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Review

Effects of substituents on the photochemical and photophysical properties of main group metal phthalocyanines[☆]

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Contents

Abstract

The review focuses on the photochemical (singlet oxygen and photobleaching quantum yields) and photophysical (triplet quantum yields and lifetimes and fluorescence lifetimes) properties of metallophthalocyanine complexes containing main group metals (Zn, Al, Ge, Si, Sn, Ga and In) and some unmetallated phthalocyanine complexes. Five tables containing photophysical and photochemical data for sulfonated phthalocyanines, tetra-, octa-substituted and unsubstituted phthalocyanines in a variety of solvents, are included in the review.

Keywords: Metallophthalocyanine; Triplet state quantum yield; Triplet lifetimes; Fluorescence quantum yield; Photobleaching

1. Introduction

Phthalocyanines were first synthesized by chance in 1907 during a study of the properties of 1,2-cyanobenzamide [1]. Linstead synthesized a vast range of phthalocyanines in the 1930s [2], and the X-ray analysis was later conducted by Robertson

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[3–5]. Metallophthalocyanine (MPc) complexes, in particular CuPc, are produced in industry on a large scale (∼50,000 t per year). These complexes have long been used as blue–green dyes and pigments. In recent years, the applications of MPc complexes have expanded to areas such as photosensitizers in photodynamic therapy, photoconducting agents in photocopying machines and electrocatalysts. Monograms on general properties of MPc complexes are available [6–9]. Phthalocyanines show exceptional thermal and chemical stability. Strong acids only protonate conventional MPc complexes [10–13]. For use in photocatalysis (photosensitization), MPc complexes containing non-transition metal ions are employed. High triplet state quantum yields and long triplet lifetimes are required for efficient photosensitization, and these criteria may be fulfilled by the incorporation of diamagnetic metals such as zinc, aluminum or silicon into the phthalocyanine macrocycle. Thus, this review focuses on the photophysical and photochemical properties of MPc complexes containing diamagnetic central metal ions. The effects of phthalocyanine ring substituents on these parameters will be reviewed. A recent review by Ishii and Kobayshi provided photophysical (singlet and triplet state parameters) data of a range of substituted and unsubstituted MPc complexes [14], and fast methods for the direct detection of triplet state such as time-resolved electron paramagnetic resonance were discussed. The present review focuses more on main group phthalocyanine complexes with emphasis on the photochemical behaviour (singlet oxygen and photostability) in addition to some photophysical studies of these complexes. The review will include mainly work from our group in comparison with work from other researchers.

2. Photochemical and photophysical parameters

Photochemical studies include singlet oxygen quantum yields and photodegradation. Photophysical studies include fluorescence lifetimes, and triplet quantum yields and lifetimes.

MPc complexes act as photosensitizers for many reactions including degradation of pollutants [15–20] and transformation of alkenes and alkanes [21]. Most notable among the uses of Pcs is as photosensitizers in oncology, particularly in photodynamic therapy (PDT) [22–29]. ZnPc complexes in particular are well known for their photosensitizing abilities [30–38], while unmetallated phthalocyanine complexes shows very little PDT effect [29]. It is believed that during photosensitization, the MPc molecule is first excited to the singlet state and through intersystem crossing forms the triplet state, and then transfers the energy to ground state oxygen, $O_2(^3\Sigma_g)$, generating excited singlet state oxygen, $O_2(^1\Delta_g)$, the chief cytotoxic species, which subsequently oxidizes the substrate by Type II mechanism [39]. Thus singlet oxygen quantum yields are expected to be comparable to triplet state yields if quenching of the latter by triplet oxygen is efficient [40].

The excited triplet state of the MPc can also interact with ground state molecular oxygen or substrate molecule, generating radical ions, superoxide and hydroperoxyl radicals, which subsequently afford oxidation of the substrate by Type I mechanism [28,41,42].

Type II mechanism is more prevalent [40] in photo-initiated oxidation reactions, thus the magnitude of singlet oxygen quantum yield (Φ_Δ) which expresses the amount of singlet oxygen generated per quanta of light, is often employed as a main criteria in choosing photosensitizers used in photocatalytic reactions.

Singlet oxygen quantum yields (Φ_Δ) for the MPc complexes may be conveniently determined using a singlet oxygen quencher such as 1,3-diphenylisobenzofuran (DPBF), or using singlet oxygen luminescence method (SOLM). The two methods give comparable results [34].

Photostability of MPc complexes is important for their applications as photocatalysts. Photodegradation (photobleaching) is characterized by the decrease in the intensity of the spectra (of both the Q and B bands) without shift in maxima or formation of new bands, on exposure of MPc to light. Photobleaching quantum yields (Φ_p) may be determined as reported in literature [10,17,35,37,38]. Phthalocyanine molecules in general photodegrade oxidatively via attack by singlet oxygen generated by them.

Both fluorescence [43–46] and triplet quantum yields [47–52] parameters may be determined by the comparative methods, using well known references such as chlorophyll. Phthalocyanines show a transient absorption due to the triplet state between 450 and 550 nm, accompanied by absorption loss in the Q band regions due to depletion of the parent compounds.

3. Sulfonated MPc complexes

For PDT action, it is necessary that the drug be easy to administer via injection into the blood stream. As the blood itself is a water-based system, water solubility then becomes an essential requirement for a PDT drug. Additionally, the drug will have to traverse lipid membranes—consequently, it should also be lipophilic. Water solubility is also essential for use of MPc complexes for the photodegradation of pollutants such as chlorinated phenols. The most common water-soluble complexes are the sulfonated MPcs [53,54]. Sulfonation [55] by the reaction of MPc complexes with fuming sulfuric acid (containing SO_3) gives a variable mixture of differently sulfonated metallophthalocyanine complexes ($MPc(SO_3^-)_n$ where M = metal ion, n is a mixture of 1, 2, 3, or 4 sulfo groups, which will be represented as $MPcS_{mix}$ in this review), each containing a variety of positional isomers. Tetrasulfonated derivatives are generally synthesized by the method of Weber and Busch [56]. Mixed-sulfonated aluminium phthalocyanine ($AlPcS_{mix}$) commercially known as Photosens® has been developed as a PDT drug with a fair measure of success [28]. Pentasulfonation has been reported in cases where tetra sulfonation was expected [57].

3.1. Aggregation behaviour

Sulfonated MPc complexes often form dimers or higher aggregates in solution. Aggregation in these complexes is easily characterized by UV–vis spectroscopy. Phthalocyanines aggregate due to electronic interactions between rings of two or more molecules. The J aggregates have been assigned to a red shifted band near 750 nm, while the blue shifted band around 630 nm is attributed to H aggregates [58]. MPc photosensitisers that form dimers and aggregates show lower photosensitization efficiency [33,53,59]. Aggregation reduces the lifetimes of the MPc's excited state, most probably due to enhanced radiationless excited state dissipation [60] and therefore lowers the quantum yields of the excited states and of singlet oxygen generation. The degree of sulfonation, isomeric composition and the nature of the central metal ion affect the extent of aggregation. Biological environments support monomerization of phthalocyanines.

$AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$ in pH 7.4 buffer showed broadening and splitting of the Q band [48,50]. This behaviour is characteristic of the formation of aggregates in sulfophthalocyanines. For these three complexes, addition of a surfactant (Triton X-100) did not bring about any noticeable change in shape and intensity of the spectra, suggesting that these complexes are in a monomeric state. Addition of Triton X-100 to solutions of $ZnPcS_{mix}$ and $SnPcS_{mix}$ brought about considerable increase in intensity of the low energy band in the visible region, suggesting that the molecules are aggregated and that addition of Triton-X-100 breaks up the aggregates.

The degree of aggregation in water increases with lipophilicity [54], hence the prevalence of the less sulfonated fractions in solution is expected to increase aggregation. High performance liquid chromatography (HPLC) confirmed [50] that $AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$, had a prevalence of fractions with higher degree of sulfonation, hence were not aggregated compared to $ZnPcS_{mix}$ and $SnPcS_{mix}$ which contained less sulfonated fraction, hence were more aggregated. For a series of $AlPcS_n$ complexes, only the di- [61] and tri-sulfonated were essentially monomeric [61,62].

3.2. *Fluorescence spectra and quantum yields*

Since the $MPcS_{mix}$ complexes are a mixture of sulfonated MPc derivatives, the determined photochemical and photophysical parameters are an average for each mixture. It is important to report these parameters for the mixtures since such mixtures are already in use for PDT for example. Each $MPcS_{mix}$ preparation may contain a mixture of tetra-, tri-, di- and mono-sulfonated metallophthalocyanine in varying proportions and each of the sulfonated derivatives will also contain a variety of positional isomers. The compositions of the mixtures were determined by HPLC, hence ensuring the consistency of the mixture [49,50]. Tetrasubstituted MPc complexes ($MPcS_4$) contain positional isomers in a statistical ratio of 1:1:2:4 (for 2,9,16,23-, 2,10,16,24-, 2,9,17,24- and 2,9,16,24-isomers). The isomers are difficult to separate.

$AlPcS_{mix}$, $SiPcS_{mix}$ and $GePcS_{mix}$ consisted of mainly (∼90%) tetrasulfonated derivatives while $ZnPcS_{mix}$ and $SnPcS_{mix}$ contained approximately the same amounts of tetra-, tri- and di-sulfonated derivatives. Thus the parameters listed in Table 1 will be an average for the mixtures and were found to remain unchanged. For the aggregated $ZnPcS_{mix}$ and $SnPcS_{mix}$ complexes [49], it was only the monomer that fluoresced. For the non-aggregated $GePcS_{mix}$ and $SiPcS_{mix}$, the excitation spectra were different from the absorption spectra, suggesting not all the components fluoresced. The fluorescence quantum yields (Φ_F) were influenced both by the heavy atom effect and by aggregation. Comparing $MPcS_{mix}$ (M = Al, Ge, Si) complexes in PBS, Table 1, Φ_F values were lower for heavier atom (e.g. Ge), due to the heavy atom effect [49]. The aggregated $SnPcS_{mix}$ and $ZnPcS_{mix}$ showed significantly lower Φ_F values than the non-aggregated complexes [49] and the Φ_F values increased when surfactant Triton X-100 was added, Table 1.

Comparing $ZnPcS_4$ with $AlPcS_4$ and H_2PcS_4, showed the former to have a low Φ_F value in DMF, and was found to be the best photosensitizer in terms of cell killing ability [63], as a result of the high singlet oxygen quantum yield compared to the other two complexes, Table 1. The low value of Φ_F for $ZnPcS_4$ could be a result of some aggregation even in organic solvents such as DMF. The Φ_F values are generally lower (Table 1) for the $MPcS_{mix}$ complexes in DMSO than in water (with or without Triton X-100) and this was attributed [49] to the presence of relatively heavier atoms in the former, which would tend to favour intersystem crossing rather than fluorescence. Bovine serum albumin (BSA) quenches the fluorescence of ZnPcS complexes [64]. The fluorescence quantum yields of the non-aggregated MPc complexes ($AlPcS_{mix}$, $GePcS_{mix}$ and $SiPcS_{mix}$) decreased in the presence of bovine serum albumin (BSA) Table 1. In other studies, it was observed that the degree of sulfonation had little effect on the fluorescence quantum yields [65]. $AlPcS_2$ gave higher Φ_F in D_2O compared to water [66].

3.3. *Triplet life times and quantum yields*

Triplet quantum yields (Φ_T) are influenced both by the heavy atom effect and aggregation for a series of $MPcS_{mix}$ complexes [49]. Φ_T values for the aggregated $SnPcS_{mix}$ and $ZnPcS_{mix}$, improved on addition of Triton X-100 (Table 1). For the monomeric $AlPcS_{mix}$, $GePcS_{mix}$ and $SiPcS_{mix}$, the Φ_T values were lower (considering the same solvent) for the smaller atom, due to the heavy atom effect. For $ZnPcS_4$, the Φ_T value was high in DMSO ($\Phi_T = 0.88$ [47], Table 1). Compared with other substituted ZnPc complexes (such as *tert*-butylphenoxy, methylphenoxy and nitro substituted ZnPc derivatives), sulfonation of the Pc ring brings about longer triplet lifetimes [47]. However, there was little effect of the degree of sulfonation on triplet lifetimes [65,66], considering the same solvent (compare $AlPcS_2$, $AlPcS_3$ and $AlPCS_4$ in PBS or D_2O, Table 1). The values of τ_T for $MPcS_{mix}$ complexes in DMSO ranged between 120 and 800 μs [49], the highest value being observed for the $AlPcS_{mix}$ (800 μs), followed by the $GePcS_{mix}$ (760 μs), and $ZnPcS_{mix}$ (530 μs). It is important to note that, triplet states of MPc complexes are quenched by oxygen [67,68], hence deoxygenation is important for accurate determinations of triplet life times, τ_T and Φ_T values for all MPcS complexes were found to be generally lower in water compared to the non-aqueous solvents or D_2O, Table 1, [64,69,70]. BSA increases the life time of $AlPcS_4$ as shown in Table 1 [64]. The triplet lifetime values for $ZnPcS_4$ and $ZnNPcS_4$ increased in the presence of detergents [71], Table 1.

Table 1
Photochemical and photophysical data of sulfonated MPc complexes[a]

Complex[b]	Φ_F	Φ_T	Φ_Δ	Φ_P ($\times 10^5$)	τ_T (μs)	Solvent[c]	Refs.
$\mathrm{ZnPcS_{mix}}$	0.16	0.53	0.45	3.65	2.95	PBS	[49]
	0.21	0.61	0.54	7.02	2.37	PBS + Triton X-100	[49]
	0.14	0.86	0.72	13.65	530	DMSO	[47,49]
$\mathrm{ZnPcS_2}$		0.46	0.52		270	Methanol	[115,116]
$\mathrm{ZnPcS_{2.1(mix)}}$[d]			≤0.01 (0.65)[e]			pH 7.4	[72]
			0.74			DMSO	
$\mathrm{ZnPcS_{2.9(mix)}}$[d]			0.10 (0.70)[e]			pH 7.4	[72]
			0.70			DMSO	
$\mathrm{ZnPcS_{3.4(mix)}}$[d]			0.10 (0.69)[e]			pH 7.4	[72]
			0.69			DMSO	
$\mathrm{ZnPcS_{3.7(mix)}}$[d]			0.49 (0.67)			pH 7.4	[72]
			0.70			DMSO	
$\mathrm{ZnPcS_4}$	0.32	0.56			245	Aqueous	[60]
					165	pH 7.1	[64]
			≤0.01 (0.30)[e]			pH 7.4	[72]
			0.52			DMF	[34]
			0.68			DMSO	[72]
	0.28	0.56				DMF	[63]
					50	Water	[70]
			0.70		490	Detergent	[71]
	0.07	0.88	0.46	4.03	470	DMSO	[47]
$\mathrm{ZnNPcS_4}$			0.25		110	Detergent	[71]
$\mathrm{AlPcS_{mix}}$	0.44	0.44	0.42	0.40	2.93	PBS	[50]
	0.34			0.59		BSA/PBS	[50]
	0.39	0.52	0.48	5.79	800	DMSO	[49]
$\mathrm{AlPcS_2}$					520	PBS	[66]
					505	H_2O	[59]
	0.54	0.23			1130	D_2O	[66,120]
	0.40	0.17			520	pH 7.4	[69,116,119]
		0.24	0.27		775	Methanol	[115,116]
					1440	CD_3OD	[66]
			0.15			pH 7.4/Triton X-100	[72]
	0.27					Micelles	[61]
			0.30			CH_3OD	[119]
$\mathrm{AlPcS_3}$					490	PBS	[66]
					1150	D_2O	[66]
			0.42			pH 7.4	[62]
	0.24					Micelles	[61]
$\mathrm{AlPcS_4}$					530	PBS	[66]
					1140	D_2O	[66]
			0.18			pH 10	[16,36]
					500	Aqueous	[60]
			0.22			pH 7.4	[62]
					440	pH 7.1	[64]
	0.56	0.28				DMF	[63]
			0.20			DMF	[34]
					1160	Water/BSA	[64]
					440	Water	[64]
$\mathrm{SiPcS_{mix}}$	0.34	0.45	0.49	0.71	2.90	PBS	[49]
	0.30			0.86		BSA/PBS	[49]
	0.29	0.58	0.52	7.35	439	DMSO	[49]
$\mathrm{GePcS_{mix}}$	0.30	0.67	0.68	0.45	2.76	PBS	[49]
	0.24			0.44		BSA/PBS	[49]
	0.21	0.79	0.78	9.74	760	DMSO	[49]
$\mathrm{SnPcS_{mix}}$	0.05	0.59	0.42	1.59	2.52	PBS	[49]
	0.19	0.68	0.52	1.77	2.32	PBS/Triton X-100	[49]
	0.13	0.87	0.65	14.01	120	DMSO	[49]

Table 1 (*Continued*)

Complex[b]	Φ_F	Φ_T	Φ_Δ	Φ_P ($\times 10^5$)	τ_T (μs)	Solvent[c]	Refs.
$GaPcS_2$		0.36	0.38		390	Methanol	[115,116]
$GaPcS_3$		0.36	0.38		425	Methanol	[10]
$GaPcS_4$			0.41			DMF	[34]
		0.36	0.38		420	Methanol	[115]
$GaPcS_1(C(CH_3)_3)_3$		0.36	0.38		440	Methanol	[115]
$GaPcS_2(C(CH_3)_3)_2$		0.36	0.38		360	Methanol	[115]
$GaPcS_3(C(CH_3)_3)_1$		0.36	0.38		300	Methanol	[115]
$GdPcS_{2(mix)}$[d]			0.37			DMSO	[72]
H_2PcS_4	0.62		0.22		170	Aqueous	[60]
			0.16			DMF	[34]
	0.60		0.24			DMF	[63]
$MgPcS_{2(mix)}$[d]			0.19			DMSO	[72]

[a] Φ_F: fluorescence quantum yield (in general the standard used for determination of Φ_F is chlorophyll *a* in ether ($\Phi_F = 0.32$) [49]); Φ_T: triplet quantum yield; Φ_Δ: singlet oxygen quantum yield; Φ_P: photodegradation quantum yield; τ_T: triplet life time.

[b] Where sulfonated MPc complexes are in a mixture, the reported parameters are an average for the mixture.

[c] BSA: bovine serum albumin, DMF: dimethylformamide, DMSO: dimethylsulfoxide, PBS: phosphate buffer saline (or solution).

[d] Subscripts: average number of sulfo groups per molecule.

[e] Values in pH 7.4 + Triton X-100 in parentheses.

3.4. Singlet oxygen and photobleaching quantum yields

Singlet oxygen quantum yield (Φ_Δ) values are expected to depend on the triplet quantum yield of the photosensitizer. Thus, the trend in variation of Φ_Δ within an array of photosensitizers should be parallel to variations in their Φ_T values. And this was observed for a range of $MPcS_{mix}$ photosensitizers [49]. Lower singlet oxygen quantum yields were observed in aqueous solutions (in the absence detergents) compared to organic solvents or in aqueous media in the presence of detergents, Table 1, for MPcS complexes [49,72]. However, for $AlPCS_4$ and H_2PcS_4, low singlet oxygen quantum yields <0.3 were observed in DMF and in aqueous solutions, Table 1. The degree of sulfonation has a dramatic influence on the production of singlet oxygen [65]. For a series of $ZnPcS_{n(mix)}$ complexes (Table 1), Φ_Δ values were almost the same in DMSO, but an increase in Φ_Δ with the value of *n* is observed in PBS (pH 7.4), in the absence of Triton X-100. The Φ_Δ value is low for the more hydrophilic (hence more aggregated) $ZnPcS_{2(mix)}$ ($\Phi_\Delta \le 0.01$), but high for the mainly monomeric $ZnPcS_{3.7(mix)}$ ($\Phi_\Delta = 0.49$ in pH 7.4 buffer), Table 1 [72]. Similar to $ZnPcS_4$, Φ_Δ value for $ZnNPcS_4$ increased in the presence of detergents [71]. The Φ_Δ values for tetrasulfonated MPc complexes were found to increase as follows in DMF: $ZnPcS_4 > GaPcS_4 > AlPcS_4 \sim H_2PcS_4$ and in general Φ_Δ values were higher in DMF than in water or water containing cetyl trimethylammonium chloride (CTAC) [34]. In reversed micelles, singlet oxygen quantum yields for the di- and tri-substituted AlPcS complexes were found to be the same as in water, even though enhanced intersystem crossing was observed in micelles [62]. For the unmetallated $H_2PCS_{n(mix)}$, intermolecular hydrogen bonding results in extensive aggregation, with the addition of Triton X-100 only leading to partial monomerisation and a low Φ_Δ value (0.02) [72].

Photodegradation (photobleaching) quantum yield (Φ_d) is a measure of the stability of a molecule under photo-irradiation. It is believed that photobleaching is a singlet oxygen-mediated process; hence its efficiency should depend on the value of Φ_Δ. However, for a series $MPcS_{mix}$ complexes, this was not the case, implying that $MPcS_{mix}$ photodegradation is probably not initiated by singlet oxygen alone [49].

4. Octa (and higher)-substituted MPc complexes

MPc complexes are notorious for their lack of solubility in common organic solvents. Introduction of substituents onto the Pc ring enhance solubility of these complexes. Substitution of the phthalocyanine ring may be at either peripheral (2, 3) or non-peripheral (1, 4) positions (see Fig. 1 for numbering), or both. Substitution at the peripheral positions results in octasubstituted derivatives, Fig. 1. The photochemical and photophysical behaviour of a variety of peripherally substituted ZnPc complexes have been studied [37,47] (Fig. 1). Some of the complexes (e.g. **1a**, **1c**, **1g**, **1j** and **ZnPc(Cl)$_8$**) showed aggregation behaviour in organic solvents even at low concentrations (<1 × 10^{-5} M). The UV–vis spectrum of **1k** showed an extra band (the so called X band, [73]) in non-polar or less polar solvents such as benzene and chloroform, but not in more polar solvents such as DMF, acetone and DMSO [38]. The origin of the X band was explained in terms of the distortion of the Pc ring due to the presence of eight phenyl groups on the peripheral positions of the phthalocyanine ring [74].

The presence of bulky groups on the axial position in MPc complexes prevents aggregation. Thus octaphenoxy SiPc complexes containing various axial ligands were studied (Fig. 2, complexes **5**). The axially ligated SiPc complexes containing phenoxy groups on the ring showed spectra typical of monomeric species [43]. For **5b**, aggregation occurs due to hydrogen bonding between the axial hydroxyl groups [75]. Octacarboxy phthalocyanines ($MPc(COOH)_8$) are water soluble and when M = Al(III)(OH) association via hydrogen bonding occurs, affects the production of singlet oxygen hence the photosensitizing ability [62].

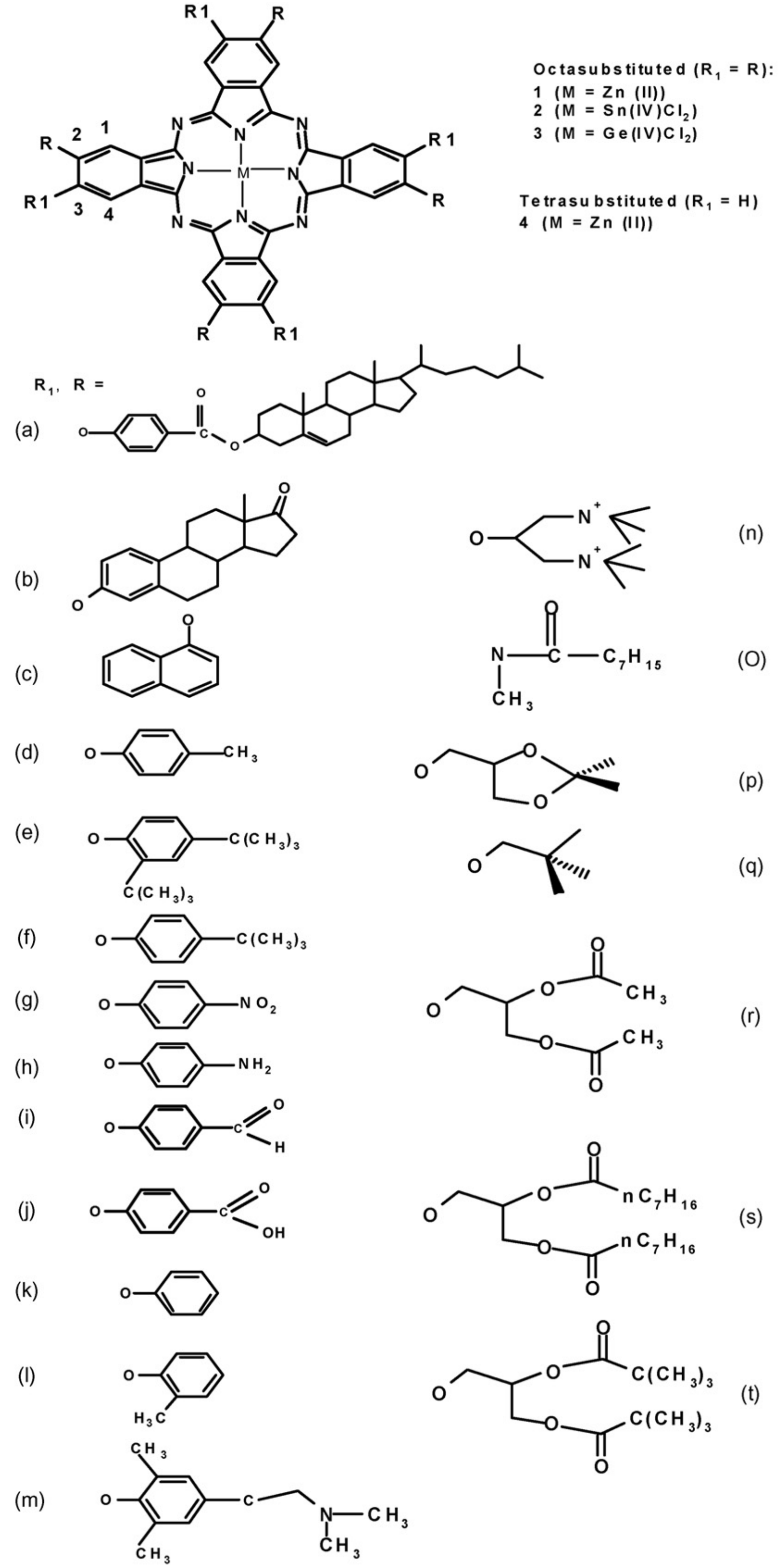


Fig. 1. Molecular structure of octasubstituted and tetrasubstituted MPc complexes.

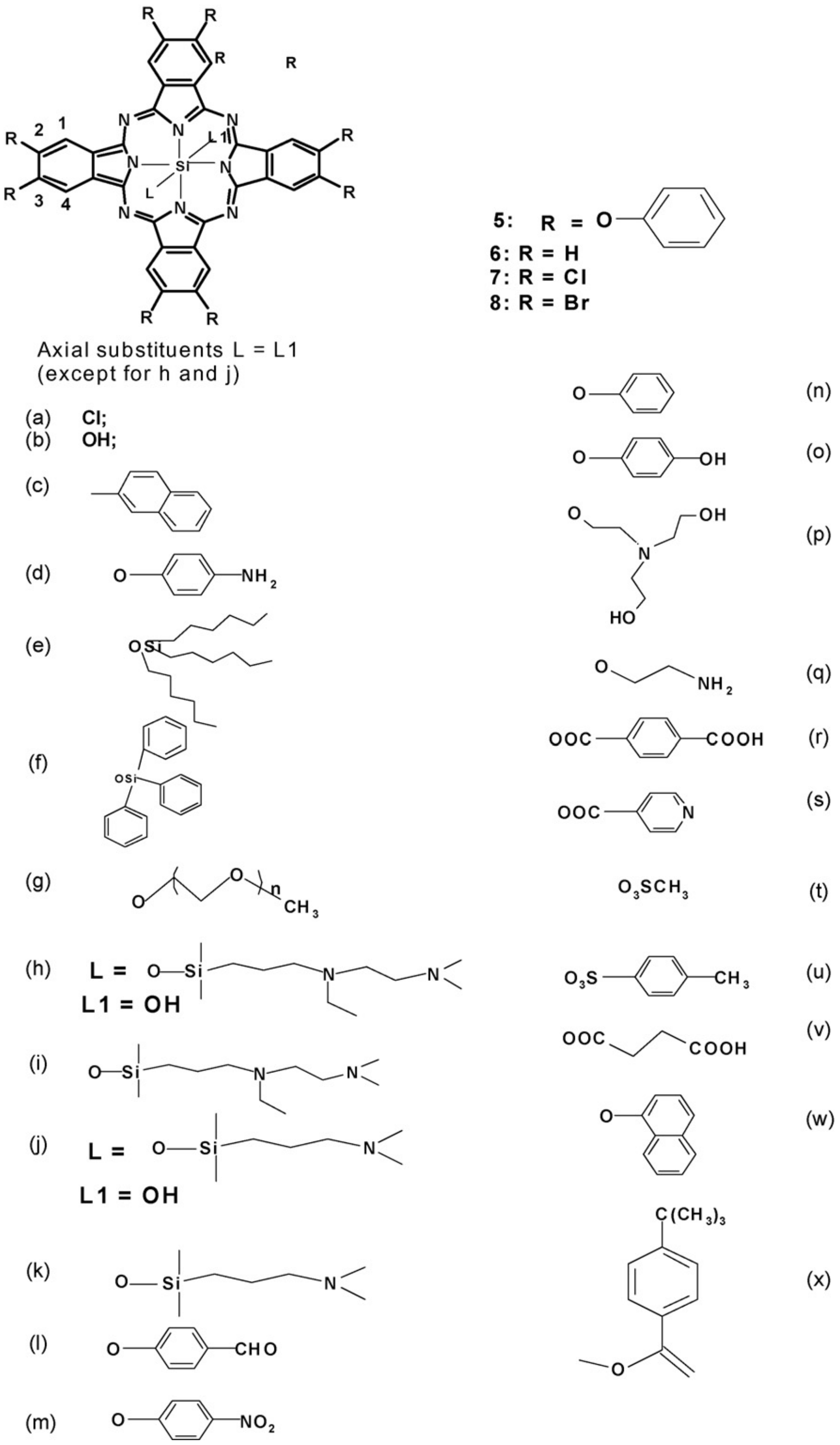


Fig. 2. Axially substituted SiPc complexes.

4.1. Fluorescence spectra and quantum yields

For **1k** (Fig. 1), the fluorescence excitation and emission spectra exhibited two bands, associated with the loss of symmetry due to the twisting of the phenyl ring, which distorts the molecule [47]. The change in the nature of axial ligand for SiPc complexes does not have a huge effect on the fluorescence quantum yields [43], Table 2, ranging from $\Phi_F = 0.02–0.34$ for **5a–5f**, containing the same ring substituent. For complexes **7g** and **8g** containing two axial poly(ethylene glycol) axial ligands, halogenation of the ring resulted in decrease in Φ_F values [76], Table 2, when compared to **6g** ($\Phi_F = 0.80$) containing the same axial ligands but not ring halogenated. A decrease in the Φ_F value was observed on going from ZnPc ($\Phi_F = 0.17$ in acetone) to $ZnPcF_{16}$ followed by an increase for the $ZnPc(C(CF_3)_2F)_8F_8$ complex [77], Table 3. This observation is consistent with the notion that aro-

Table 2
Photophysical and photochemical parameters of axially ligated and ring substituted SiPc complexes

Complex	Φ_F	Φ_T	Φ_Δ	Φ_P ($\times 10^5$)	τ_T (μs)	Solvent	Refs.
5a	0.21	0.31	0.14	1.0	194	DMSO	[43,75]
5b	0.18	0.30	0.07	–	179	DMSO	[43,75]
5c	0.02	0.29	0.20	170	260	DMSO	[43,75]
5d	0.03	0.43	0.03	3.3	271	DMSO	[43,75]
5e	0.29	0.40	0.41	4.1	311	DMSO	[43,75]
5f	0.34	0.41	0.20	3.0	356	DMSO	[43,75]
5l			0.21	200		DMSO	[75]
5m			0.19	100		DMSO	[75]
5n			0.21	160		DMSO	[75]
5o			0.18	400		DMSO	[75]
5p			0.11	1.9		DMSO	[75]
5q			0.14	1.7		DMSO	[75]
5r			0.21	1.8		DMSO	[75]
5s			0.14	7.0		DMSO	[75]
5t			0.16	1500		DMSO	[75]
5u			0.15	800		DMSO	[75]
5v			0.17	1.4		DMSO	[75]
5w			0.21	170		DMSO	[75]
6g	0.80		0.20			DMF	[76]
7g	0.73		0.38			DMF	[76]
8g	0.34		0.52			DMF	[76]

Φ_P values for complexes **5** represent phototransformation to the hydroxyl species. Φ_F: fluorescence quantum yield (in general the standard used for determination of Φ_F is chlorophyll *a* in ether ($\Phi_F = 0.32$) [49]); Φ_T: triplet quantum yield; Φ_Δ: singlet oxygen quantum yield; Φ_P: photodegradation quantum yield; τ_T: triplet life time.

matic fluorine groups in $ZnPcF_{16}$ are part of the phthalocyanine π system and thus increase the intersystem crossing. Aliphatic fluorine groups in $ZnPc(C(CF_3)_2F)_8F_8$ are not conjugated with the phthalocyanine π system, resulting in increased fluorescence lifetime [77].

The fluorescence spectra of a phthalocyanine–porphyrin complex in which eight units of zinc tetraphenyl porphyrin ($ZnPc(ZnTPP)_8$) are linked to a central ZnPc molecule via ether linkage showed extensive energy transfer between the porphyrin and phthalocyanine moeties [78]. The excitation spectra was slightly different from the absorption spectra in terms of Q band absorption wavelength, suggesting that changes in the nature of the molecules follow upon excitation. Φ_F values upon excitation at the porphyrin Q-band were found to be very small due to energy transfer taking place from the porphyrin units to the phthalocyanine moeity. This was also observed for a porphyrin-phthalocyanine hetero dimer linked by a triplebond [79,80] and $ZnPc(ZnTPP)_4$ [81].

4.2. Triplet lifetimes and quantum yields

τ_T values were found to be very low for SnPc derivatives, ranging from 10 to 32 μs (**2b**, **2k** and **2l**) compared 168–340 μs (**3b**, **3k** and **3l**) [44] for the corresponding GePc complexes, Table 3. For the axially ligated complexes **5**(**a**–**f**) [43], triplet state lifetimes vary according to the degree of aggregation, with the aggregated **5b** showing a shorter lifetime compared to the rest of the complexes in the series [43], Table 3. The Φ_T values were also lower for the SnPc (**2b**, **2k**, **2l**) derivatives compared to the corresponding GePc (**3b**, **3k**, **3l**) derivatives, contradicting the heavy atom effect phenomena.

Triplet quantum yields were not affected much by changes in axial ligands. For complexes **5**(**a**–**f**), the Φ_T were 0.31–0.43 [43], Table 2. There was a decrease in τ_T values in going from ZnPc to $ZnPcF_{16}$ followed by an increase for the $ZnPc(C(CF_3)_2F)_8F_8$ complex [77], Table 3. As discussed above, the differences are explained in terms of changes in the conjugation of the phthalocyanine π system.

For **ZnPc(ZnTPP)$_8$**, triplet lifetime decreased compared to the respective monomers, and this decrease was dependant on the number of porphyrin rings present on the molecules. **ZnPc(ZnTPP)$_4$** (containing four porphyrin units) had a triplet lifetime of 230 μs and **ZnPc(ZnTPP)$_8$** gave $\tau_T = 170$ μs [78,81]. The triplet quantum yields also decreased with the number of porphyrin rings. $\Phi_T = 0.12$ for **ZnPc(ZnTPP)$_4$** and 0.04 for **ZnPc(ZnTPP)$_8$** [78,81].

4.3. Singlet oxygen and photobleaching quantum yields

In general, zinc phthalocyanine complexes containing the more electron-withdrawing substituted phenoxy groups (e.g. **1g** and **1j**) tended to stabilize the phthalocyanine molecule in the presence of light in DMSO [37]. The more electron-donating phenoxy groups (e.g. **1e** and **1f**) tend to be easily degraded in chloroform [37], hence confirming that the photobleaching mechanism involves oxidative degradation of the ring. However in DMSO **1f** and **1e** were found to be relatively stable [82], Table 3, but less stable than **1g** and **1j**. Complexes **1a** and **1b** which contain biologically important substituents, cholesterol and estrone, respectively, were easily degraded in chloroform [37], Table 3. In THF, complex **1k** underwent phototransformation rather than photobleaching, resulting in an increase in the low energy band (the X band), due to the distortion of the ring [38]. $ZnPc(SC_6H_4CH_3)_8$ and $ZnPc(SC_4H_9)_8$ complexes containing thiol substituents were relatively stable ($\Phi_p \sim 6 \times 10^{-5}$), Table 3, with the former showing less stability than the latter, due to the ability of benzene to enhance photobleaching [35,83].

Attempts to photobleach complexes **3b**, **3k** and **3l** resulted in the reduction of the central Ge(IV) ion to Ge(II)Pc species [44], and the Ge(II)Pc species was stable towards photodegradation.

However corresponding complexes **2b**, **2k** and **2l**, did not show phototransformation to the Sn(II)Pc species. For the latter complexes, there was evidence of photoreduction of the Pc ring during the photobleaching process and a mechanism was proposed [44].

For the axially ligated complexes **5**(**a**, **c**–**f**) (Fig. 2), attempts to photobleach resulted in the well-known axial ligand transformation to the hydroxyl group (to **5b**) for all the complexes.

Electron-withdrawing and electron-donating nature of ring substituents affected singlet oxygen yields [84]. For ZnPc complexes **1a**–**k**, aggregation also played a significant role in the magnitude of the Φ_Δ values [37], Table 3. Thus the relatively low Φ_Δ values for **1j** and **1c** were explained in terms of the aggregated nature of these complexes. The octacarboxy AlPc ($(OH)AlPc(COOH)_8$) is aggregated due to hydrogen bonding, its Φ_Δ value of 0.12 (Table 3) is thus low. The **ZnPc(Cl)$_8$**

Table 3
Photophysical and photochemical parameters of octa (or more) substituted MPc complexes (except M = Si)

Complex	Φ_F	Φ_T	Φ_Δ	$\Phi_P \times 10^5$	τ_T (μs)	Solvent	Ref.
1a			0.44	111		$CHC1_3$	[37]
1b			0.64	275		$CHC1_3$	[37]
	0.15		0.43	1.74		DMSO	[38]
1c			0.01				[37]
1d	0.24	0.63	0.51	2.12	370	DMSO	[37,47]
1e			0.44	766		$CHC1_3$	[37]
1f			0.52	3.3		DMSO	[38]
			0.73	464		$CHC1_3$	[37]
1g			0.36	1.41		DMSO	[37]
1h			0.07	0.86		DMSO	[37]
1i			0.34	5.04		DMSO	[37]
1j			0.23	0.24		DMSO	[37]
1k			0.60	2.53	10	DMSO	[44]
	0.17		0.53	12.1		DMF	[10]
2b	0.01	0.15	0.23		10	DMSO	[44]
2k	0.04	0.19	0.22		30	DMSO	[44]
2l	0.06	0.45	0.34		32	DMSO	[44]
3b	0.21	0.20	0.18		205	DMSO	[44]
3k	0.12	0.30	0.18		340	DMSO	[44]
3l	0.31	0.50	0.24		168	DMSO	[44]
ZnPc(ZnTPP)$_8$ (λ_{exc} = 603 nm)	0.005	0.04			170	DMSO	[78]
$(OH)AlPc(COOH)_8$			0.12			DMSO	[36]
$H_2Pc(O(CH_2)_3CH_3)_8$	0.19					Tetrahydrofuran	[118]
$ZnPc(COOH)_8$			0.52			pH 10	[36]
ZnPc(Cl)$_8$	0.02		0.34		370	DMSO	[47]
$ZnPc(SC_6H_4CH_3)_8$			0.54	5.2		DMF	[83]
$ZnPc(SC_4H_9)_8$			0.61	6.4		DMF	[83]
$ZnPc(C_6C_{13})_7(CH_2)_{11}SH$			0.45			Toluene	[85]
$ZnPc(C_6C_{13})_7(CH_2)_{11}SH$-nanoparticles			0.65			Ethanol	[85]
$ZnPcPh_4(O(CH_3)_4)$	0.034					$CHC1_3$	[118]
$ZnPc(C_{10}H_{21})_8$		0.26	0.47			Tetrahydrofuran	[117]
$ZnPcF_{16}$	0.04		0.13		<1	Acetone	[77]
$ZnPc(C(CF_3)_2F)_8F_8$	0.39		0.21		131	Acetone	[77]
$Zn(OC_6H_{13})_8$			0.52			DMF	[34]

Φ_F: fluorescence quantum yield (in general the standard used for determination of Φ_F is chlorophyll *a* in ether ($\Phi_F = 0.32$) [49]); Φ_T: triplet quantum yield; Φ_Δ: singlet oxygen quantum yield; Φ_P: photodegradation quantum yield; τ_T: triplet life time.

complex gave relatively low Φ_Δ a value attributed to its aggregation behaviour [47]. Complex **1f** gave a larger Φ_Δ value (0.73) in chloroform [37] than in DMSO ($\Phi_\Delta = 0.52$) [82]. Comparing complexes **2k**, **3k** (Fig. 1) and **5a** (Fig. 2) containing the same peripheral and axial ligands, but different central metals (Sn, Ge and Si, respectively) showed that Φ_Δ increases with increase in the size of the central metal as follows: Si(IV) (**5a**, $\Phi_\Delta = 0.14$) < Ge(IV) (**3k**, $\Phi_\Delta = 0.18$) < Sn(IV) (**2k**, $\Phi_\Delta = 0.22$), due to the heavy atom effect [44]. This effect was also used to explain the higher Φ_Δ value for **3k** when the axial chloride ligands are replaced by the iodide ligands [45]. For complex **2b**, containing estrone ligands (structure **b** in Fig. 1) on the periphery, Table 3, the Φ_Δ value was similar to when estrone was located axially [44].

For a series of axial substituents for **5a–f**, **l–w**, the Φ_Δ values did not vary much with the axial ligand [75] and were generally low ranging between 0.03 and 0.24, Table 2. Nanoparticles of $ZnPc(C_6C_{13})_7(CH_2)_{11}SH$ complex on gold were found to generate singlet oxygen with higher quantum yields than when in solution, Table 3 [85]. For complexes **7g** and **8g** (Table 2) containing two axial poly(ethylene glycol) ligands, halogenation of the ring resulted in increase in Φ_Δ values [76], when compared to **6g** containing the same axial ligands but unsubstituted, in accordance with the heavy atom effect. A decrease in Φ_Δ value was observed in going from ZnPc to $ZnPcF_{16}$ followed by an increase for the $ZnPc(C(CF_3)_2F)_8F_8$ complex [77].

Oligomers of complex **5** containing two to five, and nine rings linked by terephthalate linkages, gave singlet oxygen quantum yields ranging from 0.11 to 0.34 [86]. The Φ_Δ values increased with the number of the rings up to five, then decreased.

5. Tetra substituted MPc complexes

Tetrasubstituted MPc complexes are more common than the octasubstituted. This could be due to the readily available starting phthalonitriles [87] for the tetrasubstituted derivatives.

5.1. Fluorescence spectra and quantum yields

$ZnPc(NO_2)_4$ and $ZnPc(NH_2)_4$ complexes are aggregated with split or broad Q bands. Fluorescence of these aggregated complexes occurred from the monomeric component [88]. The $\Phi_{\rm F}$ values were very low (Table 4) for the aggregated $ZnPc(NO_2)_4$ and $ZnPc(NH_2)_4$ as expected. Fluorescence quantum yields were not affected by addition of cyclodextrin [88] to these complexes. Cyclodextrin is known to prevent aggregation in porphyrins [89]. The fluorescence quantum yields of $AlPc(COOH)_4$ complex adsorbed onto silica particles, were found to be higher than in solution [90], Table 4. Halogenation of ZnPc derivatives resulted in a decrease in fluorescence quantum yield as expected for the heavy atom effect [31].

The $\Phi_{\rm F}$ values obtained for complexes **9** and **10** (Fig. 3) were low as is typical of MPc complexes [51,91,92]. The nature of substituents did not play an important role in determining the fluorescing capabilities of the complexes **9**, Table 4. The unmetalated form of **9b** (**H$_2$9b**) is water soluble and it is highly aggregated in water and methanol, but mainly monomeric in DMSO (with a low $\Phi_{\rm F} = 0.04$) and chloroform [92]. The fluorescence quantum yield of **H$_2$9b** in water containing a surfactant (CTAC) was $\Phi_{\rm F} = 0.12$, a value typical of MPc complexes.

Binuclear ZnPc complexes containing catechol bridges (**12a**–**c**, **e**), Fig. 3, showed UV–vis spectra with a split Q band, this is an indication that the two halves of the molecule are sufficiently uncoupled to be regarded as two mononuclear species held together by the catecholate bridge [93]. The values of the fluorescence quantum yield ($\Phi_{\rm F}$) were low, for complexes **12**, Table 4, and this was attributed to self-quenching process of the binuclear phthalocyanine complexes [93].

The $\Phi_{\rm F}$ value of ZnPc in the pentamer (**ZnPc(ZnTPP)$_4$**) ($\Phi_{\rm F} = 0.03$), Table 4, was much smaller than that in the monomer ($\Phi_{\rm F} = 0.2$), implying that ZnPc fluorescence is quenched in the presence of the porphyrin substituents. For porphyrin–phthalocyanine heterodimer (ZnTPP–O–$ZnPc(CH_3)_3)_4$ linked with an oxygen atom, selective excitation of the porphyrin chromophore resulted in very efficient energy transfer to the phthalocyanine moiety [94] with very low $\Phi_{\rm F}$ values compared to the individual components, Table 4.

In a series of positional isomers of zinc bis(1,4-didecylbenzo)bis(3,4-pyridino)porphyrazine, the isomer with the lowest symmetry (**13**, Fig. 4) gave the highest triplet lifetime [95]. The *N*, *N*′ *N*″, *N*‴-tetramethylated quaternised forms of tetrapyridinoporphyrazines (complexes **14**, Fig. 4), are known not to form aggregates in aqueous solutions. The presence of trialkylated compounds due to incomplete quarternization of the outer nitrogen atoms induces severe aggregation [96], thus complexes **14a** and **14c** were found to be highly aggregated in solution [97,98]. The $\Phi_{\rm F}$ values were lower in water (containing sodium dececylsulfate, SDS) compared to toluene for **14d** [98], Table 4.

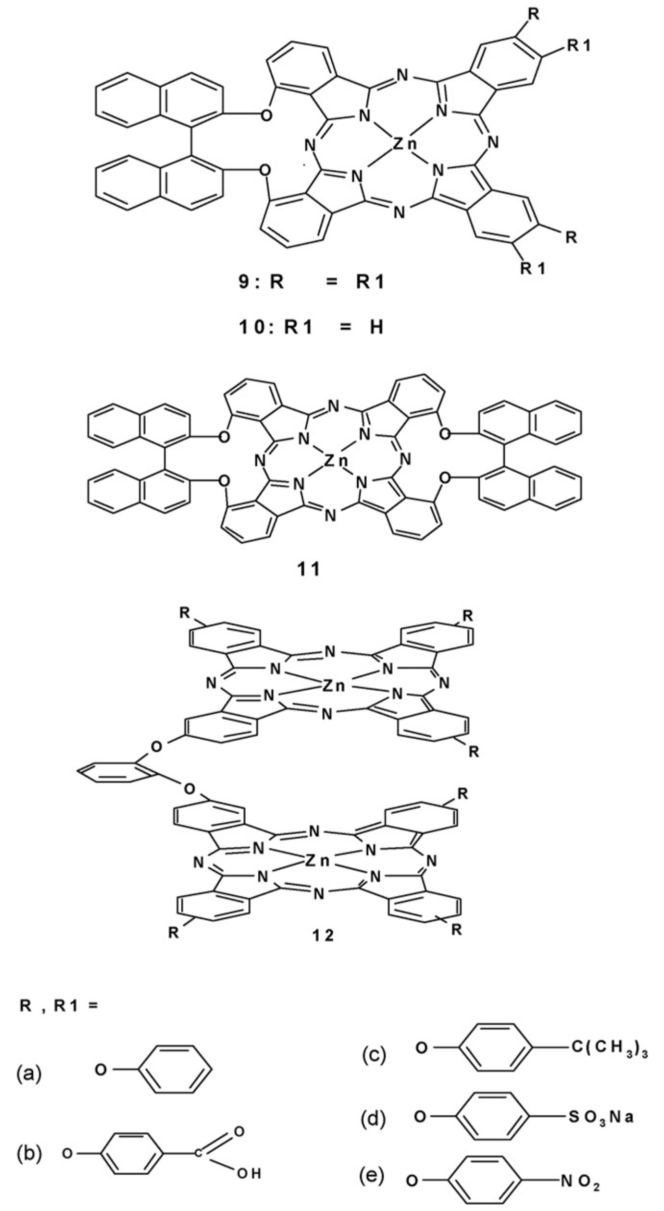


Fig. 3. Di- (**9**) or tetra-substituted (**10**) substituted binaphthalo Zn phthalocyanines. (**11**) Bisnaphthalocyanine, (**12**) binuclear ZnPc complexes containing catechol bridges.

5.2. Triplet lifetimes and quantum yields

A relatively low $\tau_{\rm T}$ value was reported for **4f** [47], $\tau_{\rm T} = 160$ μs in DMSO compared to other monomeric tetra and octasubstituted ZnPc complexes, and considering the same solvent. This was explained in terms “loose bolt” effect [99], which accelerates internal conversion. Compared with ZnPc ($\tau_{\rm T} = 350$ μs), the excited states of the complexes **9**, **10** and **11** ($\tau_{\rm T}$ ranging 90–180 μs), Table 4, were found to be more short-lived [51], due to the quenching abilities of naphthalene [51,100]. The binaphthalo complex **11**, had a relatively high $\tau_{\rm T}$, compared to complexes **9** and **10** (except **9c**), Table 4, this was attributed to its rigid structure. Complexes (**10a**–**c**) generally had lower $\tau_{\rm T}$ values compared to the corresponding **9a**–**c**. Quantum yields of the triplet state also favor the less aggregated complexes, **9c** and **10c**. For the unmettalated water soluble **H$_2$9b**, $\Phi_{\rm T}$ values were highly solvent dependent, with the highest value being observed in water containing CTAC, followed by DMSO, thus showing

Table 4
Photochemical and photophysical parameters of tetrasubstituted MPc complexes

Complex	Φ_F	Φ_T	Φ_Δ	$\Phi_P \times 10^5$	τ_T (µs)	Solvent	Refs.
4f	0.14	0.85	0.60	3.33	160	DMSO	[47,88]
	0.13		0.42	9.41		DMF	[10]
			0.55			DMF	[34]
			0.58		287	Toluene	[67]
4m			0.59		~300	Ethanol	[67]
4n			0.6		125	Water	[105]
4o	0.18	0.66	0.51		57	Toluene	[96]
4p	0.28						[102]
4q	0.3						[102]
4r	0.32						[102]
4s	0.32						[102]
4t	0.26						[102]
ZnPc(ZnTPP)$_4$ ($\lambda_{exc} = 640$ nm)	0.03	0.12			230	DMSO	[92]
9a	0.17	0.52	0.54	3.28	150	DMSO	[51]
9b	0.16	0.27	0.31	1.65	90	DMSO	[51]
9c	0.16	0.70	0.72	3.77	180	DMSO	[51]
H$_2$9b	0.04	0.34			~2	DMSO	[92]
10a	0.20	0.45	0.47	0.93	120	DMSO	[51,91]
10b	0.15	0.25	0.23	0.30	130	DMSO	[51]
10c	0.22	0.62	0.58	2.3	90	DMSO	[51,91]
10d	0.26		0.37	0.88		DMSO	[91]
11	0.19	0.58	0.68	0.38	150	DMSO	[51,91]
12a	0.07		0.22			DMSO	[93]
12b	0.06		0.06			DMSO	[93]
12c	0.08		0.14			DMSO	[93]
12e	0.06		0.24			DMSO	[93]
13					26	Toluene	[95]
14a			<0.01			DMSO	[97]
14b			0.02			DMSO	[97]
14c			0.01			DMSO	[97]
14d			0.06			DMSO	[97]
	0.25		0.71		139	Water (SDS)[a]	[96]
15d	0.09		0.55		133	Water (SDS)	[96]
16a			0.17			DMSO	[97]
16b			0.15			DMSO	[97]
16c			0.21			DMSO	[97]
16d			0.16			DMSO	[97]
(Cl)GaPc(C(CH$_3$)$_3$					257	Toluene	[103]
(C$_6$H$_2$F$_3$CH$_3$)GaPc(C(CH$_3$)$_3$)					200	Toluene	[103]
(C$_6$H$_2$F$_3$CH$_3$)InPc(C(CH$_3$)$_3$)					22	Toluene	[103]
(Cl)InPc(C(CH$_3$)$_3$)					46	Toluene	[103]
ZnPc(NO$_2$)$_4$	0.02		0.11		310	DMSO	[10,47,88]
	0.12		0.24			DMF	
ZnPc(Cl)$_4$	0.29	0.59	0.35		216	DMSO	[31]
ZnPc(Br)$_4$	0.17	0.76	0.41		96	DMSO	[31]
ZnPc(I)$_4$	0.088	0.86	0.54		55	DMSO	[31]
Zn(C(CH$_3$)$_3$)$_4$	0.26	0.58	0.54		200	Ethanol	[13]
ZnPc(NH$_2$)$_4$	<0.01		0.11			DMSO	[88]
ZnNPc[b]	0.07	0.37	0.19	16.4	126	DMSO	[47,88]
	0.12		0.24			DMF	[10]
ZnPc(OCH$_2$C(CH$_3$)$_3$)$_4$	0.25					CHC1$_3$	[118]
ZnPc((CH$_2$)$_2$O(CH$_2$)$_2$OCH$_3$)$_4$			0.44		~300	Toluene	[67]
ZnPc(COOH)$_4$			0.48			DMF/pyridine	[34]
AlPc(COOH)$_4$	0.66[c]		0.10			Adsorbed	[90]
H$_2$Pc(OCH$_2$C(CH$_3$)$_3$)$_4$	0.24					CHC1$_3$	[118]
H$_2$Pc((CH$_2$)$_2$O(CH$_2$)$_2$OCH$_3$)$_4$			0.19		~300	Toluene	[67]
ZnTPP–O–ZnPc(CH$_3$)$_3$)$_4$[d]	<0.01	0.68			75	Toluene	[94]

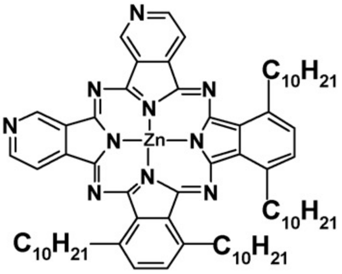
Φ_F: fluorescence quantum yield (in general the standard used for determination of Φ_F is chlorophyll *a* in ether ($\Phi_F = 0.32$) [49]); Φ_T: triplet quantum yield; Φ_Δ: singlet oxygen quantum yield; Φ_P: photodegradation quantum yield; τ_T: triplet life time. TSPP: 5,10,15,20-tetra(*p*-sulfonato-phenyl-porphyrin).

[a] SDS: sodium dececylsulfate.

[b] NPc: naphthalocyanine.

[c] Corrected for aggregation, background absorption, re-absorption and re-emission effects.

[d] TPP: tetraphenyl porphyrin.



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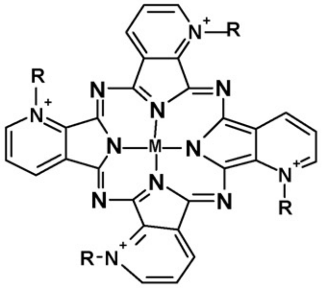
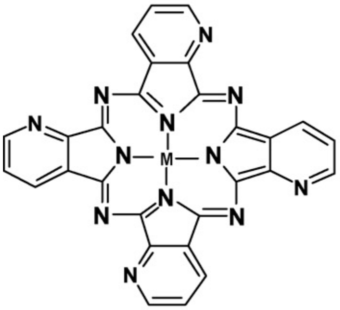


14 R = CH_3

15 R = $(CH_2)_4COOCH_2CH_3$



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(a) M = $Ge^{IV}(OH)_2$

(b) M = $Sn^{IV}(OH)_2$

(c) M = $Si^{IV}(OH)_2$

(d) M = Zn

Fig. 4. (**13**) Zinc bis(1,4-didecylbenzo)bis(3,4-pyridino)porphyrazine, the isomer with the lowest symmetry. (**14** and **15**) *N*, *N*, *N*, *N*-tetraalkylated quaternised form of Zn tetrapyridinoporphyrazines. (**16**) Zn tetrapyridinoporphyrazine complexes.

again that monomerization increases photophysical parameters. This complex however, showed very low τ_T values in all solvents [92]. Halogenation of ZnPc resulted in increased triplet quantum yields and decreased triplet lifetimes as expected for the heavy atom effect [31].

An efficient intersystem crossing was observed for the heterodimer consisting of positively charged porphyrin and a negatively charged phthalocyanine [101].

The triplet lifetimes increased with decrease in temperature for complexes **4p**, **4q**, **4r**, **4s** and **4t** [102]. The degree of aggregation decreased for complexes containing bulky substituents, and increased for long alkyl chain substituents [102]. For a series of indium and gallium monomers and bridged dimers the GaPc complexes were found to have much longer triplet lifetimes compared with the corresponding InPc complexes [103,104].

5.3. Singlet oxygen quantum yields and photobleaching

For $ZnPc(NH_2)_4$ complex containing an amine group, a low Φ_Δ (=0.11 in DMSO) value was obtained [88], due to the well-known quenching abilities of singlet oxygen by the amine group and due to the aggregated nature of this complex. A high Φ_Δ value (0.60) was observed for the monomeric **4f** in DMSO ($\Phi_\Delta = 0.60$) [47,88] and $\Phi_\Delta = 0.58$ in toluene [67], Table 4.

Complexes **14a** and **14c** were found to be aggregated [97], while **14b** and **14d** did not show aggregation. Thus the Φ_Δ values of the former two compounds were negligible ($\Phi_\Delta \leq 0.01$), but only marginally higher for the latter two, Table 4. For complex **4n** containing (*N*,*N*,*N*-trimethyl)amino-2-propyloxy groups, the singlet oxygen quantum yield of 0.6 in water decreased to 0.3 in PBS, but remained at 0.6 in DMF [105].

Of the adjacently substituted complexes (**9** and **10**), **9c** and **10c** containing bulky t-butyl phenyl substituents (hence less aggregated), gave the largest Φ_Δ value [51], Table 4. Comparing data obtained for tetra-substituted complexes **9** with that for the di-substituted complexes **10**, the latter gave lower Φ_Δ values than the corresponding complexes of the former. Polymer bound chloroaluminum tricarboxymonoamidephthalocyanine gave decreased amount of singlet oxygen compared to unbound (in solution) complex [106]. Singlet oxygen production is restricted on polymers due to decreased lifetime of the triplet state [106].

The Φ_Δ values for complexes **12** were low compared to value for monomeric ZnPc and this was attributed to intramolecular coupling of the rings as explained above [93]. A mixture of solutions of anionic 5,10,15,20-sulfonato-phenyl-porphyrin (TSPP) and a positively charged $H_2Pc(SCH_2CH_2N^+(CH_3)_3CH_3SO)_2(NH_2)_2$ gave high Φ_Δ values compared to individual components [107], metallated $ZnPc((CH_2)_2O(CH_2)_2OCH_3)_4$ gave larger Φ_Δ value than unmetallated $H_2Pc((CH_2)_2O(CH_2)_2OCH_3)_4$ Table 4 [67]. For the porphyrazine complexes **14d** and **15d**, singlet oxygen quantum yields were higher in aqueous (SDS) solutions compared to toluene or methanol/pyridine solvent mixture [96].

The aggregated complexes $ZnPc(NH_2)_4$ and $ZnPc(NO_2)_4$ did not undergo photobleaching, they underwent transformation from the aggregated to the monomeric state on photolysis [88]. Photolysis of the less aggregated tetrapyridinoporphyrazines (**14b** and **14d**) in DMSO resulted in degradation accompanied by reduction of the ring as was observed above for octasubstituted SnPc complexes. Thus the complexes exhibited a strong tendency towards reductive quenching of excited states [96]. The di-substituted complexes **10**, were found to be generally more stable to photodegradation than the corresponding tetra-substituted derivatives (complexes **9**), Table 4. The increase in stability of complexes **10** was attributed that the plurality of the bulky substituent which may destabilize the Pc ring in complexes **9**.

6. Unsubstituted phthalocyanme complexes

These complexes are less soluble than the substituted derivatives, hence there has been less study of their photophysical or photochemical properties. The most studied of these complexes are ZnPc and AlPc. Some studies on GePc, SnPc and SiPc have recently been reported. Earlier reviews [14,60] provided data for some of the unsubstituted derivatives discussed in this work.

6.1. Fluorescence and triplet quantum, and triplet lifetimes

Low Φ_F values were obtained for Zn naphthalocyanine (ZnNPc), this was explained in terms of the fast degradation of this complexes on photolysis [47,88]. Fluorescence quantum yield of unsubstituted ZnPc is ~0.2 [47,88] in DMSO and is typical of MPc complexes. This value was influenced by the vis-

Table 5
Photochemical and photophysical properties of ring unsubstituted MPc complexes

Complex	Φ_F	Φ_T	Φ_Δ	$\Phi_P \times 10^5$	τ_T (μs)	Solvent	Refs.
6e					243	Tetrahydrofuran	[98]
			0.32			$CHCl_3$	
6f					213	THF	[98]
			0.35			$CHCl_3$	
6g	0.80		0.20			DMF	[76]
6h			0.50		139	Acetonitrile	[110]
6i			0.20		188	Acetonitrile	[110]
6j			0.43		113	CH_3CN	[110]
6k			0.32		160	CH_3CN	[110]
6x	0.62					DCM	[112]
H_2Pc	0.55					$CHC1_3$	[107]
ZnPc	0.30					Ethanol	[107]
	0.3					1-C1NP^a	[60]
	0.32	0.50	0.40		250	DMSO	[31]
	0.20	0.65		0.20	350	DMSO	[93]
			0.67			DMSO	[114]
	0.20	0.50	0.67	2.61	330	Toluene/py^b	[110]
			0.19		350	DMSO	[47,88]
			0.56			DMF	[34]
	0.17		0.17		77	Acetone	[77]
ZnPc-d_{16}	0.34	0.58	0.54		330	Toluene/%py^b	[109]
(Cl)AlPc			0.29		444	DMSO	[98]
	0.58	0.4			500	CINP	[60]
(py)ZnPc^b	0.22		0.48	1.32		DMF	[10]
(pip)ZnPc^b	0.16		0.31	0.14		DMF	[10]
(CN)ZnPc	0.14		0.51	0.12		DMF	[10]
$(OH)_2SnPc$			0.26			DMSO	[97]
$(Estrone)_2SnPc$	0.02	0.08	0.22		18	DMSO	[44]
$(OH)_2GePc$			0.25			DMSO	[97]
$(OH)_2SiPc$			0.28			DMSO	[97]
SiPc			0.37			$CHC1_3$	[98]
Si(Pc)–O–Si(Pc)		0.22			116	Toluene	[114]
Si(Pc)–O–Si(Pc)–O–Si(Pc)		0.114			51	Toluene	[114]
Si(Pc)–O–Si(Pc)–O–Si(Pc)–O–SiCPc)		0.094			37	Toluene	[114]
(Cl)AlPc	0.58	0.4				1-C1NP^a	[112]
(Cl)GaPc	0.31	0.7				l-CINP^a	[112]
(Cl)InPc	0.031	0.9				l-CINP^a	[112]
MgPc	0.6					1-CINP^a	[108]
Li_2Pc	0.50	0.60				CH_3CN	[109]
Li_2NPc^c	0.50	0.60				Acetone	[109]

Φ_F: fluorescence quantum yield (in general the standard used for determination of Φ_F is chlorophyll *a* in ether ($\Phi_F = 0.32$) [49]); Φ_T: triplet quantum yield; Φ_Δ: singlet oxygen quantum yield; Φ_P: photodegradation quantum yield; τ_T: triplet life time.

[a] l-CINP: chloronaphthalene.

[b] py: pyridine, pip: piperidine.

[c] NPc: naphthalocyanine.

cocity of the solvent, lower values were obtained in less viscous solvents [38]. Triplet lifetimes of ZnPc in DMSO is relatively long (350 μs), Table 5.

The SnPc complex containing estrone (structure **b** in Fig. 1) axial ligand showed very short triplet life times ($\tau_T = 18$ μs), and uncharacteristically low triplet quantum yield ($\Phi_T = 0.08$), Table 5. Both Li_2Pc and Li_2NPc complexes gave the same Φ_T and Φ_F values of 0.6 and 0.5, respectively [108], Table 5, giving $\Phi_T + \Phi_F$ of ~1. This suggested that the dominant radiationless decay path was intersystem crossing for these complexes. There were no significant differences in τ_T, Φ_T, or Φ_F values for ZnPc when compared to the fully deuterated derivative (ZnPc-d_{16}) [109] in toluene containing 1% pyridine. Addition of HAS to DMSO/H_2O solutions of (Cl)AlPc (mimicking the transient behaviour of this photosensitiser in cells) resulted in an increase in triplet lifetime from 484 to 820 μs [100]. For complexes **6h–k**, τ_T values increased on substitution of the axial hydroxyl ligand on going from **6j** to **6k** or **6h** to **6i** [110]. The Φ_T values of the Ga, In and Al complexes increased as follows: CLAlPc < ClGaPc < ClInPc while the Φ_F values correspondingly decreased due to the heavy atom effect [111]. Complex **6x** containing axial 4-*tert*-butylbenzoic acid which gives rigid conformation gave a high Φ_F value of 0.62 [112]. μ-Oxo SiPc complexes containing two, three or four Si(Pc) units showed triplet lifetimes and yields which decreased with the number of units [113], Table 5.

6.2. *Singlet oxygen and photobleaching quantum yields*

Unmetallated MPc complexes are mainly soluble in solvents such as DMSO, DMF and pyridine. Most studies have be done in DMSO or DMF. Φ_Δ values did not vary much for $(OH)_2$GePc ($\Phi_\Delta = 0.25$), $(OH)_2$SnPc ($\Phi_\Delta = 0.26$), and $(OH)_2$SiPc ($\Phi_\Delta = 0.28$), complexes in DMSO, Table 5 [97]. These values were lower than the Φ_Δ value obtained for ZnPc [114], Table 5. In general unsubstituted ZnPc shows higher singlet oxygen quantum yield compared to its substituted derivatives, with a few exceptions such as ZnPcS$_{mix}$.

ZnPc is stable towards degradation in DMSO [47] compared to some ring substituted derivatives. This was explained in terms of intramolecular vibrations of some ring subsituents which quench singlet oxygen as soon as it is formed [47]. For example, ZnPc photodegrades, with low photodegration quantum yields [47], compared to ZnPcS$_{mix}$.

The GePc, SnPc and SiPc complexes photodegraded without undergoing reduction which was observed above for the corresponding porphyrazine complexes [97]. Axial ligation of ZnPc using cyanide, pyridine and piperidine resulted in a decrease in Φ_Δ but an increase in Φ_P values [10]. The decrease in Φ_Δ was attributed to the lowering of the triplet energy to a value where energy transfer to ground state oxygen was no longer favourable.

7. Conclusions

Triplet state, singlet oxygen, photobleaching, and fluorescence quantum yields, and triplet lifetimes of MPc complexes are largely affected by the nature of substituents and by aggregation behaviour of the complexes. These paramenters are affected by addition of BSA (or HAS), surfactants, and deuteration. The triplet quantum yields increase for the heavier central metals due to the heavy atom effect, which inevitably shortens the triplet lifetimes. There has been considerable literature on the Zn and Al phthalocyanine complexes with less attention to the other non-transition metal (e.g. Ge, Si, Sn, Ga and In). Thus future research should focus on phthalocyanines containing the latter central metals.

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