

Synthesis, photophysics and photochemistry of tin(IV) phthalocyanine derivatives

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ABSTRACT

The synthesis, photophysical and photochemical properties of peripherally (β) and non-peripherally (α) tetra-substituted aryloxy tin(IV) phthalocyanines are reported. The complexes presented are 1,(4)-(tetraphenoxypthalocyaninato) (**7a**); 2,(3)-(tetraphenoxypthalocyaninato) (**8a**); 1,(4)-(tetra *tert*-butylphenoxyphthalocyaninato) (**7b**); 2,(3)-(tetra *tert*-butylphenoxyphthalocyaninato) (**8b**); 1,(4)-(tetra 4-benzyloxyphenoxyphthalocyaninato) (**7c**) and 2,(3)-(tetra 4-benzyloxyphenoxyphthalocyaninato) (**8c**) tin(IV). The trends in triplet, fluorescence, singlet oxygen and photodegradation quantum yields are described for these compounds. The complexes exhibited high triplet quantum yields (Φ_T) ranging from 0.69 to 0.89 due to the spin-orbit coupling induced by Sn, which has a large atomic number, and this resulted in lowering of fluorescence quantum yields. The peripherally substituted derivatives (**8a**, **8b** and **8c**) showed marginally higher fluorescence quantum yield values ($\Phi_F=0.014$, 0.010 and 0.011, respectively) compared to non-peripherally substituted derivatives (**7a**, **7b** and **7c**) which gave $\Phi_F=0.008$, 0.007 and 0.008, respectively). The singlet oxygen quantum yields (Φ_{Δ}) ranged from 0.58 to 0.75 indicating a potential use of these complexes as photosensitizers. Triplet lifetimes were generally low, ranging from 30 to 50 μ s. Photoreduction of the complexes in the absence of oxygen was observed during photolysis due to ring reduction.

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1. Introduction

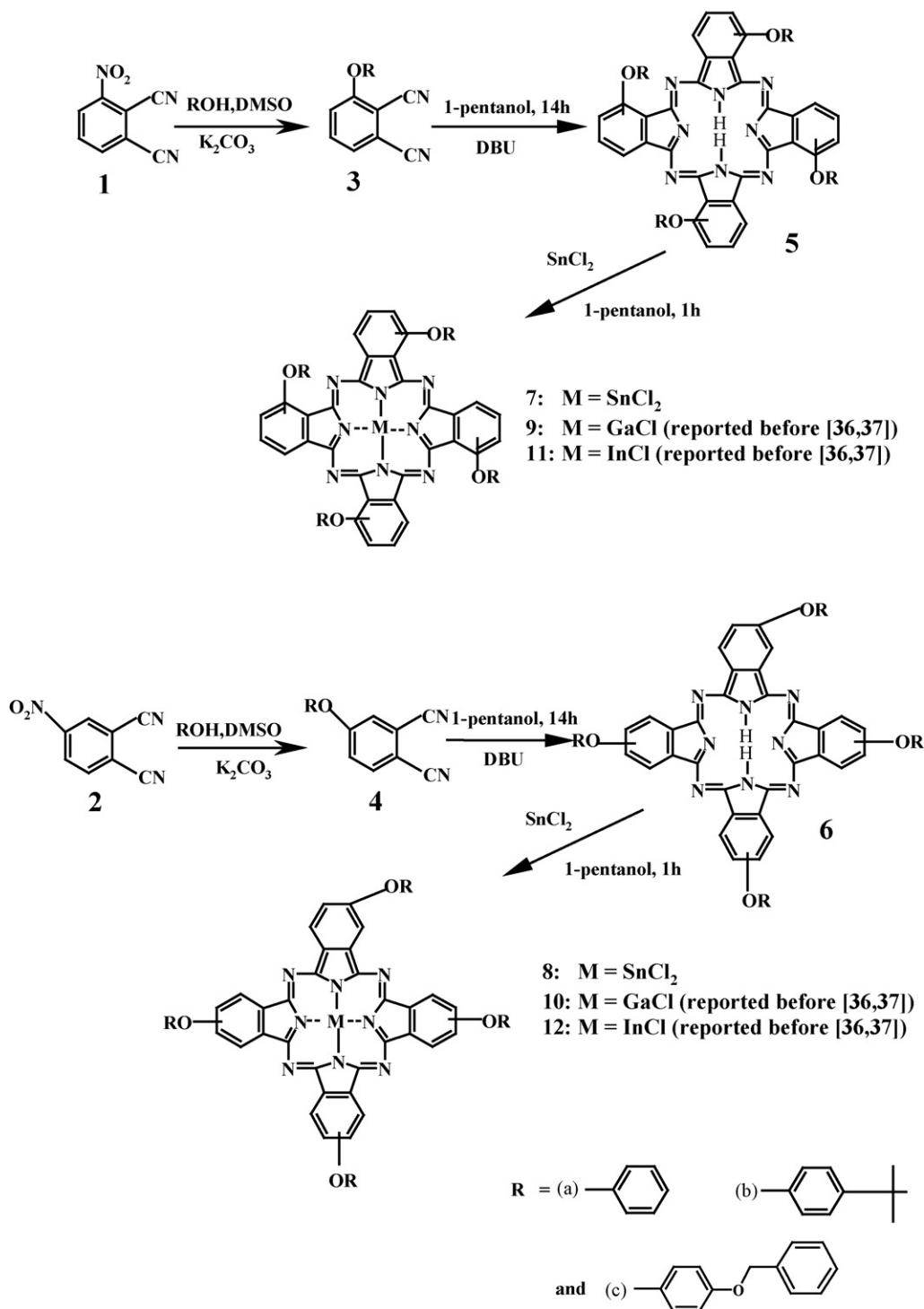
Metallophthalocyanines (MPcs) are a class of macrocyclic compounds which are very versatile because they possess a highly conjugated π -electron system. They were first developed as industrial pigments, and have been diversely applied in various fields including chemical sensors, solar cells, catalysis, liquid crystals and photodynamic therapy (PDT) [1–11], due to their stability, diverse coordination properties and spectroscopic properties. MPcs are known to have low solubility in most organic solvents, but it has been documented that tetra-substituted phthalocyanines are more soluble than their octa-substituted counterparts due to formation of constitutional isomers and high dipole moments they possess [12,13]. Alkyl or alkoxy groups introduced at the peripheral or non-peripheral positions have also been found to improve solubility and the positioning of these groups regulates the wavelength of the Q-band [14–17].

Incorporation of non-transition metal ions in the centre of the phthalocyanine (Pc) ring results in metallophthalocyanine

(MPc) complexes with high triplet state quantum yields and long triplet lifetimes, which are required for efficient photosensitization [18–20]. This work investigates the photosensitizing tendencies of some tin(IV) tetra-substituted phthalocyanine derivatives. Sn^{4+} , a closed shell diamagnetic ion, is expected to exhibit high photosensitizing abilities. Aggregation tendencies of MPcs have been documented as a setback in their use as photosensitizers [21–23] since it diminishes their photo activity. MPcs with bulky peripheral substituents especially at the non-peripheral position or axial ligands on the central metal can however overcome aggregation, since there will be less effective π - π interaction of phthalocyanine sub units [24–26].

In this work, we report on the synthesis, spectroscopic, photophysical and photochemical properties of Cl_2SnPcs tetra-substituted at the (α) non-peripheral (complexes **7a**, **7b** and **7c**) and (β) peripheral (complexes **8a**, **8b** and **8c**) positions with phenoxy, *tert*-butylphenoxy and 4-benzyloxyphenoxy groups (Scheme 1). SnPc derivatives are still relatively few. Even though the ring systems discussed in this work are not new, the use of tin metal has not been reported. Sn(IV)Pc and Sn(II)Pc complexes have been reported in the literature [27–34], and have been shown to possess interesting properties including the formation of μ -oxo Sn(IV)Pc polymers [27] and ease of photoreduction in the presence of light [30–32] rather than the more common photodegradation

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Scheme 1. Syntheses of tetra-substituted phenoxy, *tert*-butylphenoxy and 4-benzyloxyphenoxy (phthalocyaninato) tin(IV) substituted at the α and β positions (complexes **7** and **8**). The synthesis of complexes **9**, **10**, **11** and **12** has been reported before [15,36].

shown by most MPc complexes. Our group has also recently reported on the attempts to synthesize tetrasulfonated SnPc using microwave irradiation that resulted in the formation of tetrasulfonated tin α,β,γ -tetrabenzocorrole [34]. There has been very little study on the photophysical and photochemical behaviour of SnPc complexes. The triplet state quantum yields have been reported for sulfonated SnPc complexes [34] and were found to be lower than would be expected on the basis of the heavy atom

effect. SnPc_{mix} containing a mixture of differently sulfonated derivatives gave high triplet yields ($\Phi_T = 0.87$) in dimethylsulfoxide (DMSO) [20]. It has been shown that the presence of phenoxy, *tert*-butylphenoxy or 4-benzyloxyphenoxy groups improves triplet lifetimes and singlet oxygen quantum yields [15,35,36]. Peripheral substitution with phenoxy or *tert*-butylphenoxy was found to improve triplet lifetimes compared to non-peripheral substitution [15], hence we chose these substituents in this work for the

elucidation of photochemical and photophysical behaviour of SnPc complexes.

2. Experimental

2.1. Materials

Methanol, dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), chloroform (CHCl_3) and dimethylsulfoxide were dried as described by Perrin and Armarego [37] before use. Deuterated chloroform (CDCl_3), 4-*tert*-butylphenol, 4-benzyloxyphenol, phenol, 3-diphenylisobenzofuran (DPBF), 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), pentan-1-ol and tin(II) chloride were purchased from Sigma–Aldrich. Chromatography was performed on silica gel 60 (0.04–0.063 mm). 3-Nitrophthalonitrile (**1**), 4-nitrophthalonitrile (**2**), 3-phenoxyphthalonitrile (**3a**) and 4-phenoxyphthalonitrile (**4a**), 3-*tert*-butylphenoxyphthalonitrile (**3b**), 4-*tert*-butylphenoxyphthalonitrile (**4b**), 3-benzyloxyphenoxyphthalonitrile (**3c**) and 4-benzyloxyphenoxyphthalonitrile (**4c**) were all synthesized and purified according to the literature [38–40].

2.2. Equipment

UV–vis spectra were recorded on a Cary 500 UV–vis/NIR spectrophotometer. IR spectra (KBr pellets) were recorded on a Perkin-Elmer spectrum 2000 FTIR spectrometer. ^1H NMR spectra were recorded using a Bruker EMX 400 MHz NMR spectrometer. Elemental Analyses were performed at the University of Cape Town.

Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter using a 1-cm pathlength cuvette at room temperature. 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 (Pyridin 1 dye in methanol). Single pulse energy was 7 mJ. The analyzing beam source was from a Thermo Oriol xenon arc lamp, and a photomultiplier tube was used as detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360); the kinetic curves were averaged over 256 laser pulses. The triplet life times were determined by exponential fitting of the kinetic curves using the program OriginPro 7.5. Solutions for triplet yield and lifetime determinations were purged of oxygen (by bubbling with Argon) before laser irradiations. Photoirradiations for photodegradation or singlet oxygen determination were performed using a General electric Quartz line lamp (300 W). A 600-nm glass cutoff filter (Schott) and water 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 intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 5.14×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$ for photobleaching and to be 1.78×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$ for singlet oxygen studies.

2.3. Photophysical and photochemical studies

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) were determined by comparative method [41]:

$$\Phi_F = \Phi_{F(\text{Std})} \frac{FA_{\text{Std}}n^2}{F_{\text{Std}}An_{\text{Std}}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the complexes (**7a**, **7b**, **7c**, **8a**, **8b** or **8c**) and the standard, respectively.

A and A_{Std} are the absorbances of the complexes and reference at the excitation wavelength, and n and n_{Std} are the refractive indices of solvents used for the complexes and standard, respectively. ZnPc in DMSO was used as a standard, $\Phi_F = 0.20$ [42]. The complexes and the standard were excited at the same relevant wavelength.

2.3.2. Triplet quantum yields and lifetimes

Triplet quantum yields were determined using a comparative method based on triplet decay, using the following equation:

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

where $\Delta A_T^{\text{sample}}$ and ΔA_T^{Std} are the changes in the triplet state absorbance of the complexes and the standard, respectively. Φ_T^{Std} is the triplet state quantum yield for the standard. ZnPc ($\Phi_T^{\text{Std}} = 0.65$ in DMSO [43]) was used as standard. $\varepsilon_T^{\text{sample}}$ and $\varepsilon_T^{\text{Std}}$ were determined from the molar extinction coefficients of their respective ground singlet state ($\varepsilon_S^{\text{sample}}$ and $\varepsilon_S^{\text{Std}}$), the changes in absorbances of the ground singlet states ($\Delta A_S^{\text{sample}}$ and ΔA_S^{Std} and changes in the triplet state absorptions, ($\Delta A_T^{\text{sample}}$ and ΔA_T^{Std}) according to Eqs. (3a) and (3b) [44].

$$\varepsilon_T^{\text{sample}} = \varepsilon_T^{\text{sample}} \frac{\Delta A_T^{\text{sample}}}{\Delta A_S^{\text{sample}}} \quad (3a)$$

$$\varepsilon_T^{\text{Std}} = \varepsilon_T^{\text{Std}} \frac{\Delta A_T^{\text{Std}}}{\Delta A_S^{\text{Std}}} \quad (3b)$$

Quantum yields of internal conversion were obtained from Eq. (4) which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet states of the complexes.

$$\Phi_{\text{IC}} = 1 - (\Phi_F + \Phi_T) \quad (4)$$

2.3.3. Singlet oxygen and photodegradation quantum yields

Eq. (5) was employed for calculating singlet oxygen quantum yields (Φ_Δ):

$$\Phi_\Delta = \Phi_\Delta^{\text{Std}} \frac{RI_{\text{abs}}^{\text{Std}}}{R^{\text{Std}}I_{\text{abs}}} \quad (5)$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard (ZnPc; $\Phi_\Delta^{\text{Std}} = 0.67$ in DMSO [45]). R and R^{Std} are the DPBF (singlet oxygen quencher) photobleaching rates in the presence of the respective complexes under investigation and the standard, respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the complexes and the standard, respectively. To avoid chain reactions, the concentration of DPBF was kept at $\sim 3 \times 10^{-5} \text{ mol l}^{-1}$. Solutions of the complexes with an absorbance of 0.2 at the irradiation wavelength were prepared in the dark and irradiated at the Q-band region, monitoring the DPBF degradation at 417 nm. The error was $\sim 10\%$ from several values of Φ .

The values of photobleaching quantum yields (Φ_p) were determined using the following equation:

$$\Phi_{\text{Pd}} = \frac{(C_0 - C_t)VN_A}{I_{\text{abs}}St} \quad (6)$$

where C_t and C_0 are the MPC complexes concentration in mol dm^{-3} after and prior to irradiation, respectively. V is the reaction volume, S is the irradiation area of the cell, t the irradiation time, N_A is the Avogadro's number and I_{abs} the overlap integral of the irradiation light source intensity and the absorption of the MPC in the region of the interference filter transmittance [45,46].

2.4. Synthesis

2.4.1. The synthesis of the metal-free phthalocyanine (**5a**, **5b**, **6a**, and **6b**)

The synthesis was carried out using established procedures [47]. Briefly, the respective phthalonitrile derivatives (**3a**, **3b**, **3c**, **4a**, **4b** and **4c**) (0.1 mmol) were refluxed in pentan-1-ol (5 ml) in the presence of 0.1 mmol, DBU for 14 h under nitrogen atmosphere. After cooling, the solution was dropped in methanol under stirring. The dark blue product was precipitated and collected by filtration and washed with methanol. The crude product was dissolved in dichloromethane (CH₂Cl₂), filtered and concentrated. The product was purified by passing it through a silica gel column, using CH₂Cl₂ as an eluent, giving metal-free tetraphenoxy (**5a** and **6a**), tetra-*tert*-butylphenoxy (**5b** and **6b**) and tetra-4-benzyloxyphenoxy (**5c** and **6c**) phthalocyanines which gave satisfactory spectroscopic characterization and were immediately used for SnPc synthesis.

2.4.2. Tin(IV) phthalocyaninato complexes (**7a**, **7b**, **7c**, **8a**, **8b** and **8c**)

A mixture of tin(II) chloride (1 mmol) and (**5a**, **5b**, **5c**, **6a**, **6b** or **6c**) (1 mmol) was refluxed in pentan-1-ol (5 ml) for 1 h under nitrogen. The mixture was cooled and methanol was added. The dark green product was filtered off and washed with methanol. It was isolated through a silica gel column, with CH₂Cl₂:MeOH (30:1) as the eluent, giving metallated tetraphenoxy (**7a** and **8a**), tetra-*tert*-butylphenoxy (**7b** and **8b**) and tetrabenzyloxyphenoxy (**7c** and **8c**) phthalocyaninato tin(IV) complexes.

1,(4)-(Tetraphenoxyphthalocyaninato) tin(IV) (**7a**). Yield: (30%). UV-vis (DMSO): λ_{\max} (nm) (log ϵ) 339 (4.78), 652 (4.47), 733 (5.03). IR [(KBr) ν_{\max} (cm⁻¹)]: 3038 (Ar-CH), 2996 (C-H), 1580 (C=C), 1250 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 8.95–9.37 (4H, m, Pc-H), 8.04–8.25 (4H, m, Pc-H), 7.65–7.79 (4H, m, Pc-H), 7.16–7.46 (20H, m, phenyl-H). Calcd for C₅₆H₃₂Cl₂SnN₈O₄: C 62.83, H 3.01, N 10.47. Found: C 62.92, H 3.25, N 9.18.

1,(4)-(Tetra-*tert*-butylphenoxyphthalocyaninato) tin(IV) (**7b**). Yield: (37%). UV-vis (DMSO): λ_{\max} (nm) (log ϵ) 343 (4.71), 657 (4.41), 737 (5.01). IR [(KBr) ν_{\max} (cm⁻¹)]: 2964 (C-H), 1582 (C=C), 1255 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 9.24–9.38 (4H, m, Pc-H), 8.89–9.08 (4H, m, Pc-H), 8.01–8.25 (4H, m, Pc-H), 7.55–7.80 (16H, m, phenyl-H), 1.29–1.46 (36H, m, t-Bu). Calcd for C₇₂H₆₄Cl₂SnN₈O₈: C 66.78, H 4.98, N 8.65. Found: C 67.37, H 5.23, N 8.26.

1,(4)-(Tetra [4-(benzyloxy)phenoxy]phthalocyaninato) tin(IV) (**7c**). Yield: (32%). UV-vis (DMSO): λ_{\max} (nm) (log ϵ) 331 (4.85), 659 (4.51), 740 (5.18). IR [(KBr) ν_{\max} (cm⁻¹)]: 3032 (Ar-CH), 2936 (C-H), 1585 (C=C), 1231 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 9.29–9.37 (4H, m, Pc-H), 9.05–9.13 (4H, m, Pc-H), 8.08–8.21 (4H, m, Pc-H), 7.44–7.53 (20H, m, phenyl-H), 7.06–7.26 (16H, m, phenyl-H), 5.21 (8H, m, CH₂). Calcd for C₈₄H₅₆Cl₂SnN₈O₈: C 67.49, H 3.78, N 7.50. Found: C 67.98, H 4.01, N 7.65.

2,(3)-(Tetraphenoxyphthalocyaninato) tin(IV) (**8a**). Yield: (52%). UV-vis (DMSO): λ_{\max} (nm) (log ϵ) 356 (4.80), 639 (4.39), 709 (5.03). IR [(KBr) ν_{\max} (cm⁻¹)]: 3020 (Ar-CH), 2920 (C-H), 1590 (C=C), 1231 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 8.78–9.22 (4H, m, Pc-H), 8.19–8.38 (4H, m, Pc-H), 7.44–7.57 (4H, m, Pc-H), 7.14–7.32 (20H, m, phenyl-H). Calcd for C₅₆H₃₂Cl₂SnN₈O₄: C 62.83, H 3.01, N 10.47. Found: C 62.42, H 3.64, N 9.55.

2,(3)-(Tetra-*tert*-butylphenoxyphthalocyaninato) tin(IV) (**8b**). Yield: (48%). UV-vis (DMSO): λ_{\max} (nm) (log ϵ) 349 (4.82), 637 (4.42), 711 (5.10). IR [(KBr) ν_{\max} (cm⁻¹)]: 3014 (Ar-CH), 2962 (C-H), 1602 (C=C), 1234 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 9.06–9.26 (4H, m, Pc-H), 8.80–8.98 (4H, m, Pc-H), 8.51–8.67 (4H, m, Pc-H), 7.48–7.69 (16H, m, phenyl-H), 1.39 (36H, s, t-Bu). Calcd for C₇₂H₆₄Cl₂SnN₈O₈: C 66.78, H 4.98, N 8.65. Found: C 66.70, H 5.81, N 8.51.

2,(3)-(Tetra [4-(benzyloxy)phenoxy]phthalocyaninato) tin(IV) (**8c**). Yield: (44%). UV-vis (DMSO): λ_{\max} (nm) (log ϵ) 353 (4.90), 419 (4.42), 667 (4.72), 715 (5.07). IR [(KBr) ν_{\max} (cm⁻¹)]: 3033 (Ar-CH), 2934 (C-H), 1611 (C=C), 1223 (C-O-C). ¹H NMR (CDCl₃): δ , ppm 8.78–9.22 (4H, m, Pc-H), 7.70–8.11 (4H, m, Pc-H), 7.36–7.58 (24H, m, Pc-H), 6.73–7.08 (16H, m, phenyl-H), 5.19 (8H, m, CH₂). Calcd for C₈₄H₅₆Cl₂SnN₈O₈: C 67.49, H 3.78, N 7.50. Found: C 68.80, H 3.88, N 7.31.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 gives the synthetic pathways for the compounds used in this work. Substituted phthalocyanines are prepared by cyclotrimerization of substituted phthalonitriles. 4-Tetra-substituted phthalocyanines can be synthesized from 4-substituted phthalonitriles while 3-tetra-substituted phthalocyanines are obtained from 3-substituted phthalonitriles [48]. The metal-free phthalocyanine was afforded in high yield by refluxing complexes **3** or **4** for 14 h in pentan-1-ol in the presence of DBU, a strong organic base. Metallation proceeded by refluxing the metal-free derivatives in the presence of tin(II) chloride in pentan-1-ol for an average of 1 h. A high boiling solvent (pentan-1-ol) was used to insert the metal into the core of the ring because tin is a large atom.

In general, the synthesis of SnPc complexes using SnCl₂ may result in the formation of Sn(II)Pc or (Cl)₂Sn(IV)Pc species depending on the amount of SnCl₂ used in the reaction [27]. With excess SnCl₂, Sn(II)Pc derivatives are formed. In this work a ratio of 1:1 (SnCl₂: **5a**, **5b**, **5c**, **6a**, **6b** or **6c**) was employed, resulting in the formation of the (Cl)₂Sn(IV)Pcs (**7a**, **7b**, **7c**, **8a**, **8b** and **8c**). All the complexes in this study were soluble in organic solvents such as dichloromethane, chloroform, tetrahydrofuran, toluene, and dimethylsulfoxide. The phenoxy, *tert*-butylphenoxy and benzyloxyphenoxy groups were tetra-substituted at the α and β positions of the ring for comparative purposes.

The complexes were characterized by various spectroscopic methods, IR, UV-vis, ¹H NMR and elemental analysis and are in agreement with the predicted structures. The characteristic nitrile (C≡N) stretch at ~2230 cm⁻¹ of **3** and **4** disappears upon formation of the phthalocyanine. Upon metallation, the N-H stretching frequency at ~3300 cm⁻¹ disappears. All the complexes showed peaks between 1000 and 700 cm⁻¹ which may be assigned to phthalocyanines skeletal vibrations [49]. The complexes showed characteristic vibrations due to ether groups (C-O-C) at 1231–1255 cm⁻¹, aliphatic CH stretching at ca. 2920–2996 cm⁻¹ and aromatic CH stretching at ca. 3014–3038 cm⁻¹.

The ¹H NMR spectra for the complexes were complex and similar. Complex **7a**, showed three sets of multiplets at 8.95–9.37, 8.04–8.25 and 7.65–7.79 ppm for the phthalocyanine ring protons, integrating for four protons each. The phenyl protons were observed as multiplets at 7.16–7.46 ppm integrating for 20 protons. Complex **7b** also gave similar signals with the 3 sets of multiplets each integrating for 4 protons for Pc ring at 9.24–9.38, 8.89–9.08 and 8.01–8.25 ppm, 16 protons for phenyl at 7.55–7.80 ppm and a multiplet integrating to 36 protons for methyl (t-Bu) protons at 1.29–1.46 ppm. The ¹H NMR spectra of **8a** and **8b** show similar spectral features as that of **7a** and **7b** with the methyl (t-Bu) protons occurring as a singlet in **8b** and integrating to 36 protons at 1.39 ppm. The resonances belonging to the aromatic protons were observed as multiplets between 8.08–9.37 and 7.06–7.44 ppm for complex **7c** and between 7.36–9.22 and 6.73–7.08 ppm for complex **8c** integrating for a total of 48 protons for each complex as expected for aromatic protons.

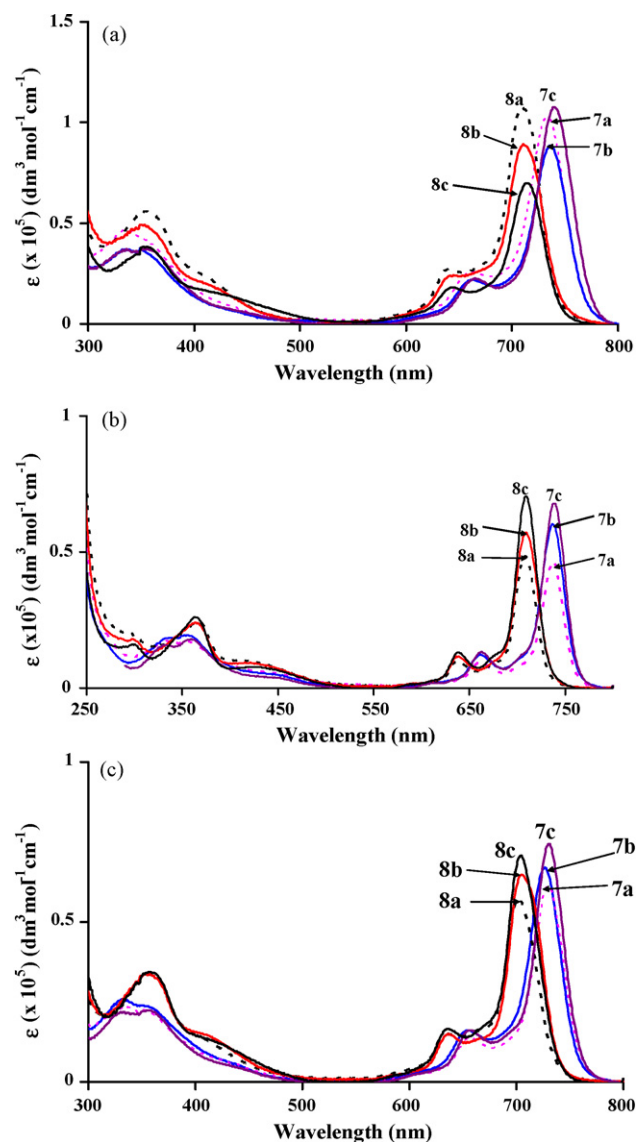


Fig. 1. Ground state electronic absorption spectra of **7a**, **7b**, **8a** and **8b** in (a) DMSO, (b) CHCl_3 and (c) THF. Concentration: $\sim 4 \times 10^{-6} \text{ mol dm}^{-3}$.

Although the presence of isomers for tetra-substituted complexes as well as phthalocyanine aggregation at the concentrations used for the NMR measurements may lead to broadening of the aromatic signals [50], the observed spectra of the complexes were relatively well resolved.

3.2. Ground state electronic absorption and fluorescence spectra

The ground state electronic absorption spectra showed monomeric behaviour evidenced by a single Q-band, typical of metallated phthalocyanine complexes (Fig. 1) [51]. The Q-bands were observed in the near infrared region between 701 to 740 nm with the B-bands between 332 and 364 nm in all the solvents Table 1. An additional broad band was observed between 400 and 460 nm, which may be due to charge transfer from the electron-rich ring to the central metal, this band was more pronounced in the β -substituted complexes compared to their α -substituted counterparts.

The Q-bands of the α -tetra-substituted complexes (**7a**, **7b** and **7c**) are red-shifted by 22–27 nm in DMSO, when com-

pared to the corresponding β -tetrasubstituted (**8a**, **8b** and **8c**) in the respective solvents. Bathochromic shifts are known to occur into the near infrared region on substitution of the Pc ring with electron-donating groups, with a greater effect observed when the substitution is at the non-peripheral (α) positions [52,53]. This has been documented [54,55] to be due to a greater destabilization effect of the HOMO level at the α position compared to the β position since linear combinations of the atomic orbitals (LCAO) coefficients at the α positions of the HOMO level are greater than those at the β positions. This results in a decreased energy gap between the HOMO and LUMO levels and a subsequent bathochromic shift. The Q-band maxima of the complexes were also found to increase in the order, phenoxy < *tert*-butylphenoxy < benzyloxyphenoxy-substituted derivatives in DMSO, Table 1. This may be due to the increase in electron donating ability of these substituents as we move from phenoxy to benzyloxyphenoxy. The trends in the rest of the solvents are not clear, but overall, the phenoxy substituents gave shorter wavelengths compared with the other two substituents. The B-bands are broad in some cases due to the superimposition of the B_1 - and B_2 -bands in the 330–360 nm region [54]. The β -substituted complexes exhibit a rarely observed N-band (Fig. 1b) in the UV transparent solvents; CH_2Cl_2 and CHCl_3 . This arises from the deeper π levels due to LUMO transitions [54]. It can be observed from an overview of the complexes that the shortest Q-band absorption wavelengths are obtained in THF, while the longest are obtained in chloroform and/or DMSO, Table 1. This observation can be explained partly by considering the refractive indices of the solvents. It has been observed that red-shifting of absorption spectra is a function of the solvent's refractive index [56]. The complexes showed monomeric behaviour up to $\sim 1 \times 10^{-5} \text{ mol dm}^{-3}$ in all solvents.

Table 1
Spectral data of MPC complexes in different solvents

Sample	Solvent	$\lambda_{\text{Q-band}}$ (nm)	$\lambda_{\text{B-band}}$ (nm)
7a	DMSO	733	339
	THF	727	333, 357
	CHCl_3	737	347
	DCM	732	345
	Toluene	730	332, 357
7b	DMSO	737	343
	THF	730	356, 331
	CHCl_3	737	347
	DCM	733	349
	Toluene	732	331, 359
7c	DMSO	740	336, 358
	THF	730	333, 356
	CHCl_3	739	331, 359
	DCM	737	332, 358
	Toluene	735	333, 359
8a	DMSO	709	356
	THF	701	354
	CHCl_3	709	366
	DCM	707	359
	Toluene	706	357
8b	DMSO	710	349
	THF	704	356
	CHCl_3	710	363
	DCM	709	358
	Toluene	707	359
8c	DMSO	715	356
	THF	705	357
	CHCl_3	709	364
	DCM	710	358
	Toluene	708	356

Table 2
Spectral, photophysical and photochemical parameters for MPc complexes in DMSO

Complex ^a	λ_Q (nm)	λ_{exc} (nm)	λ_{ems} (nm)	$\log \epsilon$	Φ_F	Φ_T	Φ_{IC}	τ_T (μ s)	Φ_{Δ}	Φ_{Pd} ($\times 10^{-4}$)	S_{Δ} ^b
7a (α Sn)	733	740	747	5.03	0.008	0.79	0.20	50	0.58	4.10	0.73
7b (α Sn)	737	742	747	5.01	0.007	0.76	0.23	40	0.74	4.31	0.97
7c (α Sn)	740	738	745	5.18	0.008	0.69	0.30	30	0.75	6.17	1.08
8a (β Sn)	709	715	721	5.03	0.014	0.89	0.10	40	0.73	2.79	0.82
8b (β Sn)	710	717	723	5.10	0.010	0.75	0.24	40	0.65	1.79	0.87
8c (β Sn)	715	713	719	5.10	0.011	0.71	0.28	30	0.73	4.29	1.01
9a (α Ga)	712	–	–	5.34	0.14	0.62	0.24	230	0.64	1.19	1.03
9b (α Ga)	717	–	–	5.31	0.15	0.54	0.31	350	0.62	2.03	1.14
9c (α Ga)	716	728	717	5.20	0.15	0.77	0.08	280	0.69	0.027	0.98
10a (β Ga)	691	–	–	4.29	0.19	0.61	0.20	350	0.64	2.82	1.04 ^c
10b (β Ga)	697	–	–	5.32	0.20	0.45	0.35	340	0.58	2.32	1.28 ^c
10c (β Ga)	693	704	696	5.24	0.23	0.75	0.02	210	0.62	0.19	0.82
11a (α In)	712	721	732	5.13	0.048	0.78	0.17	40	0.88	0.92	1.12 ^c
11b (α In)	714	725	732	5.20	0.015	0.59	0.39	40	0.92	1.39	1.55 ^c
11c (α In)	716	739	728	5.18	0.013	0.97	0.02	50	0.61	0.03	0.67
12a (β In)	696	706	715	5.09	0.032	0.69	0.28	50	0.87	2.44	1.26 ^c
12b (β In)	696	708	716	5.14	0.019	0.60	0.38	50	0.88	2.14	1.46 ^c
12c (β In)	697	716	709	5.16	0.017	0.91	0.07	50	0.87	0.097	0.95

^a Values for complexes **9**–**12** from Refs. [15,36].

^b $S_{\Delta} = \Phi_{\Delta}/\Phi_T$.

^c Reasons for values >1 explained in Ref. [15].

3.3. Photophysical studies

Photophysical studies were carried out in DMSO. The fluorescence behaviour of all the MPc complexes is similar. The fluorescence excitation and emission spectra of the complexes are typical of phthalocyanine complexes, with Stokes' shifts ($\lambda_{ems} - \lambda_{exc}$) ranging from 7 to 14 nm, Table 2. Fig. 2 shows the fluorescence excitation and emission spectra of complex **8a** in DMSO as an example. The excitation spectra are similar to the absorption spectra and are mirror images to the fluorescence emission spectra for all complexes. However, the Q-band maxima of the absorption and excitation spectra are different, especially for complexes **7a**, **7b**, **8a** and **8b**, with differences of between 5 and 7 nm, Table 2, suggesting a difference in the nuclear configuration of the ground and excited states. This was also observed for InPc derivatives bearing the same substituents as the SnPc complexes discussed in this work, Table 2, but was not observed for the GaPc derivatives. This behaviour may be due to the fact that Sn and In are metals with large atomic numbers that can be displaced from the core of the Pc ring on excitation hence, resulting into a loss of symmetry as it has been observed before in indium phthalocyanines [15]. For complexes **7c** and **8c**, the differences in the maxima of the absorption and excitation spectra were only 2 nm, suggesting that the nuclear configurations of the ground and excited states are similar and are

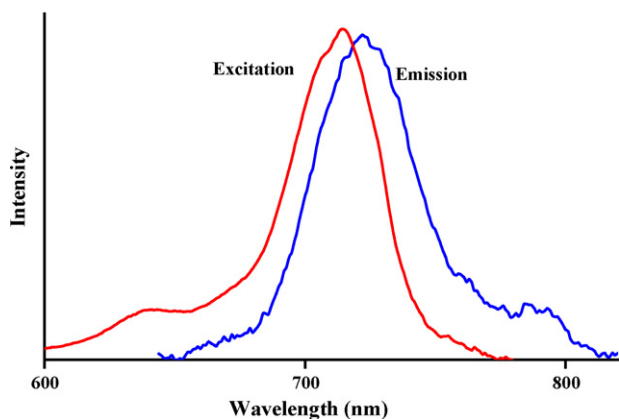


Fig. 2. Fluorescence excitation and emission spectra of **8a** in DMSO. $\lambda_{exc} = 625$ nm.

not affected by excitation in DMSO. This could be explained by the fact that the bulky benzyloxyphenoxy substituent on the periphery of the complexes may shield the central metal from displacement on excitation, for **7c** and **8c**.

The fluorescence quantum yield (Φ_F) values were very low (Table 2) due to the increased strength of spin–orbit (S–O) coupling induced by the presence of the central metal, Sn. This leads to enhancement of intersystem crossing (ISC). An aftermath of enhanced ISC is the reduction in the likelihood of fluorescence. Φ_F was found to be slightly higher in the β -substituted complexes (**8a**, **8b** and **8c**) compared to the α -substituted (**7a**, **7b** and **7c**) ones, suggesting less quenching of the excited singlet state by the former.

The efficiency of a phthalocyanine as a photosensitizer is determined by its triplet quantum yield (Φ_T) and lifetime (τ_T). Enhanced ISC results in high Φ_T and decreased τ_T in complexes **7** and **8** compared to MPcs in general [20] and to the standard ZnPc ($\Phi_T = 0.65$ [43]), Table 2. Compared to GaPc and InPc derivatives containing the same substituent, Scheme 1 (complexes **9**–**12**), SnPc derivatives show larger Φ_T values for the phenoxy and *tert*-butylphenoxy-substituted derivatives due to the large atomic number of the central metal, Sn, but the values were lower in the benzyloxyphenoxy-substituted derivatives (**7** and **8**). The τ_T values were comparable to those of InPc derivatives, Table 2 [15,36]. There was no clear general trend on the effect of the α (**7a**, **7b** and **7c**) versus β (**8a**, **8b** and **8c**) substitution in the Φ_T values of the complexes but the Φ_T values were found to decrease in the order phenoxy substituted (**7a** and **8a**) > *tert*-butylphenoxy substituted (**7b** and **8b**) > 4-benzyloxyphenoxy-substituted (**7c** and **8c**) derivatives. This could be due to a concept called the “loose bolt” effect [57] for the *tert*-butyl phenoxy and benzyloxyphenoxy-substituted SnPc complexes (**7b** and **8b**; **7c** and **8c**). The effect is associated with the vibrations of the bonds set off by the parent molecule in a similar way as a loose bolt in a moving part of the machine, which tends to be set in motion by the other moving parts of the machine. The σ C–H bonds of these bulkier substituents may show this effect. The effect increases the rate of internal conversion as electronic energy is lost through C–H vibrations [57,58], hence lower Φ_T values. The “loose bolt” effect is expected to be less pronounced in the phenoxy-substituted SnPc complexes (**7a** and **8a**) since they have less C–H bonds.

The triplet lifetimes, τ_T were generally low for complexes **7** and **8** as shown in Table 2 which is not unexpected since they exhibit

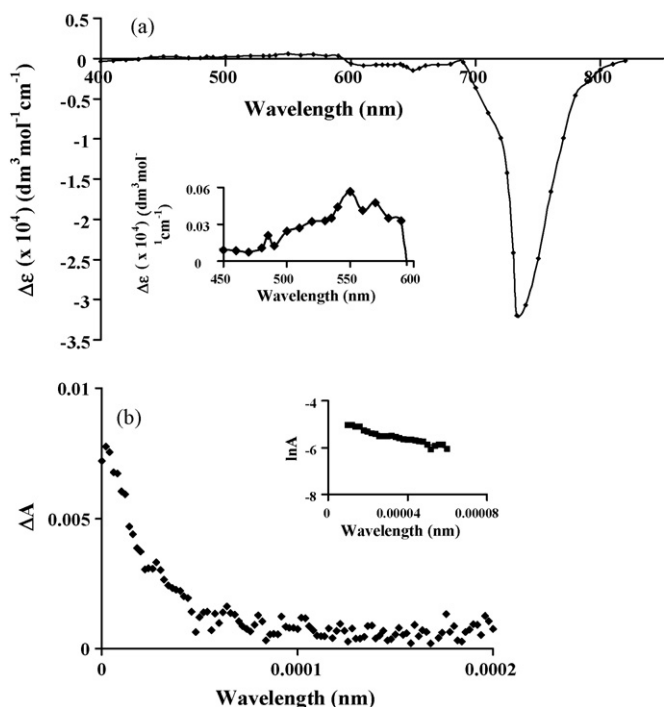


Fig. 3. (a) Transient absorption spectrum for **7a** in DMSO. Inset = magnification of the 450–600 nm area and (b) triplet decay curve of **7a**. Inset: plot of $\ln A$ versus time for **7a** in DMSO. $[7a] = \sim 1.4 \times 10^{-5} \text{ mol dm}^{-3}$, $\lambda_{\text{exc}} = 733 \text{ nm}$.

high triplet quantum yields. Fig. 3a shows the transient absorption curve of **7a**. The transient absorption curve shows the absorption of the triplet state is centered at 550 nm for complex **7a**. The triplet absorption maxima were also obtained at $\sim 550 \text{ nm}$ for all the other complexes. Monoexponential triplet decay curves are maintained even with the presence of the central metal with large atomic number as shown in Fig. 3b. Plot of $\ln A$ versus time (Fig. 3b, inset) is linear, showing a first order dependence of the triplet state.

There was a change in the absorption spectra following laser irradiation for complexes **7** and **8**, as shown in Fig. 4 for **7a**. The changes involved a decrease in the Q-band and increases in the 500–650 nm region, with an isosbestic point at 640 nm. These increases disappeared gradually on exposure of the solution to air and the Q-band increased in intensity suggesting that the emerged bands were due to reduction products of the complexes. The ease of reduction of SnPc complexes in the presence of light is well

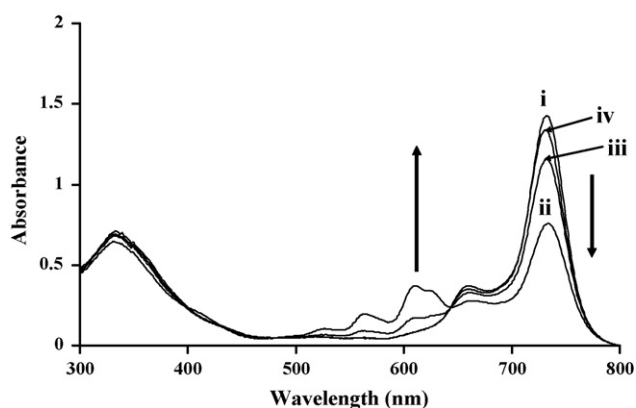
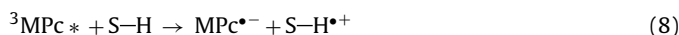


Fig. 4. Absorption spectral changes of compound **7a** before (i) and after (ii) laser irradiation. (iii) and (iv) show spectra on exposure of laser irradiated solution to air for 2 and 5 min, respectively.

documented as stated in the introduction [30–32]. The first ring reduction in MPc complexes was characterized by a decrease in the Q-band and the formation of weak bands between 500 and 600 nm [59]. Thus during laser irradiation, the complexes were partly transformed to an anion (Pc^{-3}). The mechanism for the photoreduction of MPc complexes in the presence of light has been suggested to involve H atoms from the solvent during the production of Pc^{-3} [15,46,60]:



The Φ_{IC} values were generally low (≤ 0.2) showing that the photoactivity of the complexes is high in DMSO.

3.4. Photochemical studies

Energy transfer between the triplet state of photosensitizers and ground state molecular oxygen leads to the production of singlet oxygen, Φ_{Δ} . Therefore, singlet oxygen quantum yield which is the efficiency of singlet oxygen generation, should depend on the triplet state quantum yield and lifetime, the efficiency of energy transfer, which depends on the energy of the triplet state and the ability of the substituents to quench the triplet state amongst other factors. In general the Φ_{Δ} values are expected to be related to Φ_{T} values. Table 2 shows that even though **7c** had the lowest Φ_{T} value, its Φ_{Δ} was not the lowest, and this may be due to the photoreduction occurring following laser irradiation. Though photoreduction occurred in all the complexes, it may have been enhanced in the benzyloxyphenoxy-substituted derivatives due to more electron donating ability of this substituent compared to the phenoxy or *tert*-butylphenoxy substituents. S_{Δ} which represents the efficiency of quenching of the triplet excited state by singlet oxygen, is near unity for complexes **7a**, **7b**, **8a** and **8b** (Table 2), suggesting efficient quenching of the triplet state by singlet oxygen. It was however slightly higher than unity in complexes **7c** and **8c** due to the low Φ_{T} values as a result of photoreduction following laser irradiation as discussed above. Photoreduction was not experienced during singlet oxygen quantum yield determinations because of the presence of oxygen during such determination.

The stability of MPc complexes in the presence of light plays an important role in their functionality and therefore it is vital to determine the stability of these complexes when exposed to light and determine any possible pathways of degradation. The photodegradation studies were done in air-saturated solutions, using the experimental set-up described in Section 2. Complexes **7** and **8** exhibited stability within the same range, with Φ_{pd} of the order of 10^{-4} , which is higher than reported for some known MPc derivatives [20] but the values are in the range for GaPc and InPc phenoxy and *tert*-butylphenoxy-substituted derivatives. No photoreduction (to other species absorbing in the visible region) of the complexes was observed during photodegradation studies.

In order to further confirm if the photoreduction that occurred after laser irradiation (performed in argon) also occurred during photodegradation, the latter experiments were repeated in solvent solutions that were argon purged or oxygen saturated. Fig. 5a and b shows typical set of curves for each of these experiments for complex **7c**. Similar results were obtained for other complexes. The photobleaching was very slow in argon purged solutions Fig. 5b (the little that occurred was due to some residual oxygen), compared to solutions containing oxygen Fig. 5a and in air only (figure not shown). Bubbling with oxygen resulted in enhanced photodegradation Fig. 5a compared to in air or in argon only, Fig. 5b due to the increased kinetics. Fig. 5b shows that in the presence of argon there

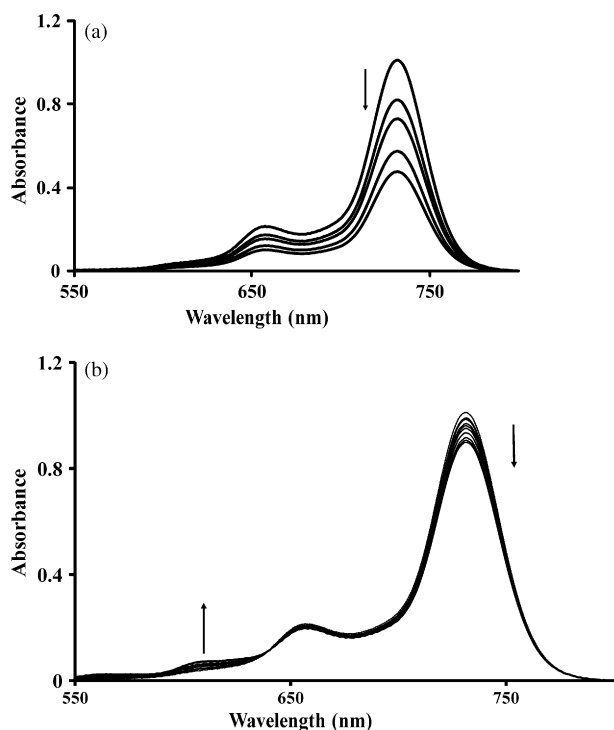


Fig. 5. Photodegradation curves of complex **7c** in DMSO in the presence of oxygen (10 min bubbling) (a) and argon (10 min bubbling) (b).

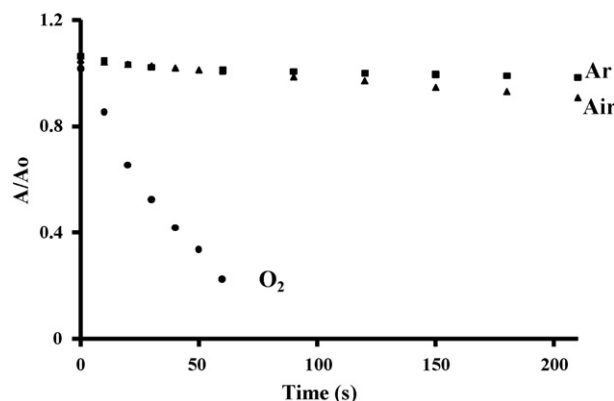


Fig. 6. Kinetic plots for the photodegradation curves of complex **7c** in DMSO in argon (Ar), air and oxygen (O_2).

was some photoreduction (as judged by increase in the absorption between 550 and 600 nm) as was observed for laser flash photolysis, but to a lesser extent in the former.

Oxidative attack on the excited triplet state of MPCs by singlet oxygen brings about photodegradation, since the triplet state is sufficiently long lived to participate in photochemical reactions. It is believed that singlet oxygen has the ability to react with macrocyclic metal complexes [61,62]. Fig. 6 shows the kinetic plots for the photodegradation in the different media, and the results all point to the involvement of singlet oxygen in the photodegradation process.

4. Conclusions

Peripherally and non-peripherally phenoxy, *tert*-butyl phenoxy and 4-benzyloxyphenoxy tetra-substituted tin(IV) phthalocyanines have been synthesized and shown to be monomeric in various organic solvents. The photophysical and photochemical param-

eters of the complexes reveal that the complexes would find use in applications requiring photosensitizers. A difference in the nuclear configuration of the ground and excited states was observed in the complexes due to the central metal (tin) with large atomic number leading to a displacement of the metal from the core of the phthalocyanine ring, hence a loss of symmetry, which is more pronounced on excitation.

Photoreduction of the complexes was observed during photolysis in the absence of oxygen due to ring reduction. Photodegradation was found to be dependent upon the singlet oxygen generating capabilities of the complexes.

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