



Photophysical, photochemical and electrochemical properties of water soluble silicon, titanium and zinc phthalocyanines

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ABSTRACT

The photophysical, and photochemical properties of titanium, silicon and zinc octacarboxy phthalocyanine (OTiOCPc, (OH)₂SiOCPc and ZnOCPc) and their tetrasulfonated counterparts (OTiTSPc, (OH)₂SiTSPc and ZnTSPc) in phosphate-buffer solution (PBS), pH 10 were studied. The tetrasulfonated derivatives were also studied in the presence of a surfactant, cremophore EL (CEL) due to their high aggregation tendency in aqueous solutions. Triplet quantum yields ranged from 0.20 to 0.48 for MOCPCs and 0.32–0.65 for MTSPcs in the presence of CEL and in pH 10. High triplet lifetimes were observed for ZnTSPc (270 μs, in the presence of CEL) or ZnOCPc (130 μs) compared to values ranging from 50 to 70 μs for the rest of the complexes.

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1. Introduction

Metallophthalocyanines (MPcs) have been a focus of attention because of their exclusive properties. Their intense absorption in the red and near infra-red regions of the solar spectrum, their non-toxicity coupled with their ease of oxidation and reduction has made them attractive as chromophores for light-driven processes. MPcs and their substituted derivatives function as active components in various processes driven by visible light such as, photoredox reactions in solutions [1,2], photodynamic therapy of cancer [3–5], photoelectrochemical and photovoltaic cells [6–10].

Fossil fuels account for a great deal of energy source to mankind. However, technological advancement and improvement in living standards have imposed a huge demand on this natural energy source, which is being rapidly depleted. It is therefore imperative that renewable energy sources should be developed. In recent years, building integrated photovoltaic modules has become popular. An approach is to assemble models that mimic the natural photosynthetic systems. An essential requirement for a good photosynthetic mimicker is the ability to undergo excited state

charge transfer with ease. MPcs are favoured candidates in this respect, as their excited states are known to be easily reducible [11–14].

The report herein is based on the photophysical and electrochemical properties of tetrasulfo ((MTSPcs) and octacarboxy (MOCPCs) substituted zinc, silicon and titanium metallophthalocyanines, Fig. 1). The effect of the central metals on their electrochemical and photophysical properties will be evaluated. Electrochemical studies were performed in order to study the influence of substituents on the redox potentials.

Carboxylic and sulfonic groups are electron withdrawing hence they are expected to make the Pc ring easy to reduce which is useful for photoelectrochemistry [15,16]. The carboxylic and sulfonic groups confer water solubility on the MPc macrocycle which is essential in photosensitized reactions. The stability of these macrocycles to visible light is important, hence their photochemical properties are investigated in this work. The singlet oxygen quantum yield for ZnOCPc has been reported [17]. Less attention has been paid to the photophysical behavior of the molecule. Recently the photophysical behavior of SiTSPc complex was reported [18]. However the photophysical behavior of the corresponding SiOCPc and of TiTSPc has not been explored. MOCPC complexes are water soluble and are known to be monomeric in aqueous media, and thus give better photosensitizing behavior compared to MTSPc [19].

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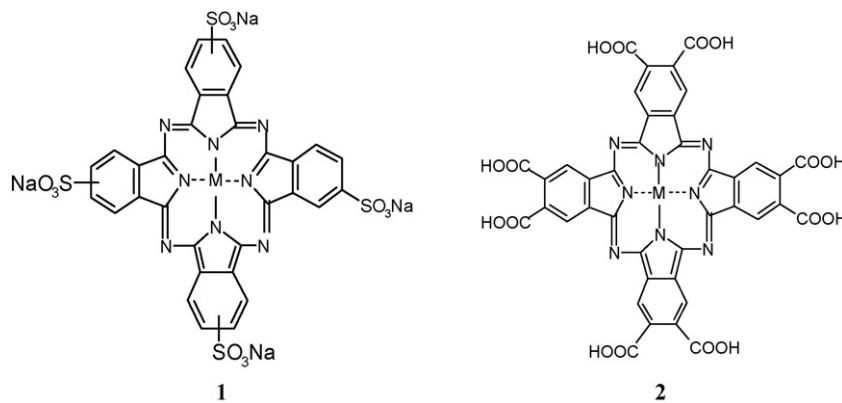


Fig. 1. Chemical structure of the tetrasulfonated (1) and octacarboxyl (2) substituted metallophthalocyanines. M = TiO, Si(OH)₂ and Zn.

2. Experimental and method

2.1. Materials and synthesis

Creomophore EL (CEL), pyromellitic dianhydride, 4-sulfophthalic acid, titanium tetrachloride, silicon tetrachloride, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and anthracene-9,10-bis-methylmalonate (ADMA) were obtained from Aldrich. Phosphate-buffered saline (PBS) solution (0.01 M, pH 10.0) was prepared using appropriate amounts of Na₂HPO₄ (1.37 g) and NaOH (0.014 g) dissolved in 100 ml ultra pure water (of resistivity 18.2 MΩ), obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA). All other reagents were obtained from commercial supplies and used as received.

The syntheses of tetrasulfophthalocyanine complexes of Si ((OH)₂SiTSPc [18]) and zinc (ZnTSPc [20]) and of the octacarboxyphthalocyanine complexes of Zn (ZnOCPc [16]) have been reported in the literature. OTiTSPc was synthesized using the microwave method reported for the SnTSPc counterpart [21].

Briefly, a mixture of commercially available 50% aqueous 4-sulfophthalic acid solution (4 g, 8.12 mmol), urea (1.95 g, 32 mmol), and Ti butoxide (4.1 mmol) in the presence of ammonium chloride (1.56 g, 29 mmol) and ammonium molybdate (0.17 g, 0.14 mmol) as catalysts, was irradiated in a microwave oven at 560 W for 11 min. The mixture was then added to aqueous sodium hydroxide solution (100 ml, 10 wt.%), heated until boiling, and cooled to the room temperature. The solution was then poured into methanol (50 ml), and then *i*-propyl alcohol (100 ml) was added for precipitation. The complex was purified by following the literature methods [21] in addition to Soxhlet extraction of impurities using methanol and ethanol.

Yield: (47%). IR (KBr, cm⁻¹): 3467(OH), 2176, 1639, 1662(C=C), 1451, 1197, 1131, 1040(S=O), 962(Ti=O), 904, 865, 834(C-S), 686, 560. ¹H NMR (400 MHz, D₂O): (ppm) 8.13–8.11 (s, 8H, Pc-H), 8.05–8.03 (d, 4H, Pc-H'), 7.81–7.79 (d, 4H, Pc-H), 7.75–7.76 (s, 2H, (O-H)₂). λ_{max} (nm) (log ε) (pH 10/CEL): 340 (4.30), 610 (3.67), 677 (4.98) nm.

OTiOCPc and (OH)₂SiOCPc were synthesized, purified and characterized according to established literature methods [16] as follows: benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride, 2.50 g, 11.5 mmol), urea (13.0 g, 0.22 mol), titanium (IV) butoxide or SiCl₄ (23.5 mmol) and DBU (0.1 g, 0.7 mmol) were heated to 250 °C in a flask until the reaction mixture was fused. The reaction products were washed with water, acetone and 6 M hydrochloric acid (HCl). After being dried, the solid obtained was hydrolyzed in 20% H₂SO₄ for a period of 72 h. The products were purified further as explained in the literature.

2.1.1. OTiOCPc

Yield: (25%). IR (KBr, cm⁻¹): 3441(OH), 3029, 2782, 2357, 1725, 1644, 1469, 1399, 1283, 1054, 930(Ti=O), 772, 536. ¹H NMR (400 MHz, D₂O): (ppm) 7.75–7.67 (s, 8H, Pc-H), 4.13–4.15 (s, 8H, Carboxylic-H). λ_{max} (nm) (log ε) (pH 10): 338 (3.72), 620 (3.94), 693 (4.75) nm.

2.1.2. (OH)₂SiOCPc

Yield: (32%). IR (KBr, cm⁻¹): 3433(OH), 1752, 1631, 1574, 1403, 1282, 1024, 756 (C-S), 625, 602, 511. ¹H NMR (400 MHz, D₂O): (ppm) 7.92–7.96 (s, 8H, Pc-H), 7.69–7.70 (s, 2H, (OH)₂-H), 4.63–4.64 (s, 8H, Carboxylic-H). λ_{max} (nm) (log ε) (pH 10): 346 (4.97), 618 (4.42), 690 (5.10) nm.

2.2. Equipment

Cyclic voltammetry (CV) and square wave voltammetry (SWV) data were obtained under purified nitrogen gas with BioAnalytical Systems (BAS) model 100B/W Electrochemical Workstation. The data were collected using a conventional three-electrode set-up with glassy carbon electrode (GCE, 3 mm diameter) as a working electrode, platinum wire as a counter electrode and Ag/AgCl wire as pseudo-reference electrode. Electrochemical experiments were performed in doubly distilled water containing 0.1 M Na₂HPO₄ and 0.1 M NaOH. Prior to scans, the working electrode was polished with alumina paste on a Buehler felt pad, followed by washing with deionised water and rinsing with methanol, then with acetone and pH 10 phosphate buffer. Phosphate buffer saline solution was employed for aqueous solutions.

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

Laser flash photolysis experiments were performed with light pulses produced by a Quanta-Ray Nd:YAG laser providing 400 mJ, 90 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL3002 dye (Pyridin 1 dye in methanol). Single pulse energy ranged from 2 to 7 mJ. The analyzing beam source was from a Thermo Oriol 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 life times were determined by exponential fitting of the kinetic curves using the program OriginPro 7.5.

Photoirradiations for photodegradation or singlet oxygen determination were performed using a General Electric Quartz line lamp (300 W). A 600-nm glass cut off filter (Schott) and water were used to filter off ultraviolet and infra-red radiations respectively. An interference filter (Intor, 670 nm with a band width of 20 nm) was

additionally placed in the light path before the sample. Light intensity was measured with a POWER MAX5100 (Molelectron detector incorporated) power meter and was found to be 3.12×10^{16} photons s^{-1} for photobleaching and to be 1.25×10^{16} photons s^{-1} for singlet oxygen studies.

2.3. Photophysical and photochemical studies

Fluorescence quantum yields (Φ_F) were determined by comparative method [22] (Eq. (1))

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

where F and F_{Std} are the areas under the fluorescence curves of the 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, $\Phi_F = 0.2$ [23]. At least three independent experiments were performed for the quantum yield determinations. Both the sample and the standard were excited at the same relevant wavelength.

Natural radiative (τ_0) life times were determined using PhotochemCAD program which uses the Strickler–Berg equation [24]. Lifetimes of fluorescence (τ_F) were then calculated from the radiative lifetime using fluorescence quantum yields, Eq. (2).

$$\Phi_F = \frac{\tau_0}{\tau_F} \quad (2)$$

Triplet quantum yields were determined using a comparative method based on triplet decay, using Eq. (3)

$$\Phi_T^{\text{Sample}} = \Phi_T^{\text{Std}} \frac{\Delta A^{\text{Sample}} \epsilon_T^{\text{Std}}}{\Delta A^{\text{Std}} \epsilon_T^{\text{Sample}}} \quad (3)$$

where A_T^{Sample} and A_T^{Std} are the changes in the triplet state absorbance of the sample and the standard, respectively. $\epsilon_T^{\text{Sample}}$ and ϵ_T^{Std} are the triplet state extinction coefficients for the sample and standard, respectively. Φ_T^{Std} is the triplet state quantum yield for the standard. ZnTSPc in aqueous solution, $\Phi_T^{\text{Std}} = 0.56$ [25] was used as standard. 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.

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

The values of photobleaching quantum yields (Φ_P) were determined using Eq. (5)

$$\Phi_{\text{Pd}} = \frac{(C_0 - C_t)VN_A}{I_{\text{abs}}St} \quad (5)$$

where C_t and C_0 are the MPc 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 is the irradiation time, N_A is the Avogadro's number and I_{abs} , the overlap integral of the radiation light source intensity and the absorption of the MPc in the region of the interference filter transmittance [26,27]. Eq. (6) was employed for calculating singlet oxygen quantum yields

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{Std}} \frac{R_{\text{abs}}^{\text{Std}}}{R_{\text{abs}}^{\text{Std}} I_{\text{abs}}} \quad (6)$$

where $\Phi_{\Delta}^{\text{Std}}$ is the singlet oxygen quantum yield for the standard (ZnTSPc, $\Phi_{\Delta}^{\text{Std}} = 0.3$ in aqueous solution in the presence of Triton X) [28], R and R^{Std} are the ADMA photobleaching rates in the presence of the respective MPcs under investigation and the standard

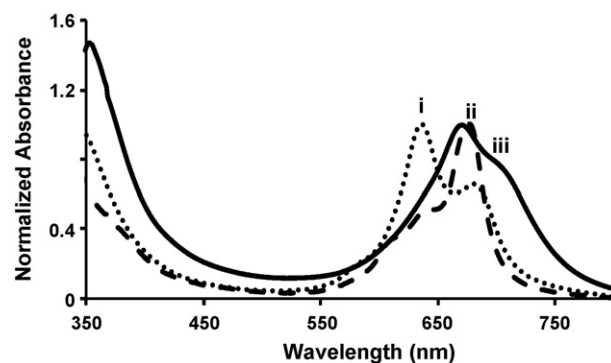


Fig. 2. Ground state electronic absorption spectra of the sulfonated MPc complexes in aqueous solution: (i) ZnTSPc, (ii) $(\text{OH})_2\text{SiTSPc}$ and (iii) OTiTSPc ($\sim 8 \times 10^{-6} \text{ mol dm}^{-3}$).

respectively. I_{abs} and $I_{\text{abs}}^{\text{Std}}$ are the rates of light absorption by the MPcs and the standard, respectively. To avoid chain reactions, the concentration of ADMA was kept at $\sim 6 \times 10^{-5} \text{ mol l}^{-1}$.

Solutions of the MPcs with an absorbance of 0.2 at the irradiation wavelength were prepared in the dark and irradiated at the Q band region, monitoring the ADMA absorption at 380 nm. The error was $\sim 10\%$ from several values of Φ_{Δ} .

3. Results and discussion

3.1. Ground state electronic absorption and fluorescence spectra

Tetrasulfonated and octacarboxy metallophthalocyanines (MTSPcs and MOCPC) complexes are known and the complexes: $(\text{OH})_2\text{SiOCPC}$, ZnOCPC, OTiOCPC, $(\text{OH})_2\text{SiTSPc}$, ZnTSPc and OTiTSPc gave satisfactory UV–vis, IR and NMR spectroscopic characterization.

The ground state electronic spectra of the tetrasulfonated metallophthalocyanine (MTSPcs) complexes in Fig. 2 shows they are aggregated in aqueous solution (pH 10) with the presence of two main bands one at $\sim 680 \text{ nm}$ due to the monomeric species and the other at $\sim 640 \text{ nm}$ due to the aggregated species. Aggregation in MPc complexes is usually depicted as a coplanar association of rings, progressing from dimer to higher aggregates, resulting in splitting and broadening of spectra, with a blue shifted peak at $\sim 630 \text{ nm}$ due to the aggregate. Tetrasulfonated phthalocyanines, exist as loosely associated species that are not chemically bonded dimers in aqueous solution which can be dissociated by surfactants or in non-aqueous solvents [25,29,30]. The addition of a surfactant, CEL, resulted in a decrease in the intensity of the band due to the aggregates with an increase in the intensity of the band due to the monomeric species (Fig. 3), which confirms that the complexes are aggregated in aqueous solution of pH 10 with Q band maxima given in Table 1. The disaggregation of $(\text{OH})_2\text{SiTSPc}$ was total on addition of CEL, but ZnTSPc and OTiTSPc still shows some aggregation suggesting that strong forces are responsible for their aggregation or that a high equilibrium between the monomer and the aggregated species occurs in these complexes. Unlike the tetrasulfonated complexes, the ground state electronic absorption spectra of $(\text{OH})_2\text{SiOCPC}$, ZnOCPC and OTiOCPC, in pH 10 (Fig. 4) show characteristic monomeric absorption in the Q band region at $\sim 690 \text{ nm}$ which was evident by a single narrow Q band typical of metallated phthalocyanine complexes [29].

Fluorescence excitation spectra of these MOCPCs complexes are similar to their absorption spectra and are mirror images of the fluorescence emission spectra which is usual for MPc derivatives as shown in Fig. 5a (for OTiOCPC). There is however a lack of agreement

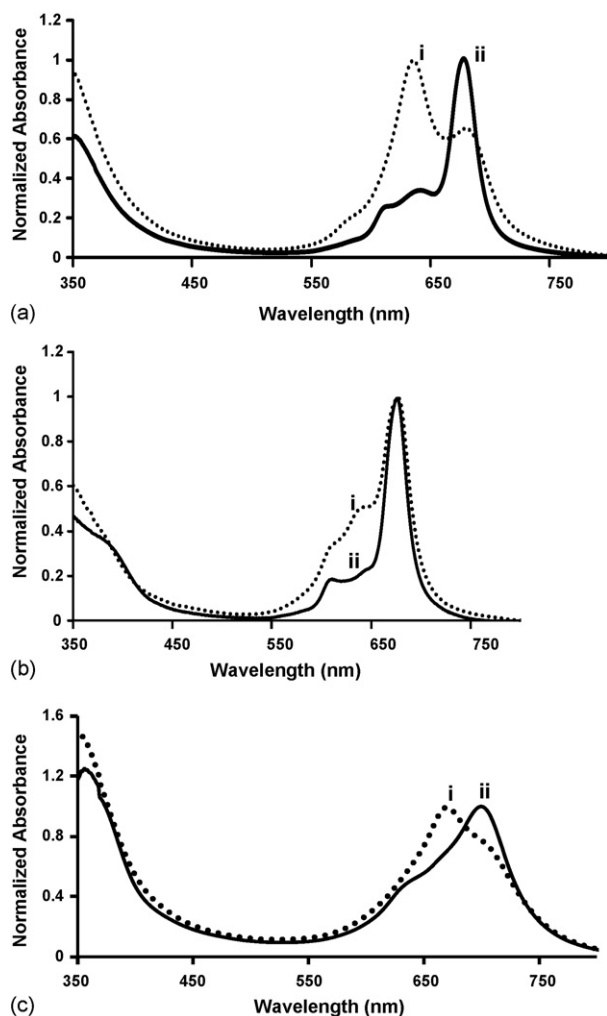


Fig. 3. Absorption spectra of $1 \times 10^{-5} \text{ mol dm}^{-3}$ (a) ZnTSPc, (b) $(\text{OH})_2\text{SiTSPc}$ and (c) OTiTSPc in the absence (i) and in the presence (ii) of $4 \times 10^{-4} \text{ mol dm}^{-3}$ CEL.

between the absorbance and emission spectra for the tetrasulfonated counterparts as shown in Fig. 5b (for SiTSPc). The band around 640 nm, associated with the dimer is not seen in the fluorescence excitation spectrum since only the monomer fluoresces. It has been documented before that dimers are non-photoactive [25]. The Stokes' shifts were in the neighbourhood of 10 nm typical of MPC complexes. Fig. 6 shows the fluorescence excitation and emission spectra of the MTSPc complexes in aqueous medium in

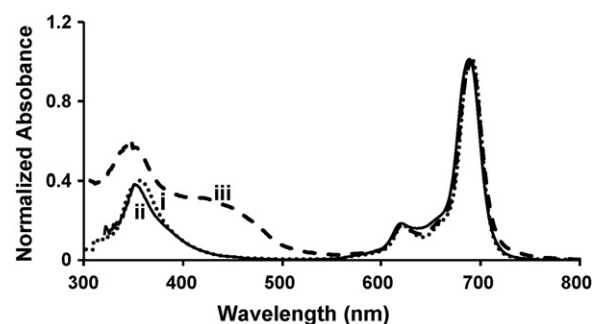


Fig. 4. Ground state electronic absorption spectra of the octacarboxy MPC complexes in aqueous solution: (i) ZnTOCPC, (ii) $(\text{OH})_2\text{SiOCPC}$ and (iii) OTiOCPC ($\sim 6 \times 10^{-6} \text{ mol dm}^{-3}$).

the presence of CEL. For ZnTSPc and OTiTSPc, the absorption spectrum still had some aggregation even in CEL as evidenced by a more clear splitting in the Q band, hence the absorption is not a mirror image of emission. For SiTSPc there is no clear splitting, but there is broadening. Emission will be from unaggregated species for these complexes.

3.2. Photophysical parameters

The fluorescence quantum yields Φ_F of the complexes are listed in Table 1. The tetrasulfonated complexes have relatively low yields of fluorescence in the absence of CEL due to aggregation, but improve on addition of CEL. The ZnTSPc in the presence of CEL however showed the highest Φ_F in this set. Aggregation is known to dissipate the electronic energy of the excited singlet state, thereby lowering fluorescence. Monomerization of aggregates leads to enhanced fluorescence and this is noticed in the Φ_F of the complexes in the presence of CEL in aqueous medium. The Φ_F values are however low compared to MPCs in general [17]. Φ_F values were relatively higher for the MOCPCs probably due to their monomeric nature even in aqueous medium.

Lifetimes of fluorescence (τ_F) were determined using the Strickler–Berg equation as stated above and are listed in Table 1. Using this equation, a good correlation has been [31] found for the experimentally determined fluorescence lifetimes and the theoretically determined lifetimes. Thus we believe that the values obtained using this equation are a good measure of fluorescence lifetimes. τ_F values were generally low for all the complexes, though they were higher with the MOCPCs suggesting quenching of fluorescence in aqueous medium. The addition of the CEL however slightly increased the τ_F values for MTSPc complexes. The rate constants for fluorescence (k_F) were about the same for all the complexes

Table 1

Spectral, photophysics and photochemical parameters for the MPC complexes in pH 10 and in pH 10 + CEL^a.

Sample	Solvent	λ_Q (nm)	λ_F (nm)	Φ_F	τ_F (ns)	Φ_T	Φ_{IC}	Φ_{Δ}	$^cS_{\Delta}$	$\Phi_{Pd} (\times 10^{-4})$	τ_T (μs)
ZnOCPC	pH 10	689	699	0.18	1.40	0.48	0.34	0.52 [17] ^b	1.0	4.90	130
OTiOCPC	pH 10	693	700	0.07	1.59	0.20	0.73	0.24	1.2	19.8	70
$(\text{OH})_2\text{SiOCPC}$	pH 10	690	699	0.06	0.54	0.30	0.64	0.33	1.1	5.40	70
ZnTSPc	pH 10	678,640	673	<0.01	0.02	0.56 [25] ^b	0.44	0.03	0.05	9.42	190
	pH 10 + CEL	678	676	0.20	3.71	0.65	0.15	0.12	0.18	14.2	270
OTiTSPc	pH 10	672,660	686	<0.01	0.01	0.03	0.97	0.03	1.0	4.95	50
	pH 10 + CEL	695	687	0.012	0.09	0.32	0.67	0.13	0.41	6.12	60
$(\text{OH})_2\text{SiTSPc}$	pH 10	677,639	684	0.04	0.28	0.53	0.43	0.20	0.38	1.15	40
	pH 10 + CEL	677	688	0.05	0.30	0.58	0.37	0.52	0.89	1.52	60

^a CEL = cremophore EL.

^b References in brackets.

^c $S_{\Delta} (= \Phi_{\Delta} / \Phi_T)$.

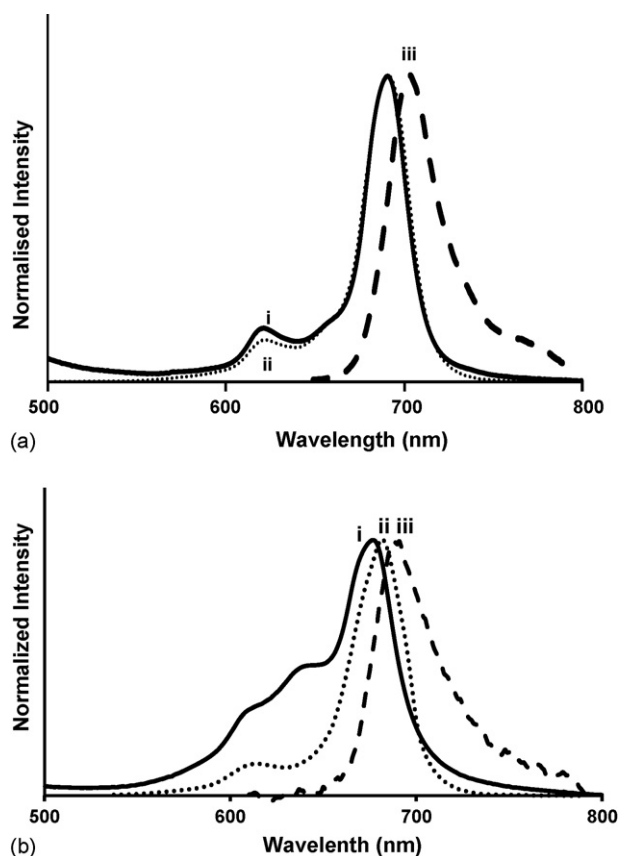


Fig. 5. Normalized absorption (i), fluorescence excitation (ii) and emission (iii) spectra of (a) OTiOCPc and (b) $(\text{OH})_2\text{SiTSPc}$ (in the absence of CEL) in pH 10. Excitation wavelength = 630 nm.

except for OTiOCPc and ZnTSPc (the latter in the presence of CEL), Table 2.

Φ_T is the measure of the fraction of absorbing molecules that undergoes intersystem crossing (isc) to the triplet state. The efficiency of a phthalocyanine as a photosensitizer is determined by its triplet state quantum yield (Φ_T) and lifetime (τ_T). The MTSPc complexes all have high Φ_T values both alone and in the presence of CEL except for OTiTSPc which is low without CEL. It should be noted that the d orbitals of the Ti metal are not fully filled and this may result in quenching of the triplet state. Φ_T values were higher in the presence of CEL since the MTSPc complexes are disaggregated in this case, monomers have greater tendencies to undergo intersystem crossing because less energy is lost through internal conversion. Again of the MOCPCs, the OTiOCPc complex has the lowest Φ_T value compared to zinc and silicon as observed for the tetrasubstituted derivatives. Fig. 7 shows the triplet decay curve for ZnOCPc which obeyed second order kinetics. This is typical of MPC complexes at high concentrations ($>1 \times 10^5 \text{ M}$) [32] due to the triplet–triplet recombination. The concentrations employed in this work were in this range hence triplet–triplet recombination is expected. The triplet life times were determined from Fig. 7 by exponential fitting of the kinetic curves using the program OriginPro 7.5.

The triplet lifetime, τ_T values range from 40–270 μs , which is a usual range for many MPC complexes. For the tetrasulfonated complexes in Table 1, ZnTSPc with the highest Φ_T has the longest triplet lifetime, however $(\text{OH})_2\text{SiTSPc}$ and OTiTSPc have shorter triplet lifetimes (40 and 50 μs). Lifetimes were longer in the presence of CEL compared to pH 10 alone for MTSPc complexes, which may be due to the reduction in the exposure of the phthalocyanine to the aqueous medium because of the presence of the CEL. The same trend

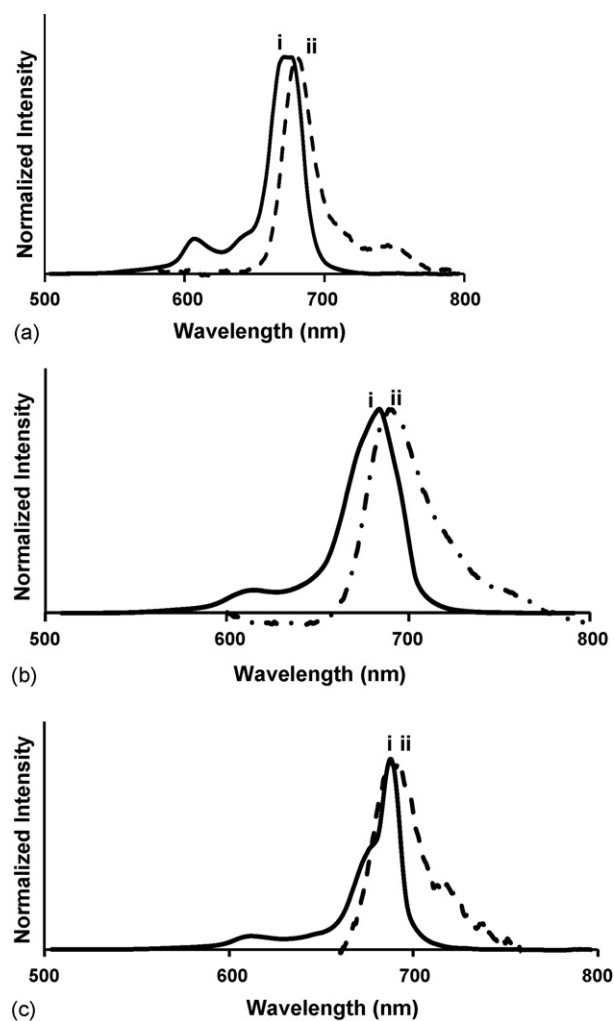


Fig. 6. Normalized fluorescence excitation (i) and emission (ii) spectra of ZnTSPc (a), $(\text{OH})_2\text{SiTSPc}$ (b) and OTiTSPc (c), in the presence of CEL, pH 10. Excitation wavelength = 568 nm.

was also observed in the τ_T values of the MOCPCs, with ZnOCPc having the longest lifetime.

Φ_{IC} values were generally high in the MTSPcs due to aggregation, which is due to the dissipation of electronic energy by the aggregates. A decrease in Φ_{IC} values in the presence of CEL was observed due to the monomerizing effect of CEL on the MTSPc complexes. Φ_{IC} values were also found to be high for the MOCPCs except for ZnOCPc. The rate constants for internal conversion (k_{IC}) in pH 10 buffer

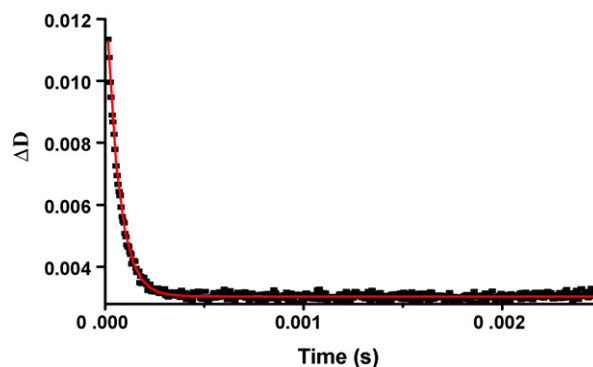


Fig. 7. Triplet decay curve of ZnOCPc in pH 10. Excitation wavelength = 689 nm.

Table 2
Rate constants for various excited state deactivation processes of the MPc complexes in pH 10 and pH 10+CEL.

Compound	Solvent	^a k_f ($\times 10^8$ s ⁻¹)	^b k_{ISC} ($\times 10^9$ s ⁻¹)	^c k_{IC} ($\times 10^9$ s ⁻¹)	^d k_d (s ⁻¹)
ZnOCPC	pH 10	1.28	0.18	0.24	3.77
OTiOCPC	pH 10	0.44	0.15	0.46	28.3
(OH) ₂ SiOCPC	pH 10	1.01	0.56	1.20	7.71
ZnTSPc	pH 10	1.44	25.5	20.0	4.96
	pH 10+CEL	0.54	0.18	0.04	5.26
OTiTSPc	pH 10	1.11	5.42	164	12.2
	pH 10+CEL	1.46	3.44	7.20	8.25
(OH) ₂ SiTSPc	pH 10	1.46	0.26	1.53	2.53
	pH 10+CEL	1.64	3.22	1.25	13.2

^a k_f is the rate constant for fluorescence. Values calculated using $k_f = \Phi_f/\tau_f$.

^b k_{ISC} is the rate constant for intersystem crossing. Values calculated using $k_{ISC} = \Phi_T/\tau_T$.

^c k_{IC} is the rate constant for internal conversion. Values calculated using $k_{IC} = \Phi_{IC}/\tau_F$.

^d k_d is the rate constant for photodegradation. Values calculated using $k_d = \Phi_d/\tau_T$.

(Table 2) are higher for the MTSPcs compared to the corresponding MOCPCs, this could be due to aggregation of the former. On addition of CEL to MTSPc complexes, the k_{IC} values decrease drastically showing the effects of aggregation, Table 2. Larger rate constants for intersystem crossing (k_{ISC}) were observed for the MTSPc complexes compared to the MOCPCs, indicating that the sulfonic substituents may encourage intersystem crossing to the triplet state more than the carboxyl ones.

3.3. Singlet oxygen and photodegradation quantum yield, Φ_Δ

Energy transfer between the triplet state of photosensitizers and ground state molecular oxygen leads to the production of singlet oxygen, Φ_Δ . There is a necessity of high efficiency of transfer of energy between excited triplet state of MPc and ground state of oxygen to generate large amounts of singlet oxygen. The Φ_Δ values (Table 1) are high for the MOCPC complexes. Φ_Δ values were very low for the MTSPcs, probably due to their aggregated nature. There was however an improvement in the singlet oxygen yields on addition of CEL. The efficiency of quenching of the triplet excited state by oxygen, $S_\Delta (= \Phi_\Delta/\Phi_T)$, were near unity (Table 1) for the MOCPCs while they were low for the MTSPcs except for OTiTSPc and (OH)₂SiTSPc (the latter in the presence of CEL).

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 [33]. Photodegradation quantum yields in the MPc complexes were generally within the range for MPc complexes, Table 1. The addition of CEL increased the photodegradation quantum yields in all the complexes. There was no clear trend with regards to the rate constants for photodegradation (k_d), Table 2. There was an increase in k_d values for (OH)SiTSPc and ZnTSPc on addition of CEL, but a decrease for OTiTSPc, Table 2.

Table 3
Half wave potential ($E_{1/2}$) of the MPc complexes in pH 10 buffer (vs. Ag/AgCl).

Complex	$E_{1/2}$ (mV)	
	I (Pc ⁻³ /Pc ⁻⁴)	II (Pc ⁻² /Pc ⁻³)
OTiOCPC	-714	-512
(OH) ₂ SiOCPC	-632	-482
ZnOCPC	-776	-596

3.4. Electrochemical properties

Cyclic and square wave voltammetry studies (Fig. 8, for ZnOCPC and (OH)₂SiOCPC) were undertaken for the MOCPC complexes which were not aggregated in order to determine the relative ease of reduction of the complexes. All the MOCPC complexes are expected to show only ring-based processes. Two ring-based reduction processes were observed for the complexes Fig. 8 and their redox potentials are summarized in Table 3. All the processes showed reversible to quasi-reversible behavior with cathodic to anodic peak separations (ΔE) of 90 mV to 120 mV. A ΔE of the ferrocene standard was 120 mV in the same solvent. SWV showed reversibility of the couples (Fig. 8 inset). The redox processes labeled I are assigned

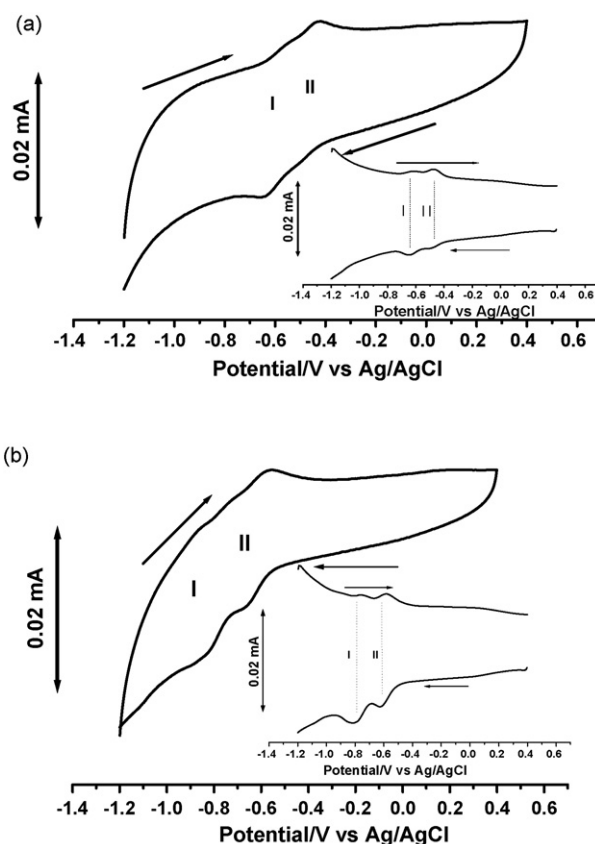


Fig. 8. Cyclic and square wave voltamograms of (a) (OH)₂SiTSPc and (b) ZnOCPC in a buffer solution of pH 10 at a scan rate of 50 mV s⁻¹.

to $\text{MPC}^{-3}/\text{MPC}^{-4}$ and **II** to $\text{MPC}^{-2}/\text{MPC}^{-3}$ according to the literature [34] for water soluble and redox inactive central metals. Table 3 shows that the Si and Ti complexes are more easily reduced due to the tetra positive nature of the central metal.

4. Conclusion

The photophysical, photochemical and electrochemical properties of oxotitanium, silicon and zinc octacarboxy and tetrasulfonated phthalocyanine were studied. Electrochemical studies showed that TiPc and SiPc derivatives were more easily reduced than the ZnPc derivatives. Ease of reduction is a requirement for possible use of these complexes in photoelectrochemistry. Triplet quantum yields ranged from 0.20 to 0.48 for MOCPCs and 0.32 to 0.65 for MTSPCs in the presence of CEL and in pH 10. High triplet lifetimes were observed for ZnTSPc (270 μs , in the presence of CEL) or ZnOCPC (130 μs) compared to values ranging from 50 to 70 μs for the rest of the complexes. Singlet oxygen quantum yields were very low for the tetrasulfophthalocyanines in pH 10, but improved in the presence of CEL. Overall the MOCPC gave better singlet oxygen values.

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