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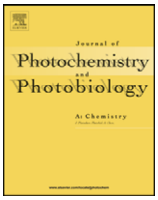

Solvent and central metal effects on the photophysical and photochemical properties of peripherally tetra mercaptopyridine substituted metallophthalocyanines

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ABSTRACT

The synthesis of peripherally tetra 2-mercaptopyridine substituted phthalocyanines containing Si, Ga, Sn and In as central metal ions is reported for the first time in this study. Photophysical and photochemical studies were carried out on these compounds in order to determine the potential of the complexes as photosensitizers for use in photodynamic therapy. Fluorescence quantum yields (Φ_F) ranged from 0.012 to 0.2 and triplet quantum yields (Φ_T) from 0.54 to 0.89 in dimethylformamide (DMF) and from 0.65 to 0.93 in dimethylsulfoxide (DMSO). The triplet lifetimes ranged from 20 to 130 μs, the low values are due to the heavy atom effects of the central metal. The triplet lifetimes were larger in DMSO when compared with DMF.

1. Introduction

The study of phthalocyanines (Pcs) has been carried out quite extensively over the past decades. Phthalocyanines have diverse applications in many fields of science and as a result they have gained widespread attention in research. These complexes may be exploited as dyes and pigments, sensors, electronic devices, in non-linear optics, Langmuir–Blodgett films and as photosensitizers in photodynamic therapy (PDT) [1–7].

PDT is a non-invasive binary therapy for the treatment of small tumours and it involves the use of visible light in combination with a photosensitizer [8–10]. During the course of PDT, the photosensitizer is thought to be excited to its triplet state. In this metastable state the photosensitizer then transfers energy to the ground state oxygen $^3O_2$ ($^3\Sigma_g{}^-$) resulting in the generation of the excited state singlet oxygen $^1O_2$ ($^1\Delta_g$) which is the main cytotoxic species through the type II mechanism [10].

Phthalocyanines are generally known to be insoluble in common organic solvents. The solubility of these complexes is improved by introduction of substituents onto the phthalocyanine ring [11–14]. The presence of substituents on the ring is known to cause significant changes in the photophysical, photochemical and spectral properties of phthalocyanine complexes [15].

The nature and presence of the central metal ion strongly influences the photophysical behaviour of metallophthalocyanines (MPcs). It is known that diamagnetic ions with a closed shell such as Zn^{2+}, Al^{3+}, Si^{4+} result in both high triplet quantum yields (Φ_T) and long triplet lifetimes (τ_T) [16,17]. Apart from AlPc and SiPc, there has been less attention paid to the other group 5 and 6 metals or metalloids for possible use in PDT. Large central metals such as indium increase Φ_T but decrease τ_T values. Also excitation of MPcs containing large metals such as In leads to loss of symmetry [14] which is observed as a split or broadening in the Q band. Thus MPc complexes containing large central metals are of interest.

In this work the photophysical and photochemical properties of the synthesised tetra {2,(3)-(2-mercaptopyridine) phthalocyaninato} (MTMPyPc) complexes of Si, Ga, In, and Sn whose synthetic procedure is shown in Scheme 1 are presented here for the first time. The MPc's were linked to pyridine groups by sulfur. The sulfur leads to red shifting of the Q band in the MPc which may enhance their photochemical and photophysical properties.

2. Experimental

2.1. Materials

Phthalimide, 1-pentanol, 2-mercaptopyridine, 1,3-diphenylisobenzofuran (DPBF) and silicon tetrachloride, gallium(III)chloride,

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indium(III)chloride, and tin(II)chloride were obtained from Sigma–Aldrich. Potassium carbonate, ethanol, tetrahydrofuran (THF), chloroform, hexane, diethylether, acetone, and dimethylformamide (DMF), were obtained from Saarchem. Pyridine, dimethyl sulphoxide (DMSO) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) were obtained from Fluka. 4-(2-Mercaptopyridine)phthalonitrile (**2**) was synthesised and purified according to reported methods [18]. Ultra pure water was obtained from a Milli-Q Water System (Millipore Corp, Bedford, MA, USA).

2.2. Equipment

Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. UV–visible spectra were recorded on a Varian 500 UV–Vis/NIR spectrophotometer.

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 MAX5100 (Mol-electron detector incorporated) power meter and were found to be 1.25×10^{16} photons s^{-1} cm^{-2} for singlet oxygen studies.

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 ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a digital real-time oscilloscope (Tektronix TDS 360). The triplet lifetimes were determined by exponential fitting of the kinetic curves using the program OriginPro 7.5. Elemental analyses were carried out on a Vario EL III MicroCube CHNS Analyzer.

2.3. Photophysical studies

2.3.1. Fluorescence quantum yield determinations

Fluorescence quantum yields (Φ_F) were determined by a comparative method [19], using Eq. (1):

$$\Phi_F = \Phi_{F(Std)} \frac{F A_{Std} n^2}{F_{Std} A n_{Std}^2} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence curves of the MPc derivatives and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, and n and n_{Std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc in DMSO was used as a standard, $\Phi_F = 0.20$ [20], for the determination of fluorescence quantum yields. The sample and the standard were both excited at the same relevant wavelength. The fluorescence quantum yields for the MPc complexes are represented as $\Phi_{F(MPc)}$ (where MPc represents $(Cl)_2$SiTMPyPc, (Cl)GaTMPyPc, (Cl)InTMPyPc and, SnTMPyPc).

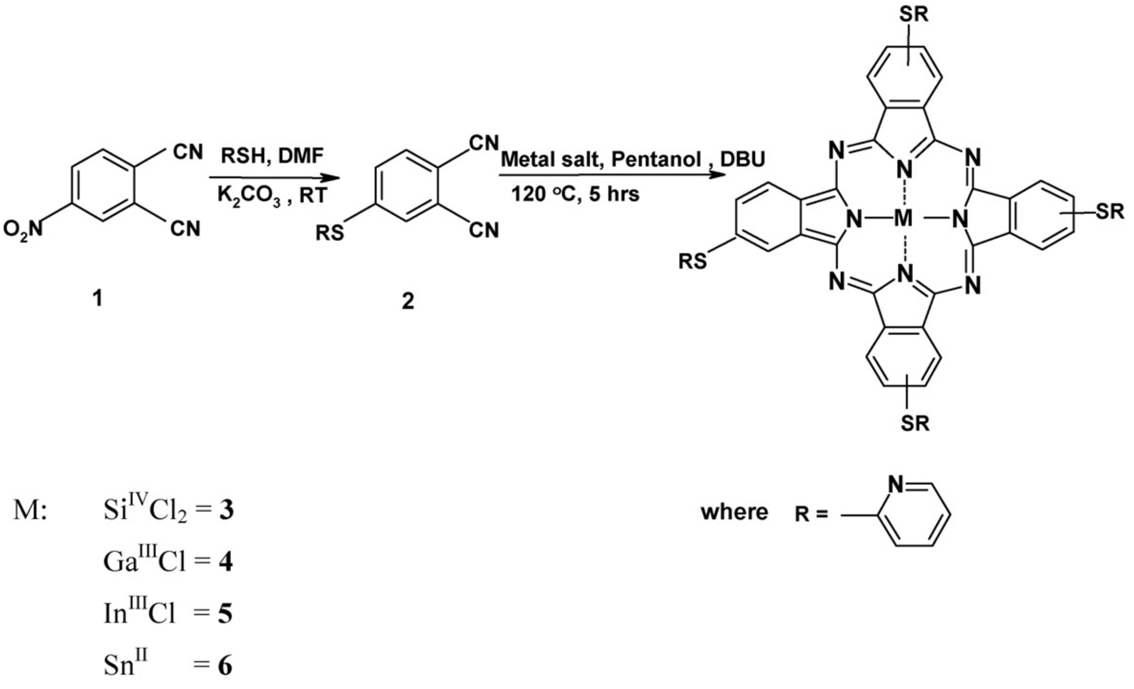
2.3.2. Triplet state quantum yields and lifetimes

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

$$\Phi_T^{Sample} = \Phi_T^{Std} \frac{\Delta A_T^{Sample}\ \varepsilon_T^{Std}}{\Delta A_T^{Std}\ \varepsilon_T^{Sample}} \tag{2}$$

where ΔA_T^{Sample} and ΔA_T^{Std} are the changes in the triplet state absorbance of the MPc derivatives and the standard, respectively. ε_T^{Sample} and ε_T^{Std} are the triplet state extinction coefficients for the MPc derivative and standard (ZnPc), respectively. Φ_T^{Std} is the triplet state quantum yield for the standard, ZnPc in DMSO, $\Phi_T^{Std} = 0.65$ [21] and in DMF, $\Phi_T^{Std} = 0.58$ [22]. Φ_T was determined for the MPcs and is represented as $\Phi_{T(MPc)}$ and the corresponding triplet lifetime as $\tau_{T(MPc)}$.

Quantum yields of internal conversion (Φ_{IC}) were obtained from Eq. (3). This equation assumes that only three processes



Scheme 1. Synthetic route of 2-mercaptopyridine tetra substituted metallophthalocyanine derivatives.

(fluorescence, intersystem crossing (ISC) and internal conversion), jointly deactivate the excited singlet state of the MPc derivatives.

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_T) \tag{3}$$

Natural or radiative lifetimes (τ_N) (hence fluorescence lifetimes) were determined with the use of the program PhotochemCAD [23]. This determination is based on the Strickler Berg equation [24].

The determined fluorescence lifetimes and $\Phi_{F,}$ Φ_T and Φ_{IC} values were used to calculate the rate constants of the processes deactivating the excited singlet state, which are fluorescence (k_F), intersystem crossing (k_{ISC}) and internal conversion (k_{IC}) rate constants.

2.3.3. Singlet oxygen quantum yields

The singlet oxygen quantum yield (Φ_Δ) determinations were carried out using an experimental set-up that is described in detail elsewhere [25]. In this work Φ_Δ values were determined using DPBF as a singlet oxygen quencher and ZnPc as a standard, Eq. (4):

$$\Phi_\Delta = \Phi_\Delta^{Std} \frac{W_{DPBF} I_{abs}^{Std}}{W_{DPBF}^{Std} I_{abs}} \tag{4}$$

where Φ_Δ^{Std} is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_\Delta^{Std} = 0.67$ [26] in DMSO and $\Phi_\Delta^{Std} = 0.56$ [27] in DMF), and W_{DPBF} and W_{DPBF}^{Std} are the DPBF photobleaching rates in the presence of the MPc derivatives under investigation and the standard (ZnPc), respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by the MPc complexes and the standard, respectively. The initial DPBF concentration used was kept the same for both the MPc complexes and ZnPc. The molar extinction coefficients for DPBF at λ = 417 nm have been reported to be: ε = 23,000 dm^3 mol^{-1} cm^{-1} (DMSO) and ε = 23,000 dm^3 mol^{-1} cm^{-1} (DMF) [28].

2.3.4. Synthesis

The method of synthesis that has been employed in this work is known and has been used to date to synthesise the corresponding Zn, Mn phthalocyanine derivatives [18,29], but it has not been used to synthesise the Si, Ga, Sn and In MPc complexes.

2.3.4.1. [2,(3)-Tetra-(2-mercaptopyridine)phthalocyaninato silicon(IV)]Cl$_2$ (3,(Cl)$_2$SiTMPyPc Scheme 1). A mixture of SiCl$_4$ (0.25 g, 1.5 mmol), 4-(2-mercaptopyridine)phthalonitrile (**2**) (0.5 g, 2.1 mmol), DBU (1.66 mL, 12 mmol) and 1-pentanol (10 mL) was stirred at 160 °C for 5 h under nitrogen atmosphere. After cooling, the solution was mixed with n-hexane. The green solid product was precipitated and collected by filtration and washed with n-hexane. The crude product was re-dissolved in DMF. After concentrating, the green product was precipitated with hot ethanol and filtered then washed with ethanol, acetone, n-hexane and diethyl ether. The green product was further purified by passing through a column of biobeads Sx-1 using DCM as the eluting solvent. Yield: 0.298 g (50%). UV/vis (DMSO): λ_{max} nm (log ε); 692 (5.07), 623 (4.39), 368 (4.66); IR (KBr): ν_{max}/cm^{-1}; 3052 (ν_{Ar-H}), 1337 ($\nu_{C=C}$), 1093 (ν_{C-S-C}). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.48–8.52 (dd, 4H, Pyridyl-H), 8.12–8.097 (s, 4H, Pc-H), 7.94–7.88 (d, 4H, Pyridyl-H), 7.85 (m, 8H, Pyridyl-H), 7.83–7.77 (d, 8H, Pc-H). Calc. for $C_{56}H_{46}N_{12}S_4SiCl_2$: C 59.59; H 2.69; N 16.06; S 12.24. Found: C 58.75, H 3.22, N 14.95, S 11.41.

2.3.4.2. [2,(3)-Tetra-(2-mercaptopyridine)phthalocyaninato gallium(III)]Cl (4,(Cl)GaTMPyPc, Scheme 1). The method employed for synthesis of **4** was the same as used for **3**, except GaCl$_3$ instead of SiCl$_4$ was employed. The amounts of all the reagents were the same (in terms of mmol) as for **3**. Yield: 0.215 g (39%). UV/vis (DMSO): λ_{max} nm (log ε); 691 (5.43), 624 (4.65), 363 (4.68); IR (KBr): ν_{max}/cm^{-1}; 3061 (ν_{Ar-H}), 1312 ($\nu_{C=C}$), 1077 (ν_{C-S-C}). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 9.86–9.76 (d, 4H, Pyridyl-H), 9.7–8.56 (d, 8H, Pc-H), 7.89–7.82 (dd, 4H, Pyridyl-H), 7.61–7.46 (m, 8H, Pyridyl-H), 7.36–7.33 (bs, 4H, Pc-H). Calc. for $C_{56}H_{46}N_{12}S_4GaCl$: C 59.24; H 2.68; N 15.95; S 12.16. Found: C 58.99, H 3.61, N 15.95, S 10.47.

2.3.4.3. [2,(3)-Tetra-(2-mercaptopyridine)phthalocyaninato indium(III)]Cl (5,(Cl)InTMPyPc, Scheme 1). The method employed for synthesis of **5** was the same as used for **3**, except InCl$_3$ instead of SiCl$_4$ was employed. The amounts of all the reagents were the same (in terms of mmol) as for **3**. Yield: 0.126 g (54%). UV/vis (DMSO): λ_{max} nm (log ε); 698 (5.09), 630 (4.47), 360 (4.65); IR (KBr): ν_{max}/cm^{-1}; 3067 (ν_{Ar-H}), 1335 ($\nu_{C=C}$), 1091 (ν_{C-S-C}). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 9.25 (m, 8H, Pyridyl-H), 8.58 (d, 8H, Pc-H), 7.45 (dd, 4H, Pyridyl-H), 7.3 (s, 4H, Pc-H), 7.07 (d, 4H, Pyridyl-H). Calc. for $C_{56}H_{46}N_{12}S_4InCl$: C 56.81; H 2.57; N 15.29, S 11.67. Found: C 57.51, H 2.96, N 14.53, S 11.10.

2.3.4.4. [2,(3)-Tetra-(2-mercaptopyridine)phthalocyaninato tin(II)] (6,SnTMPyPc, Scheme 1). The method employed for synthesis of **6** was the same as used for **3**, except SnCl$_2$ instead of SiCl$_4$ was employed. The amounts of all the reagents were the same (in terms of mmol) as for **3**. Yield: 0.137 g (48%). UV/vis (DMSO): λ_{max} nm (log ε); 711 (4.32), 636 (3.63), 373 (3.84); IR (KBr): ν_{max}/cm^{-1}; 3050 (ν_{Ar-H}), 1336 ($\nu_{C=C}$), 1080 (ν_{C-S-C}). ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 8.50–8.47 (m, 8H, Pyridyl-H), 7.95–7.79 (d, 8H, Pc-H), 7.86–7.11 (s, 4H, Pc-H), 7.32–7.295 (d, 8H, Pyridyl-H). Calc. for $C_{56}H_{46}N_{12}S_4Sn$: C 58.49; H 2.64; N 15.73; S 12.01. Found: C 58.8, H 3.39, N 14.2, S 10.83.

3. Results and discussion

In general, the synthesis of SnPc complexes using SnCl$_2$ may result in the formation of Sn(II)Pc or (Cl)$_2$Sn(IV)Pc species depending on the amount of SnCl$_2$ used in the reaction [30,31]. With excess SnCl$_2$, Sn(II)Pc derivatives (SnTMPyPc) are formed as is the case in this work. For the rest of the complexes: (Cl)$_2$SiTMPyPc, (Cl)GaTMPyPc and (Cl)InTMPyPc, the central metals have their usual oxidation states. The presence of chloride axial ligands (with weak metal-halide vibrations in the 320–350 cm^{-1} region) was confirmed by IR spectroscopy.

After conversion into gallium, tin, silicon or indium phthalocyanines, the characteristic C≡N stretch at ~2230 cm^{-1} of phthalonitrile **2** disappeared, indicative of metallophthalocyanine formation. Generally, phthalocyanine complexes are insoluble in most organic solvents; however introduction of substituents on the ring increases the solubility. All complexes (**3**–**6**) exhibited excellent solubility in organic solvents such as dichloromethane, chloroform, THF, DMF, and DMSO. The new compounds were characterized by UV–vis, IR and NMR spectroscopies, and elemental analysis and the analyses are consistent with the predicted structures as shown in the experimental section, with the percent carbon values differing by less than 1% from the calculated values.

The ^{1}H NMR spectra of tetrasubstituted phthalocyanine derivatives (**3**–**6**) show complex patterns owing to the mixed isomer character of these compounds. The complexes were found to be pure by ^{1}H NMR with all the substituents and ring protons observed in their respective regions.

3.1. Absorption and fluorescence spectra

The absorbance and fluorescence emission spectra of MTMPyPc (M = Si, Ga, Sn, and In) complexes in DMSO are shown in Fig. 1a–d. The MPc complexes obeyed Beer's law for concentrations ranging from 2.0 × 10^{-6} to 1 × 10^{-5} mol dm^{-3} and all showed a monomeric behaviour in DMSO, DMF, THF, CHCl$_3$, and DCM. It has been reported

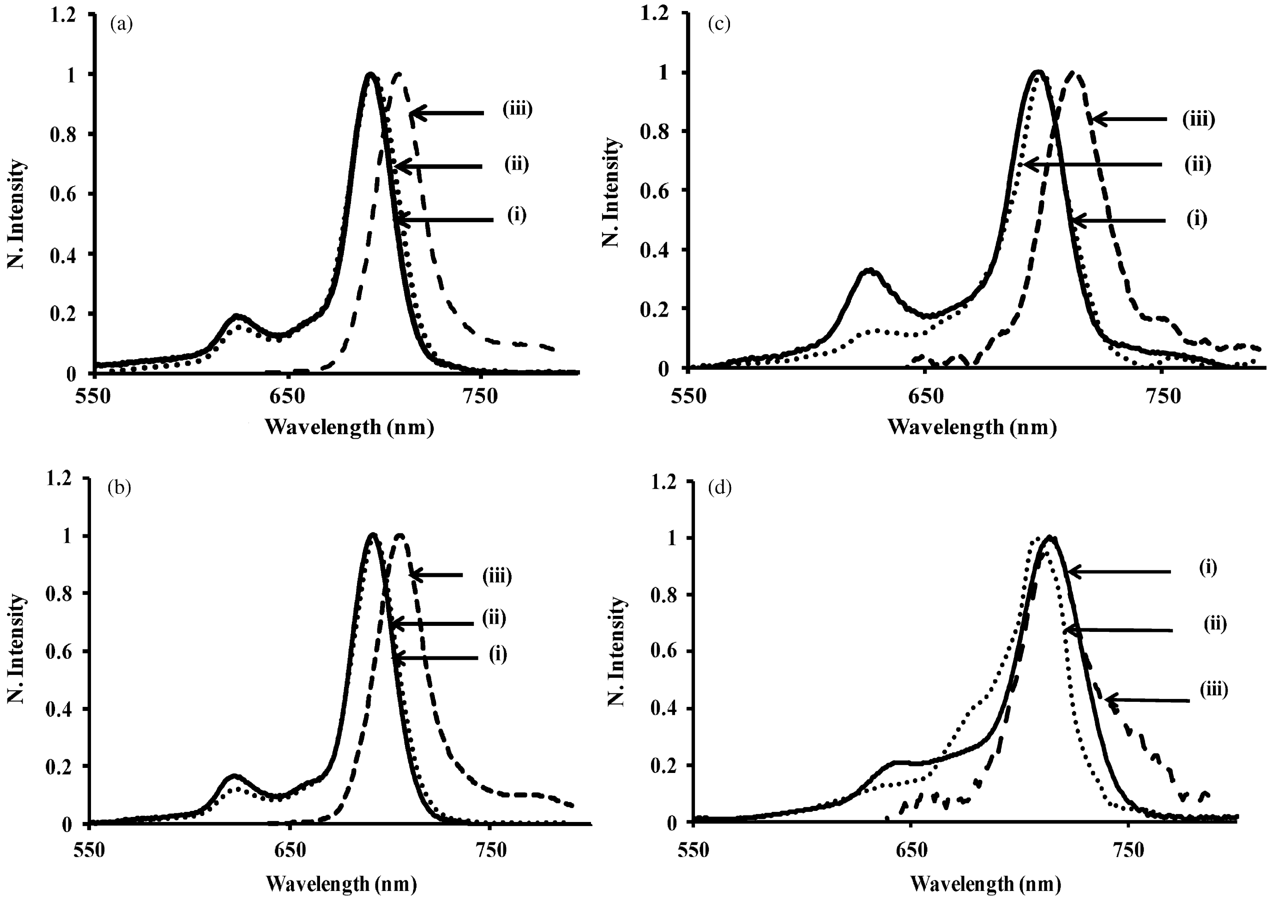


Fig. 1. Absorbance (i), excitation (ii) and emission (iii) spectra of (a) (Cl)$_2$SiTMPyPc, (b) (Cl)GaTMPyPc, (c) (Cl)InTMPyPc and (d) SnTMPyPc in DMSO (excitation wavelength = 620 nm).

that a shift in the Q band to the red occurs with increase in the refractive index of the solvent [28]. The red shifting of the Q band with increase in refractive index of the solvent is not clear in Table 1. In general a red shift in the Q band was observed with increase in size of the central metal and the order of the Q band positions is SnTMPyPc > (Cl)InTMPyPc > (Cl)GaTMPyPc ≅ (Cl)$_2$SiTMPyPc. This trend in Q band positions can be explained through a consideration of the degree of destabilization of the highest occupied molecular orbital (HOMO) in the MPc complexes. Since tin (Sn) has more electrons in its atomic structure it has greater reducing properties than the rest of the central metal ions and thus will destabilize the HOMO more than In, Ga and Si. Consequently, the greater destabilization

Table 1
Absorbance and fluorescence data for MPc complexes in different solvents.

Solvent	MPc	Q band λ_{max} (nm)	Fluorescence emission[a] λ_{max} (nm)	Stokes shift $\Delta\lambda_{stokes}$ (nm)	Log ε
DMSO	(Cl)$_2$SiTMPyPc	692	705	13	5.07
	(Cl)GaTMPyPc	691	703	12	5.43
	(Cl)InTMPyPc	698	710	12	5.09
	SnTMPyPc	711	711	0	4.32
DMF	(Cl)$_2$SiTMPyPc	689	702	13	5.06
	(Cl)GaTMPyPc	688	702	14	5.20
	(Cl)InTMPyPc	690	695	5	4.96
	SnTMPyPc	705	710	5	4.23
$CHCl_3$	(Cl)$_2$SiTMPyPc	702	712	10	5.20
	(Cl)GaTMPyPc	702	711	9	5.13
	(Cl)InTMPyPc	704	712	8	5.08
	SnTMPyPc	710	721	11	4.37
DCM	(Cl)$_2$SiTMPyPc	702	712	10	5.09
	(Cl)GaTMPyPc	702	711	9	5.17
	(Cl)InTMPyPc	703	710	7	4.99
	SnTMPyPc	710	723	13	4.5
THF	(Cl)$_2$SiTMPyPc	694	707	13	5.17
	(Cl)GaTMPyPc	693	703	10	5.22
	(Cl)InTMPyPc	701	709	8	4.98
	SnTMPyPc	709	718	9	4.55

[a] Excitation at 620 nm for all MTMPyPc derivatives.

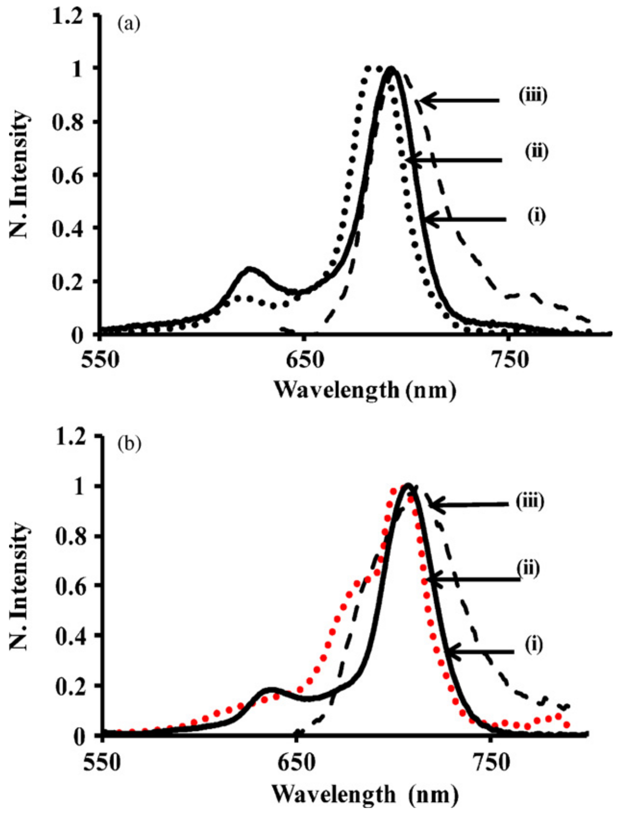


Fig. 2. Absorbance (i), excitation (ii) and emission (iii) spectra of (a) (Cl)InTMPyPc and (b) SnTMPyPc in DMF (excitation wavelength = 620 nm).

resulting from tin will result in a smaller HOMO–LUMO separation, hence the largest red-shifted spectra.

For the MTMPyPc complexes (Fig. 1) in DMSO, the fluorescence emission spectra were mirror images of the absorption spectra for Si (**3**), Ga (**4**) and In (**5**) phthalocyanine derivatives. For the SnPc derivative (**6**), excitation spectra were different from the absorption spectrum in that the excitation spectrum was split and blue shifted from the absorption spectrum, indicating a change of symmetry on excitation, most likely due to demetallation [32]. The loss of symmetry upon excitation for MPc complexes containing large central metals has been reported before for InPc [14], PbPc [32] and HgPc [15] derivatives.

In DMF, for (Cl)GaTMPyPc (**4**) and $(Cl)_2SiTMPyPc$ (**3**), the absorption and excitation spectra were similar and mirror images of emission. However for (Cl)InTMPyPc (**5**) and SnTMPyPc (**6**) derivatives (Fig. 2), there was broadening or splitting in the Q band of the excitation spectra and the excitation spectra was slightly blue shifted compared to absorption spectra, again indicative of loss of symmetry on excitation. Stokes shifts observed as shown in Table 1 ranged from 0 to 14 nm. Stokes shift were very small for **5** and **6**, Table 1.

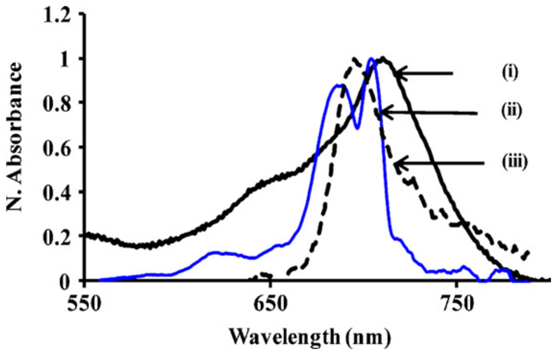


Fig. 3. Absorbance (i), excitation (ii) and emission (iii) spectra of SnTMPyPc (**6**) in DMF (excitation wavelength = 620 nm) when left standing for about an hour.

The splitting in the Q band of the excitation spectra was reported [33] for InPc derivatives (but not for corresponding GaPc derivatives), and the difference in the behaviours of ClGaPc and ClInPc on excitation was attributed to the larger In metal being more displaced from the core of the Pc ring, and the displacement being more pronounced on excitation hence a loss of symmetry [33]. Similarly in this work, the differences in the fluorescence behaviour of InPc and SnPc compared to GaPc and SiPc could be attributed to the large sizes of the former pair. The observation of the emission spectra occurring at higher energy compared to absorption, is a result of the loss of symmetry on excitation due to demetallation, thus emission occurs from the demetallated species, hence the blue shift. In DCM, $CHCl_3$ and THF, again SiPc and GaPc derivatives showed excitation spectra similar to absorption spectra and mirror images of the emission spectra. And the excitation spectra was split or broad for InPc and SnPc derivatives for the same reasons given above.

A split in the Q band of the excitation spectra for **5** and **6** in DMSO and DMF was clearer when the solution was left standing for a while before recording the spectra, Fig. 3 (for complex **6** in DMF). Broadening of the absorption and emission spectra was also observed coupled to the clear splitting of the excitation spectra. As stated above, the split of the Q band in the excitation spectra may be attributed to the lowering of symmetry following excitation of the complexes [32]. The other reason being that Sn^{2+} and In^{3+} central metal ions are quite large and as a result these central metal ions in the MPc molecules protrude out of the planar phthalocyanine ring, making the molecules prone to loss of symmetry.

3.2. Fluorescence quantum yields, lifetimes and rate constants

Fluorescence quantum yield (Φ_F) values of the MPc complexes are shown in Table 2 for excitation at 620 nm in both DMSO and DMF and were calculated by use of Eq. (1). The Φ_F values of

Table 2
Photophysical parameters for $(Cl)_2SiTMPyPc$, (Cl)GaTMPyPc, (Cl)InTMPyPc and SnTMPyPc.

Solvent	MPc	$\Phi_{F(MPc)}$ λ_{exc} = 620 nm	$\tau_{F(MPc)}$/ns	$\Phi_{T(MPc)}$	$\tau_{T(MPc)}$/μs	Φ_{IC}	Φ_Δ	S_Δ[a]	$k_F/10^{-8}\ s^{-1}$[b]	$k_{ISC}/10^{-9}\ s^{-1}$[b]	$k_{IC}/10^{-8}\ s^{-1}$[b]
DMSO	$(Cl)_2SiTMPyPc$	0.2	13.18	0.80	130	0	0.62	0.78	0.15	0.061	–
	(Cl)GaTMPyPc	0.3	1.59	0.65	110	0.05	0.34	0.52	1.89	0.409	0.31
	(Cl)InTMPyPc	0.03	0.24	0.93	60	0.04	0.33	0.35	1.25	3.88	1.67
	SnTMPyPc	0.012	0.49	0.88	40	0.11	0.59	0.67	0.55	1.79	2.24
DMF	$(Cl)_2SiTMPyPc$	0.2	11.82	0.62	80	0.18	0.47	0.76	0.17	0.053	0.15
	(Cl)GaTMPyPc	0.26	2.09	0.54	20	0.20	0.33	0.61	1.25	0.25	0.96
	(Cl)InTMPyPc	0.03	0.26	0.89	50	0.08	0.53	0.59	1.15	3.42	3.08
	SnTMPyPc	0.04	2.96	0.75	30	0.21	0.57	0.76	0.39	0.25	0.71

[a] $S_\Delta = \Phi_\Delta/\Phi_T$.

[b] $k_{ISC} = \Phi_T/\tau_F$, $k_F = \Phi_F/\tau_F$, and $k_{IC} = \Phi_{IC}/\tau_F$.

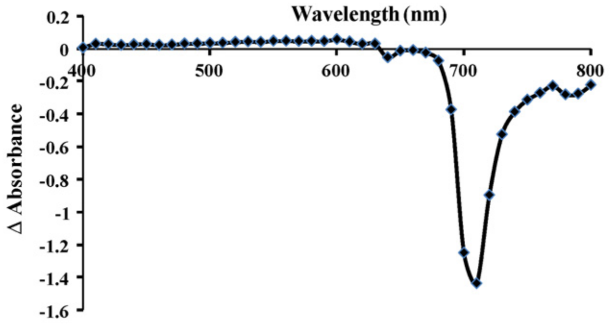


Fig. 4. A transient differential spectrum for $(Cl)_2$SiTMPyPc (excitation wavelength = 692 nm in DMSO).

the MTMPyPc complexes decreased in the order (Cl)GaTMPyPc > $(Cl)_2$SiTMPyPc > (Cl)InTMPyPc > SnTMPyPc in DMSO. The same trend was observed in DMF, except (Cl)InTMPyPc and SnTMPyPc had about the same Φ_F value within experimental error. For SnTMPyPc in DMSO and SnTMPyPc and (Cl)InTMPyPc in DMF, the Φ_F values are due to the demetallated species. However, the In and Sn central metals are still in solution hence affecting Φ_F values. Thus InPc and SnPc derivatives give small Φ_F values due to the heavy atom effect which encourages intersystem crossing to the triplet state, hence the diminished spin allowed fluorescence. An increase in the size of the central metal ion results in a reduced fluorescence lifetime (τ_F) as shown in Table 2. The order of the τ_F values with respect to the central metal ion is $(Cl)_2$SiTMPyPc > (Cl)GaTMPyPc > SnTMPyPc > (Cl)InTMPyPc in DMSO and $(Cl)_2$SiTMPyPc > SnTMPyPc > (Cl)GaTMPyPc > (Cl)InTMPyPc in DMF. This pattern indicates that a greater number of (Cl)InTMPyPc molecules would be expected to undergo intersystem crossing to the triplet state. The τ_F values were used to determine the rate constants of fluorescence (k_F), internal conversion (k_{IC}) and intersystem crossing (k_{ISC}). The order of the k_{ISC} values for the MPcs is (Cl)InTMPyPc> SnTMPyPc > (Cl)GaTMPyPc > $(Cl)_2$SiTMPyPc in DMSO. The trend in DMF is as follows: (Cl)InTMPyPc > (Cl)GaTMPyPc = SnTMPyPc > $(Cl)_2$SiTMPyPc. This trend gives an indication that the heavy atom effect plays a major role in the results observed and it implies that the major pathway through which the excited singlet state is deactivated is through intersystem crossing. The trend for k_F in both DMSO and DMF is (Cl)GaTMPyPc > (Cl)InTMPyPc > SnTMPyPc > $(Cl)_2$SiTMPyPc, thus Ga with the highest Φ_F value had the largest k_F value. The overall trend however does not match the trend in Φ_F. For k_{IC}, the trend was as follows for DMSO: SnTMPyPc > (Cl)InTMPyPc > (Cl)GaTMPyPc > $(Cl)_2$SiTMPyPc and for DMF: (Cl)InTMPyPc > (Cl)GaTMPyPc > SnTMPyPc > $(Cl)_2$SiTMPyPc. Thus the SiPc derivative had the smallest k_{IC} value and also had the large Φ_F value (as well as with the GaPc derivative).

3.3. Triplet quantum yields (Φ_T) and lifetime (τ_T) studies

The transient absorption spectra were recorded for TMPyMPc in argon degassed DMSO by exciting the MPc photosensitizer in the Q band region and recording the transient absorption spectra point by point from 400 to 830 nm (Fig. 4, using $(Cl)_2$SiTMPyPc as an example). The Q band is rather broadened upon laser excitation and is slightly red-shifted compared to the ground state absorption spectra, indicative of distortion of the symmetry of the $(Cl)_2$SiTMPyPc complex upon excitation. Fig. 5 (using (Cl)GaTMPyPc in DMSO as an example) shows 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) [34] due to triplet–triplet recombination. The concentrations employed in this work were in this range hence triplet–triplet recombination is expected.

The values of Φ_T obtained by using Eq. (2), provide a measure of the fraction of absorbing molecules that undergo intersystem crossing (ISC) to the triplet state (Φ_T). The variation of Φ_T values of MTMPyPcs are shown in Table 2. The order of the Φ_T values with respect to the central metals is (Cl)InTMPyPc > SnTMPyPc > $(Cl)_2$SiTMPyPc > (Cl)GaTMPyPc in both DMSO and DMF. The Φ_T values of the MTMPyPc complexes were fairly high and this indicates that a considerable number of the MPc molecules undergo ISC. As was expected, the Φ_T values were high because the complexes contain central metal ions with closed d shells, and are also large, encouraging ISC. (Cl)InTMPyPc and SnTMPyPc had the largest Φ_T values in both DMSO and DMF compared to the other MTMPyPc's, due to the heavy atom effect.

The Φ_T values are higher in DMSO because the heavy sulfur atoms in DMSO encourage ISC thereby allowing a greater number of MPc molecules to cross from their lowest excited singlet states into their lowest excited triplet states, Table 2.

The triplet lifetime (τ_T) values of the MPc complexes were fairly short (Table 2). The lower τ_T value of the MPcs corresponds well with the high value of the Φ_T of the MTMPyPc complexes. The order of the τ_T values is $(Cl)_2$SiTMPyPc > (Cl)GaTMPyPc > (Cl) InTMPyPc > SnTMPyPc in DMSO and $(Cl)_2$SiTMPyPc > (Cl)InTMPyPc > SnTMPyPc > (Cl)GaTMPyPc in DMF. A general observation was that τ_T values were much higher in DMSO compared to DMF. High values of τ_T are desired as this would allow the excited MPc molecules to stay longer in the triplet state thus giving an opportunity for increased collisional and diffusional interactions between the MPc molecules and ground state molecular oxygen ($^3O_2$) molecules, which would encourage a greater production of singlet oxygen ($^1O_2$) which is the cytotoxic species in photosensitized reactions [10]. However the heavy central metal ions Sn^{2+} and In^{3+} tend to encourage non-radiative decay from T_1 to S_0 because of the heavy atom effect thus lowering the τ_T values of the SnTMPyPc and (Cl)InTMPyPc complexes more, compared to the (Cl)GaTMPyPc and $(Cl)_2$SiTMPyPc counterparts in DMSO. In DMF however, (Cl)InTMPyPc had a longer τ_T value than (Cl)GaTMPyPc.

The internal conversion quantum yields (Φ_{IC}) were obtained through the use of Eq. (3). Internal conversion is one of the deactivation processes for a molecule in the excited state and it involves the radiationless transition between energy states of the same spin state. Φ_{IC} values indicate the extent of deactivation of excited state molecules with the result that the thermal energy of their surroundings increased. As shown in Table 2, the values of Φ_{IC} for the MPc's decreased in the order SnTMPyPc > (Cl)GaTMPyPc ∼ (Cl)InTMPyPc > $(Cl)_2$SiTMPyPc in DMSO and the order in DMF was SnTMPyPc ∼ (Cl)GaTMPyPc > $(Cl)_2$SiTMPyPc > (Cl)InTMPyPc. In both cases SnTMPyPc Φ_{IC} values were larger than the values of the other

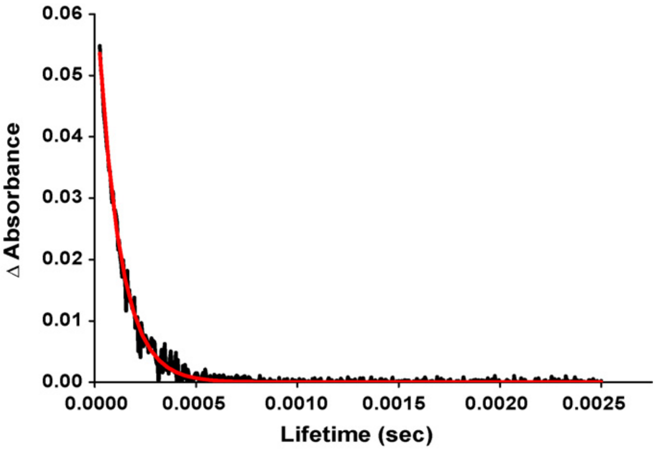


Fig. 5. A representative triplet decay curve for (Cl)GaTMPyPc (in DMSO).

MPc complexes indicating that SnTMPyPc molecules are more deactivated through radiationless transitions compared to their counterparts. Φ_{IC} values were lower in DMSO than in DMF indicating that deactivation through radiationless transitions is more prone in DMF than in DMSO. Generally the Φ_{IC} values were low suggesting that deactivation through radiationless transitions is minimal for all the MPcs. It further points to the high possibility of deactivation of the lowest excited singlet state through ISC as MPc molecules move from the lowest excited singlet state to the lowest triplet state, hence the relatively high Φ_T values observed.

3.4. Photochemical studies

3.4.1. Singlet oxygen quantum yields

Singlet oxygen quantum yield Φ_Δ is a measure of singlet oxygen generation and the Φ_Δ values were obtained using Eq. (4). Singlet oxygen is formed *via* interaction of the triplet state of a photosensitizer and ground state molecular (triplet) oxygen $^3O_2(^3\Sigma_g{}^-)$. Consequently the efficiency of singlet oxygen generation depends on the triplet state quantum yield Φ_T and the triplet state lifetime τ_T. High Φ_T and τ_T would result in high Φ_Δ values because of the increased molecular interactions between the photosensitizer in the triplet state and the ground state oxygen $^3O_2(^3\Sigma_g{}^-)$ causing formation of more singlet oxygen $^1O_2(^1\Delta_g)$. Table 2 shows that the Φ_T for the MPc complexes are relatively high, however, the values of Φ_Δ shown in the table are low to moderate for these MPc's. The general trend indicated that the Φ_Δ values were higher in DMSO than in DMF with a few exceptions, for the same reason that DMSO encourages spin orbit coupling, hence more MPc molecules will populate the excited triplet state which will interact with ground state oxygen thereby resulting in higher Φ_Δ values in DMSO. The Φ_Δ values did not follow the trend that the Φ_T values set.

The S_Δ values are a reflection of the efficiency of energy transfer from the triplet state of the MPc complexes to the ground state of molecular oxygen. S_Δ values close to unity are an indication of a high efficiency of energy transfer. The S_Δ values for the MPcs decreased in the order $(Cl)_2$SiTMPyPc > SnTMPyPc > (Cl)GaTMPyPc > (Cl)InTMPyPc in DMSO and the order applies for DMF except the S_Δ values for $(Cl)_2$SiTMPyPc and SnTMPyPc are the same. The less than unity values for S_Δ in some cases such as for (Cl)InTMPyPc and (Cl)GaTMPyPc, suggest low efficiency of energy transfer in these complexes.

4. Conclusions

This work shows that the synthesised MTMPyPc (M = Si, Ga, Sn, and In) complexes are soluble in a wide variety of solvents. The MPc complexes showed monomeric behaviour in all the solvents used; DMSO, DMF, DCM, $CHCl_3$, and THF. These complexes had fairly low Φ_F values, but gave high Φ_T values and corresponding low triplet lifetimes. The Φ_Δ values obtained were higher in DMSO than in DMF except for (Cl)InTMPyPc. The efficiency of the transfer of energy from the triplet state of the complexes to ground state molecular oxygen is reasonably good for $(Cl)_2$SiTMPyPc and SnTMPyPc and low for (Cl)InTMPyPc and (Cl)GaTMPyPc. The combined photophysical parameters show that these complexes have potential as candidates for applications as photosensitizers in PDT.

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