Phi_{\text{T}}$  is the triplet quantum yield.

## 2.4.2. Photodegradation quantum yields

For the determination of photodegradation quantum yields, Eq. (3) was employed:

(3)

$$\Phi_{\text{pd}} = \frac{(C_0 - C_t) V N_A}{I_{\text{abs}} S t}$$

where  $C_0$  and  $C_t$  ( $\text{mol dm}^{-3}$ ) are the respective CdPc derivative's concentrations before and after irradiation, respectively;  $V$  is the reaction volume;  $S$  the irradiated cell area ( $2.0 \text{ cm}^2$ );  $N_A$ , the Avogadro's number;  $t$ , the irradiation time (in seconds) and  $I_{\text{abs}}$ , the overlap integral of the radiation source intensity and the absorption of the MPc.

## 2.5. Photophysical parameters

### 2.5.1. Fluorescence quantum yields

Fluorescence quantum yields ( $\Phi_F$ ) were determined by the comparative method [26] and [27] (Eq. (4)),

(4)

$$\Phi_F = \Phi_{F(\text{Std})} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2}$$

where  $F$  and  $F_{\text{Std}}$  are the areas under the fluorescence curves of the MPc (5a, 6a, 5b, 6b) and the reference respectively.  $A$  and  $A_{\text{Std}}$  are the absorbances of the sample and reference at the excitation wavelength respectively, and  $n$  and  $n_{\text{Std}}$  are the refractive indices of solvents used for the sample and reference, respectively. Chlorophyll a in ether ( $\Phi_F = 0.32$  [28]) was employed as a reference. Both the sample and reference were excited at the same wavelength (620 nm). The absorbance of the solutions at the excitation wavelength ranged between 0.04 and 0.05.

### 2.5.2. Triplet quantum yields and lifetimes

The de-aerated solutions of the respective MPc complexes were introduced into a 1 cm pathlength spectrophotometric cell and irradiated at the Q band with the laser system

described above. Triplet quantum yields ( $\Phi_T$ ) of the MPc complexes were determined by the triplet absorption method. A comparative method [29] using ZnPc as standard was employed for the calculations, Eq. (5).

(5)

$$\Phi_T = \Phi_T^{Std} \frac{\Delta A_T \epsilon_T^{Std}}{\Delta A_T^{Std} \epsilon_T}$$

where  $\Delta A_T$  and  $\Delta A_T^{Std}$  are the changes in the triplet state absorbances of the MPc derivative and the standard respectively;  $\epsilon_T$  and  $\epsilon_T^{Std}$ , the triplet state molar extinction coefficients for the MPc derivative and the standard respectively;  $\Phi_T^{Std}$ , the triplet quantum yield for the standard ( $\Phi_T^{Std} = 0.65$  for ZnPc in DMSO [29], 0.58 for ZnPc in DMF [30] and 0.65 for ZnPc in toluene [31]).

Triplet lifetimes ( $\tau_T$ ) were determined by exponential fitting of the kinetic curves using OriginPro 7.5 software.

Quantum yields of internal conversion ( $\Phi_{IC}$ ) were obtained from Eq. (6), which assumes that only the three intrinsic processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of an MPc molecule.

(6)

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T)$$

### 3. Results and discussion

#### 3.1. Syntheses and characterizations

The MPc complexes were prepared by the known [32] and [33] template reaction of the phenoxy substituted phthalonitrile precursors (3a, 3b and 4a) with cadmium acetate in the presence of DBU forming 5a, 5b and 6a. The synthesis of 6b has been reported before [12]. DBU acts as a nucleophilic base which permits the reaction to proceed under more mild conditions while also preventing the formation of side products typical of reactions that make use of strong bases [32]. Yields of between 19 and 35% were obtained following purification by column chromatography and Soxhlet extraction. For confirmation of the predicted structures, the new compounds have been characterized by IR, NMR, UV–Vis and mass spectroscopies. All were consistent with the predicted data. The disappearance of the sharp C≡N vibration at

$\sim 2265\text{ cm}^{-1}$  confirmed the formation of the desired MPc molecules. The  $^1\text{H}$  NMR spectra of the complexes showed broad and often complex splitting patterns. Aggregation and the high concentrations used for NMR measurements resulted in poorly resolved signals. However, on close investigation, the data gave the correct number of protons in accordance with the predicted structures.

All complexes exhibit excellent solubility in most common organic solvents. This may be attributed in part to the substituent groups attached to the periphery of the phthalocyanine ring in addition to the presence of positional isomers known to be present for tetra-substituted derivatives [11]. Attempts to quaternize 5b and 6b have so far been unsuccessful.

### 3.2. Ground state electronic absorption and fluorescence spectra

The ground state electronic absorption spectra for 5a, and 6a; 5b and 6b are shown in Fig. 1a and b respectively. Spectra typical of monomeric phthalocyanines are evident in all solvents studied ( $\text{CHCl}_3$ , THF, DCM, DMF and DMSO) for 5b. The spectrum corresponding to 6b is monomeric only in DMF and DMSO; possibly a consequence of the strong co-ordinating nature of such solvents, i.e. with donor numbers of 26.6 and 29.8  $\text{kcal mol}^{-1}$  respectively [34], [35] and [36]. The behaviour of 6b in other solvents has been explained in terms of the difference in solvent properties [12]. Although substituted with similar groups, the differences in solubility and spectral characteristics (monomeric behaviour) of 5b and 6b can be attributed to the pattern of substitution where literature has shown that  $\alpha$ -substitution, such as in 5b, reduces aggregating tendencies [37] and [38]. The spectrum corresponding to 5a is typical of a monomeric species, whereas that of 6a tends to be slightly broad in DMF and DMSO, Fig. 1a. The unusual nature of spectra corresponding to 6a is carried forward to other solvents (chlorinated solvents in particular) as shown in Fig. 2. In this case, spectra are characterized by a very broad absorption band extending from  $\sim 550$  to 700 nm. Previous work [12] with 6b showed broadened spectra in chlorinated solvents, where the addition of Triton X-100 led to partial disaggregation into monomers. However in this work, no change occurred on addition of the surfactant to solutions of 6a, which is an indication that these complexes are in monomeric states. The observed spectra may be attributed to differences in solvent properties, i.e. co-ordinating nature, where co-ordinating solvents such as pyridine, DMF and DMSO are capable of axial ligation to the central metal in MPc complexes. The oxidizing nature of the solvents may also play a role, chlorinated solvents are known to oxidize some MPc complexes [12] and [39]. The presence of two sharp peaks in the 700 nm area for 6a in  $\text{CHCl}_3$  and DCM, Fig. 2,



suggests partial demetallation. A recent report by Chambrier et al. has shown that successive additions of iodine (an oxidizing agent) give rise to phthalocyanines with similar absorption spectra to that shown in [Fig. 2](#) with absorptions between 550 and 650 nm [\[40\]](#). It was shown that such spectra is typical of triple-decker and higher oligomeric complexes often formed more readily with phthalocyanine ligands substituted with alkenyl substituents at the ring periphery [\[41\]](#). However there was no evidence of such oligomers for 6a. The addition of a reducing agent ( $\text{NaBH}_4$ ) to solutions that gave rise to the spectra in [Fig. 2](#), gave some form of reversal of the observed spectrum, i.e. a change to more monomeric species ([Fig. 3a](#)); suggesting the presence of an initially oxidized form. The oxidation was only observed in solvents of low coordination number, i.e. THF,  $\text{CHCl}_3$  and DCM, which are prone to promoting oxidation [\[12\]](#) and [\[39\]](#).  $\text{CHCl}_3$  in particular is slightly acidic and is known to result in the oxidation of the phthalocyanine molecule [\[39\]](#), [\[42\]](#) and [\[43\]](#). Demetalation of 6a occurred in toluene. Oxidation behaviour of 6a in a co-ordinating solvent, i.e. DMSO resulted in spectra similar to that obtained in  $\text{CHCl}_3$ , DCM and THF ([Fig. 3b](#)), suggesting that the spectra in [Fig. 2](#) is partly due to oxidation. However, what is unusual is the increase in absorption intensity on increments of  $\text{Br}_2$ . Typical phthalocyanine oxidation is often expected to give a decrease in absorption intensity in the Q-band region. Addition of bromine to solutions of 6a in  $\text{CHCl}_3$  resulted in spectral changes shown in [Fig. 3c](#). The two sharp peaks near 700 nm increased in intensity, suggesting that oxidation with bromine results in demetalation. Addition of zinc acetate to solution of 6a in DCM resulted in the collapse of the two sharp bands confirming that the peaks were due to demetalation. Thus in DCM,  $\text{CHCl}_3$ , THF and toluene, complex 6a showed some oxidation and partial demetalation.

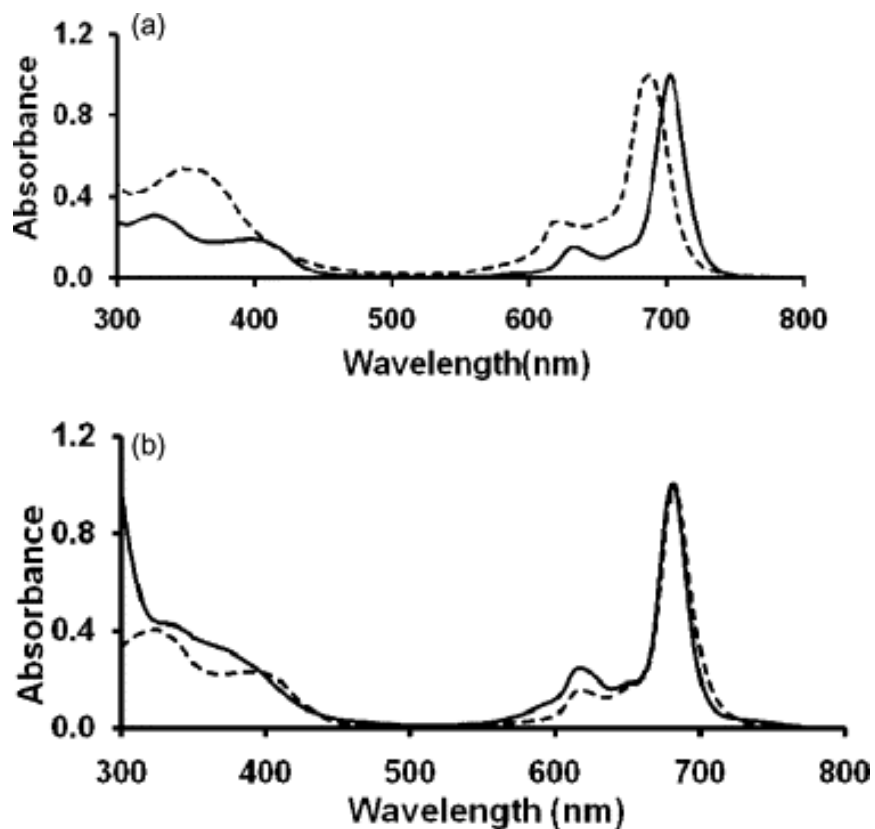


Fig. 1. Normalised ground state electronic absorption spectra of (a) 5a (—) and 6a (- - -) in DMSO, concentration =  $\sim 4.80 \times 10^{-6} \text{ mol dm}^{-3}$ , and (b) 5b (—) and 6b (- - -) in DMF. Concentration =  $\sim 7.80 \times 10^{-6} \text{ mol dm}^{-3}$ .

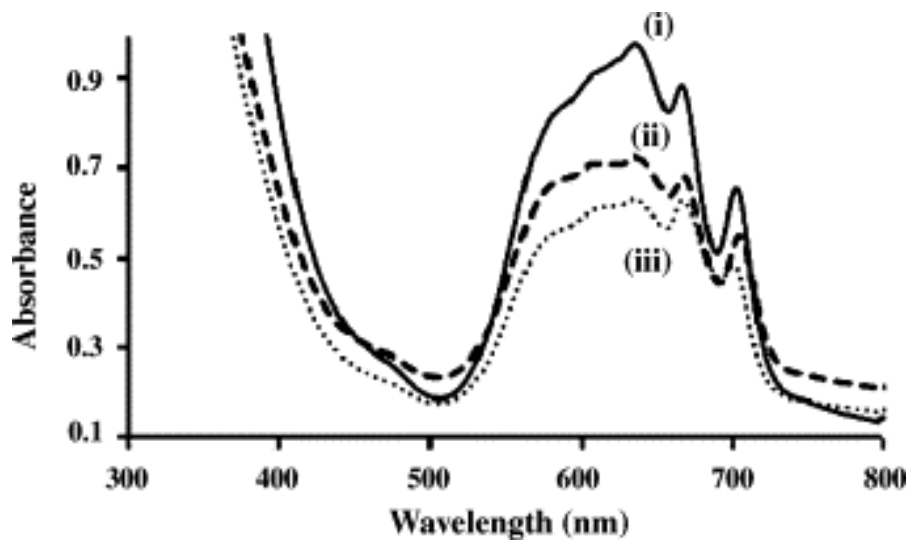


Fig. 2. Ground state electronic absorption spectra of 6a in (i) DCM (concentration =  $4.63 \times 10^{-5} \text{ mol dm}^{-3}$ ), (ii) CHCl<sub>3</sub> (concentration =  $2.55 \times 10^{-5} \text{ mol dm}^{-3}$ ) and (iii) THF (concentration =  $2.42 \times 10^{-5} \text{ mol dm}^{-3}$ ).

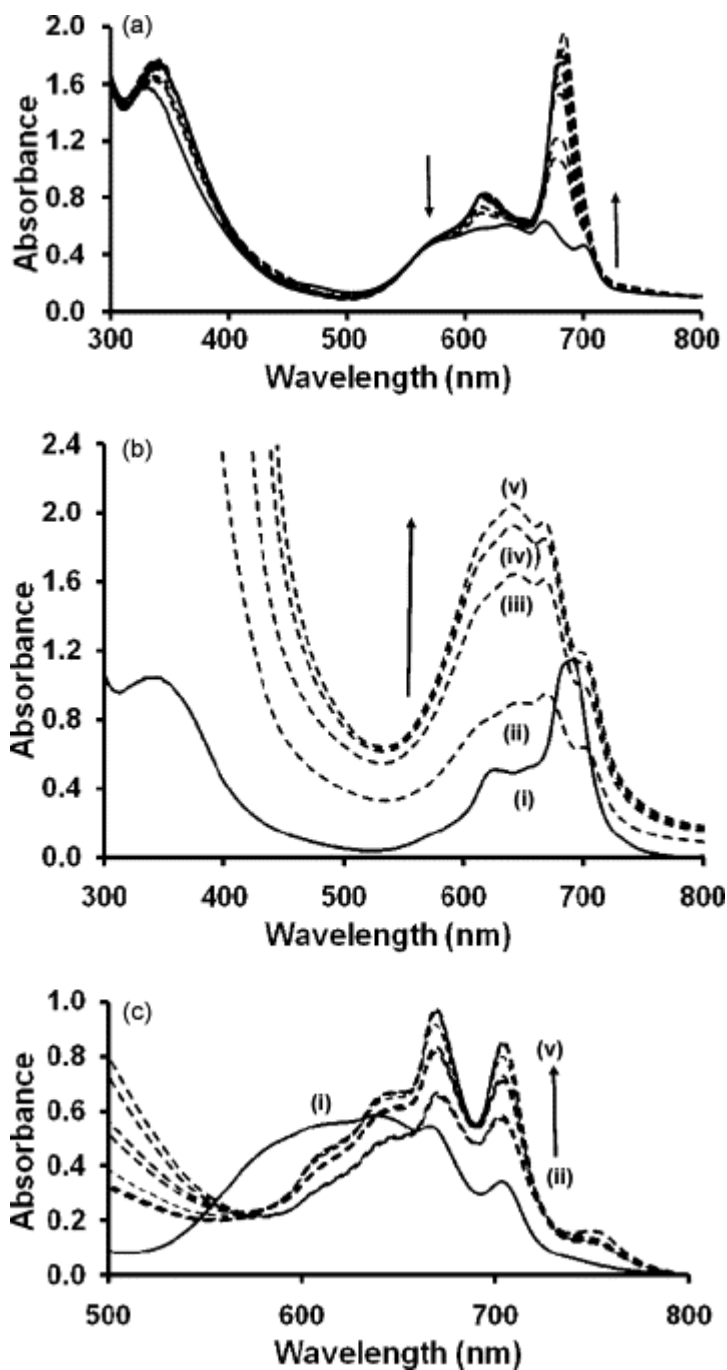


Fig. 3. Electronic absorption spectra of (a) 6a (initial concentration =  $\sim 2.84 \times 10^{-5} \text{ mol dm}^{-3}$ ) in THF on successive addition of  $\text{NaBH}_4$ , (b) 6a (concentration =  $\sim 7.29 \times 10^{-5} \text{ mol dm}^{-3}$ ), in DMSO (i), on addition of  $\text{Br}_2$  fumes (ii–v) and (c) 6a (concentration =  $2.73 \times 10^{-5} \text{ mol dm}^{-3}$ ) in  $\text{CHCl}_3$  (i) on successive addition of  $\text{Br}_2$  fumes (ii–v).

Significant bathochromic shifts into the near infrared region of the spectrum are known to occur in the presence of electron-donating groups, therefore this can be used to account for the red-shifted Q bands of the (benzyloxy)phenoxy derivatives 5a and 6a relative to those of 5b and 6b in similar solvents, e.g. DMF, [Table 1](#). Also substitution at the non-peripheral positions results in red shifting as expected (compare complexes 5 with corresponding complexes 6,

though there is no red shift when comparing 5b and 6b in DMF or DMSO). In general for all complexes 5a, 5b, 6a and 6b, a change in the solvent is accompanied by a change in the position of the Q band. Solvents with strong co-ordinating properties, i.e. DMF and DMSO interact with the phthalocyanine molecule (through either the sulfur or oxygen atoms [44] and [45]) which gives rise to a more stable lowest unoccupied molecular orbital (LUMO) and thus results in a smaller HOMO–LUMO band separation resulting in red-shifted Q bands in these solvents, however this is not clear in [Table 1](#) (except for 6b). Fluorescence emission and excitation spectra of the complexes in DMSO are of the form shown in [Fig. 4](#). In most cases, the emission spectra are similar to the absorption spectra, although slightly broadened spectra occur in some solvents. The excitation spectrum of 6a consistently shows a split Q-band peak in toluene, CHCl<sub>3</sub>, DCM and THF, suggesting a change in the nature of the molecule following absorption of light and excitation, probably due to a change in symmetry ([Fig. 5](#)). The excitation spectrum for 6a was similar to the absorption spectrum of an unmetallated derivative, suggesting that the loss of symmetry is due to demetallation. For 6b and 5a (in all solvents) and 5b (in all solvents except chloroform, where there is splitting), the closeness of the Q-band maxima for absorption and excitation spectra shows that there are no changes in the configuration of the complexes following excitation.

Table 1.

Absorption, fluorescence excitation and emission spectral data for MPc complexes 5a, 5b, 6a and 6b in various solvents. Excitation at 630 nm for fluorescence studies.

Solvent	MPc	Q band $\lambda_{\max}/\text{nm}$	Log $\epsilon$	Emission <sup>a</sup> $\lambda_{\max}/\text{nm}$	Excitation $\lambda_{\max}/\text{nm}$	$\Phi_F$	$\Phi_\Delta$	$\Phi_{Pd}/10^4$
Toluene	5a	701	5.08	714	704	0.14	0.33	5.63
	5b	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
	6a	668, 704	5.08	709	668, 705	0.14	0.042	<sup>c</sup>
	6b	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
CHCl <sub>3</sub>	5a	707	5.56	722	713	0.15	0.26	6.15
	5b	684	4.89	701	684, 697	0.17	0.50	<sup>d</sup>
	6a	636, 667, 703	4.35, 4.30, 4.12	711	669, 706	0.25	0.015	<sup>c</sup>
	6b	673	<sup>b</sup>	701	673	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>

Solvent	MPC	Q band $\lambda_{\max}/\text{nm}$	Log $\epsilon$	Emission <sup>a</sup> $\lambda_{\max}/\text{nm}$	Excitation $\lambda_{\max}/\text{nm}$	$\Phi_F$	$\Phi_{\Delta}$	$\Phi_{Pd}/10^4$
THF	5a	699	5.33	710	697	0.18	0.42	1.09
	5b	682	4.86	699	683	0.18	0.52	5.57
	6a	634, 664, 700	4.38, 4.34, 4.15	707	668, 705	0.21	0.025	<sup>c</sup>
	6b	677	<sup>b</sup>	684	677	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
DCM	5a	703	5.27	719	707	0.15	<sup>e</sup>	11.8
	5b	683	4.75	696	685	0.18	<sup>e</sup>	<sup>d</sup>
	6a	634, 666, 701	4.32, 4.24, 4.03	709	668, 705	0.27	<sup>e</sup>	<sup>c</sup>
	6b	672	<sup>b</sup>	676	672	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
DMF	5a	698	5.29	713	699	0.19	0.41	1.63
	5b	682	5.11	695	684	0.16	0.60	<sup>d</sup>
	6a	684	5.29	697	685	0.13	0.39	3.58
	6b	682 <sup>f</sup>	5.11 <sup>f</sup>	695 <sup>f</sup>	682 <sup>f</sup>	0.017 <sup>f</sup>	0.64 <sup>f</sup>	<sup>d</sup>
DMSO	5a	702	5.32	718	706	0.045	0.31	0.92
	5b	684	5.30	705	689	0.16	0.44	6.11
	6a	688	5.32	699	689	0.10	0.23	<sup>c</sup>
	6b	685 <sup>f</sup>	5.30 <sup>f</sup>	698 <sup>f</sup>	685 <sup>f</sup>	0.013 <sup>f</sup>	0.74 <sup>f</sup>	<sup>d</sup>

<sup>a</sup> Excitation at 630 nm for all derivatives.

<sup>b</sup> Values undetermined due to limited or inadequate solubility.

<sup>c</sup> No change in absorption intensity with time.

<sup>d</sup> Phototransformation.

<sup>e</sup> Values undetermined due to lack of reference standards.

<sup>f</sup> Values from Reference [12].

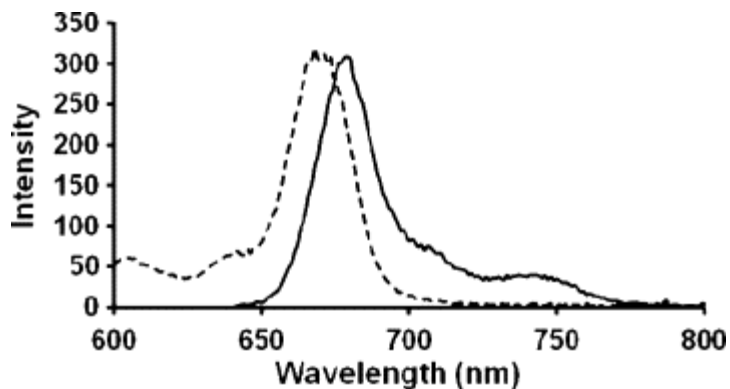


Fig. 4. Fluorescence emission (—) and excitation (- - -) spectra of 5a in DMF. Concentration of 5a =  $2.39 \times 10^{-6}$  mol dm<sup>-3</sup>. Excitation wavelength = 620 nm.

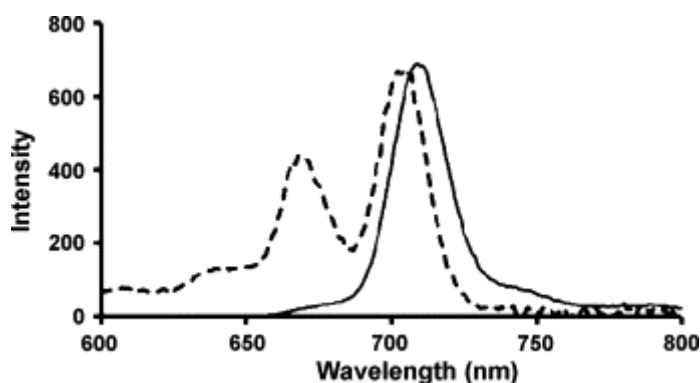


Fig. 5. Fluorescence emission (—) and excitation (- - -) spectra of 6a in DCM. Concentration of 6a =  $5.25 \times 10^{-5}$  mol dm<sup>-3</sup>. Excitation wavelength = 620 nm.

### 3.3. Photochemical studies

#### 3.3.1. Singlet oxygen quantum yields

The determination of singlet oxygen quantum yields ( $\Phi_{\Delta}$ ) was carried out in a number of solvents listed in [Table 1](#), but the lack of a suitable reference in DCM restricted calculations in this solvent. The amount of singlet oxygen produced was determined by monitoring the decrease in DPBF, a chemical quencher, by UV-Vis spectroscopy over a period of time. Eq. (1) was thus used to calculate the overall yields. The magnitude of these yields varies as a function of the triplet excited state energy, solvent and singlet oxygen quenching abilities of the substituent, triplet lifetime and efficiency of energy transfer ( $S_{\Delta}$ ). There was no decrease in the Q band or formation of new bands in the phthalocyanine spectrum during the analysis, only the decrease in the intensity of the DPBF absorption is observed, [Fig. 6](#) (for 5a in THF). The values of  $\Phi_{\Delta}$  were higher for the  $\beta$ -substituted complex 6b compared to the corresponding  $\alpha$ -derivative 5b, [Table 1](#) in DMF and DMSO only. The reverse is true for 5a and 6a, in DMSO

and DMF, where yields are lowest for the peripherally substituted derivative 6a in all solvents where values could be obtained. The very low  $\Phi_{\Delta}$  values of 6a compared to 5a in THF,  $\text{CHCl}_3$  and toluene are due to the partial oxidation and demetalation discussed above, [Fig. 2](#). The behaviour of the pyridyloxy and (benzyloxy)phenoxy derivatives also differs when considering complexes with the same substitution pattern, i.e. 5a versus 5b and 6a versus 6b. There is a trend towards lower yields for those phthalocyanines substituted with (benzyloxy)phenoxy groups, suggesting that these groups quench the ability of the molecules to produce singlet oxygen efficiently.

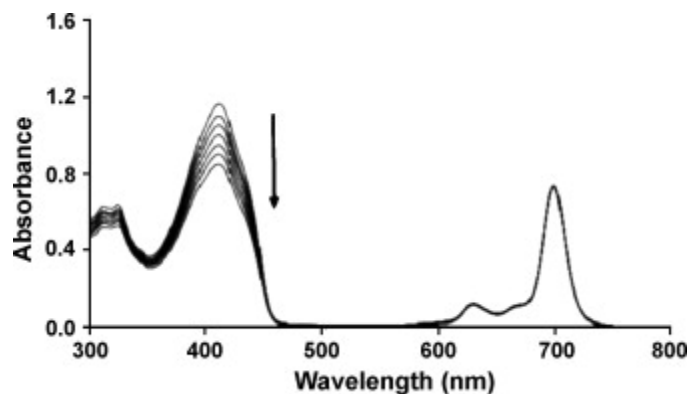


Fig. 6. A typical electronic absorption spectrum for the determination of singlet oxygen quantum yield for 5a in THF (concentration =  $3.4 \times 10^{-6} \text{ mol dm}^{-3}$ ). DPBF initial concentration =  $5.0 \times 10^{-5} \text{ mol dm}^{-3}$ .

Eq. (2) was used to give a measure of  $S_{\Delta}$ , which represents the efficiency of quenching of the excited triplet state by singlet oxygen. The  $S_{\Delta}$  values in [Table 2](#) indicate values close to unity for some complexes, suggesting efficient transfer of energy from the triplet state to oxygen. From the data obtained it seems that the highest efficiencies are obtained for 5b in DMF and 6b in DMSO. 6a consistently has the lowest transfer efficiencies in all solvents, due to partial oxidation and demetalation discussed above.

Table 2.

Photophysicochemical parameters of MPc derivatives in various solvents.

Solvent	MPc	$\Phi_T$	$\Phi_{IC}$	$\Phi_{\Delta}$	$S_{\Delta}^a$	Lifetime ( $\mu$ s)
Toluene	5a	0.51	0.53	0.33	0.65	30
	5b	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
	6a	0.82	0.14	0.042	0.058	30
	6b	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
DMF	5a	0.53	0.28	0.41	0.77	7
	5b	0.70	0.14	0.60	0.86	10
	6a	0.77	0.10	0.39	0.51	5
	6b	0.85 <sup>c</sup>	0.13 <sup>c</sup>	0.64	0.75 <sup>c</sup>	5 <sup>c</sup>
DMSO	5a	0.38	0.57	0.31	0.81	9
	5b	0.61	0.23	0.44	0.72	40
	6a	0.36	0.54	0.23	0.64	30
	6b	0.83 <sup>c</sup>	0.16 <sup>c</sup>	0.74	0.89 <sup>c</sup>	30 <sup>c</sup>

<sup>a</sup>  $S_{\Delta} = \Phi_{\Delta}/\Phi_T$ .<sup>b</sup> Values undetermined due to inadequate or limited solubility.<sup>c</sup> Values from Reference [12].

### 3.3.2. Photodegradation studies

Monitoring the photo-induced decomposition of MPc complexes can be used to determine the stability of these derivatives under intense light. It is especially important when considering phthalocyanines that may be applied as photocatalysts for the degradation of pollutants and transformation of alkenes and alkanes [46], [47], [48] and [49]. The degradation of phthalocyanine molecules occurs via attack by singlet oxygen in an oxidative process [50] and [51]. It is characterized by the decrease in intensity of the spectra, of the Q and B bands, without the appearance of new bands or a shift in the maxima on exposure of the MPc to intense light. Theory suggests that the efficiency of the process should depend on the  $\Phi_{\Delta}$



values. Variations in solvent properties and molecular structure may be used to account for the photodegradation data. Electron-donating ring substituents are expected to enhance degradation. Photodegradation quantum yields could not be expressed as such for the pyridyloxy-substituted derivatives (5b and 6b), as they underwent a phototransformation process, as indicated by a shift in the Q-band maxima (Fig. 7). These changes depict some distortion of the pyridyloxy-substituted phthalocyanine macrocycle on exposure to intense light. A similar effect has been observed on exposure to laser light in this (for 5b and 6b) and previous work (for 6b) [12].

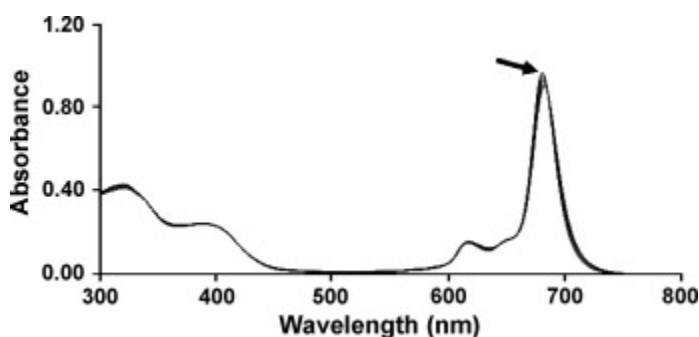


Fig. 7. Changes in absorption spectra of 5b (initial concentration =  $\sim 1.50 \times 10^{-5}$  mol dm<sup>-3</sup>) in DMF on photolysis.

Attempts to degrade complex 6a in most solvents (toluene, CHCl<sub>3</sub>, THF, DCM and DMSO) were unsuccessful, with no decrease in absorption intensity. Except for DMSO, these are the same solvents in which 6a is shown to have unusual or broadened absorption spectra. This suggests that these complexes are very stable, and may be a consequence of the initial partial oxidation mentioned earlier and low  $\Phi_{\Delta}$  values. Only data for 5a could be obtained in all solvents. The results indicate similar stability in most solvents ( $\Phi_{Pd}$  of the order of  $10^{-4}$ ). Co-ordinating solvents such as DMSO are capable of protecting the molecule against oxidative attack [52] and thus accounts for the low quantum yield of degradation value found for 5a in this solvent. Non-co-ordinating solvents however leave the molecule prone to oxidative attack, which usually gives rise to the highest  $\Phi_{Pd}$  values, e.g. 5a in DCM (Table 1).

### 3.4. Photophysical studies

#### 3.4.1. Fluorescence quantum yields

The fluorescence quantum yields of the cadmium aryloxy complexes 5a, 5b, 6a and 6b are typical of MPc complexes and in most cases marginally lower than previously reported cadmium derivatives [12] and [21]. Fluorescence yields are often influenced by the heavy atom effect as well as aggregating tendencies. The yields of the  $\beta$ -substituted derivative 6a are much higher relative to those of the  $\alpha$ -substituted 5a in all solvents, except in DMF and toluene in which case 5a has a slightly larger (or similar) value. The lowest values occur in DMSO in general, the heavy sulfur atoms present enhance intersystem crossing (ISC) to the triplet state to give increased triplet quantum yields as opposed to high  $\Phi_F$  values.

#### 3.4.2. Triplet quantum yields and lifetimes

Fig. 8 shows that the triplet decay curve for the complexes obeyed second order kinetics. This is typical of MPc complexes at high concentrations ( $>1 \times 10^{-5}$  M) [53] due to the triplet–triplet recombination. The concentrations employed in this work were in this range hence triplet–triplet recombination is expected.

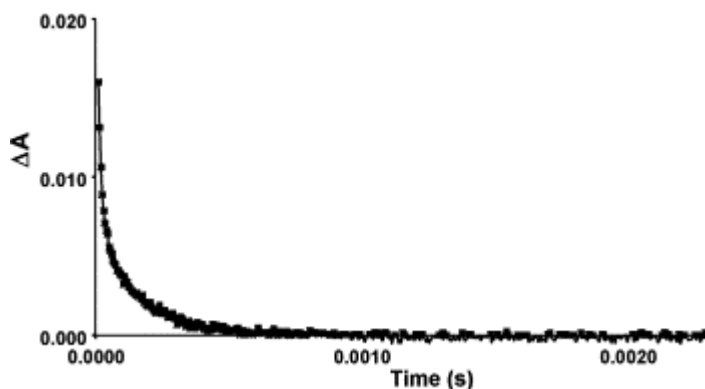


Fig. 8. Second order triplet decay curve for 6a in DMSO. Excitation = 688 nm.

All triplet data was obtained in toluene, DMF and DMSO. The lack of reference standards in  $\text{CHCl}_3$ , THF and DCM prevented the determination of data in these solvents. Phthalocyanines typically show a triplet transient absorption between 450 and 550 nm, and in this work this was observed between 490 and 520 nm for all the complexes, the triplet lifetimes and yields were determined at the appropriate wavelengths for each complex. The lifetimes were relatively short and varied between 5 and 40  $\mu\text{s}$  for 5a, 5b, 6a and 6b. Lifetimes were in general

relatively long-lived in DMSO relative to data obtained in DMF and toluene (except for 5a which had a longer lifetime in toluene) as a result of the highly viscous nature of DMSO, making it a more competent deactivator of non-radiative transitions of excited state molecules. The triplet quantum yield ( $\Phi_T$ ) is used to quantify the fraction of molecules that undergo rapid intersystem crossing from the lowest excited singlet state to populate the lowest excited triplet state ( $T_1$ ). The (benzyloxy)phenoxy derivative 5a shows considerably low  $\Phi_T$  in DMSO, which does not correspond to the low value of  $\Phi_F$  in Table 1. The value of  $\Phi_T$  for peripherally substituted 6a is larger than for non-peripherally substituted 5a in toluene and DMF and are almost equal in DMSO, Table 2, whereas the reverse was true for  $\Phi_\Delta$  values discussed above. This suggests that even though 6a is efficient in populating the triplet state, it is inefficient in generating singlet oxygen. Larger triplet yields (in DMSO and DMF) were also observed for peripherally substituted 6b than for non-peripherally substituted 5b, Table 2, suggesting that peripheral substitution enhances intersystem crossing to the triplet state. Comparing pyridyloxy and (benzyloxy)phenoxy substituents (i.e. 5a with 5b and 6a with 6b), Table 2, shows that complexes give lower triplet quantum yields as was observed for singlet oxygen quantum yields above. Thus the (benzyloxy)phenoxy seems to quench the excited state.

Changes in the structure of the phthalocyanine molecules upon excitation with intense light, has been reported before [12], [20], [21] and [54]. Following laser irradiation, most of the complexes discussed in this work were partly degraded, however the spectrum of the pyridyloxy derivative 5b shows a slight broadening in addition to a shift towards the red. On exposure to air there was no reversal to the original form. This is similar to spectra obtained for 6b [12] and has been attributed to photo-induced twisting of the pyridino groups about the flexible  $\sigma$ -bond. The extent of this twisting varies with the intensity of light applied where more intense light (i.e. laser light) results in a more significant drop in intensity and shift in wavelength.

#### 4. Conclusions

We have successfully managed to synthesize new  $\alpha$  and  $\beta$  tetra-substituted (4-benzyloxy)phenoxy cadmium phthalocyanine derivatives (5a and 6a) as well as the  $\alpha$ -pyridyloxy cadmium derivative (5b). The spectral characteristics of these molecules have been discussed with respect to the influence of the different solvents in which they are either completely or partially soluble. The  $\alpha$ -derivatives (5a and 5b) have shown excellent solubility in all solvents, whereas that of the  $\beta$ -derivatives tends to be limited at times. The oxidizing ability

of chlorinated and poorly co-ordinating solvents has been used to account for the unusual spectrum of 6a, which consists of a broad absorption band ranging from 550 to 650 nm. Substitution with (benzyloxy)phenoxy groups appears to have a quenching effect on the  $\Phi_{\Delta}$ , since lower values are obtained. The triplet quantum yield ( $\Phi_T$ ) for the non-peripherally substituted 6a in DMF and toluene (e.g.  $\Phi_T = 0.82$  in toluene) were larger than for the non-peripherally substituted 5a ( $\Phi_T = 0.51$  in toluene) containing the same substituents. The same applies to 6b and 5b in DMSO and DMF, showing the significance of the substitution point. The triplet lifetimes ranged from 5 to 40  $\mu$ s due to the heavy atom effect of Cd. The work presented here has thus accounted for differences and changes in the spectra and photophysical and photochemical properties of the newly synthesized molecules.

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