

THE PHOTOPHYSICS AND PHOTOSTABILITY OF ZINC(II) AND ALUMINIUM(III) SULPHONATED NAPHTHALOCYANINES

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Summary

The photophysical properties of aluminium(III) and zinc(II) sulphonated naphthalocyanines have been compared with those of the corresponding metallophthalocyanines, leading to the conclusion that the former class of compounds may be useful as sensitizers in certain applications. A comparison of the relative stability of aluminium phthalocyanine and aluminium naphthalocyanine indicated that the latter compound is significantly less stable to photo-oxidation.

1. Introduction

Systematic studies of the phthalocyanines were first carried out by Linstead [1] and these proved to be the starting point for a substantial commercial interest in phthalocyanine compounds which has continued until the present day, principally because of their use as dye pigments [2]. More recently, attention has focused on the capacity of phthalocyanines to act as photosensitizers, whether as chromophores for solution phase electron transfer reactions [3], as dopants for the enhancement of semiconductor electrodes [4] or as dispersed semiconductors [5].

The first synthesis of a naphthalocyanine (for structure, see Fig. 1) was also reported by Bradbrook and Linstead [6] and, despite recent interest in these compounds for similar applications to those of the phthalocyanines [7, 8], little photophysical information is available on these molecules. In this paper the photophysical properties of aluminium(III) sulphonated naphthalocyanine (AlSN) and ZnSN are compared with those of the corresponding metallophthalocyanines.

2. Experimental details

Both AlSN and ZnSN were donated by Dr. S. Beavan of Unilever Research Ltd. The compounds had been sulphonated by addition of fuming

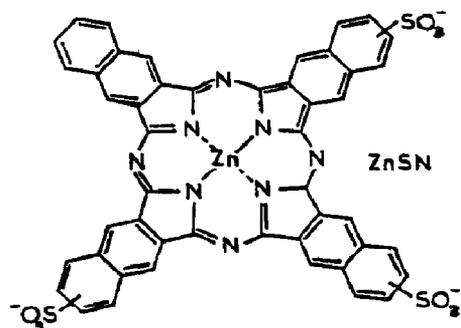


Fig. 1. Structure of zinc sulphonated naphthalocyanine (ZnSN).

sulphuric acid [9] (elemental analysis indicated an average of three sulphonic acid groups per molecule). H_2O was doubly distilled from a Fison's Fi-stream still. Methanol (MeOH) was the BDH AnalaR reagent and was used without further purification, as was deuterium oxide (BDH) in experiments on the photostability of aluminium(III) sulphonated phthalocyanine (AlSP) and AlSN. Hexadecyltrimethylammonium chloride (CTAC) (Eastman Kodak) was used as a cationic micelle-forming surfactant.

Fluorescence lifetimes were measured by the time-correlated single-photon counting technique, using a Spectra Physics synchronously pumped cavity-dumped dye laser [10]. Degassed solutions for such experiments had optical densities at λ_{max} of smaller than 0.1. In order to detect the IR fluorescence emission from the naphthalocyanines, a red-sensitive photomultiplier tube (Mullard 56 TUVP) was necessary. Conventional (micro-second) flash photolysis was carried out using an Applied Photophysics K200 system, the solutions for such experiments having been degassed by repeated freeze-pump-thaw cycles to at least 10^{-4} Torr. Steady state fluorescence and absorption spectra were recorded using a Perkin-Elmer MPF4 spectrofluorometer and a Perkin-Elmer 554 spectrophotometer.

Quantum yield measurements for the photodestruction of AlSP and AlSN were carried out on aerated solutions using the apparatus shown schematically in Fig. 2. The output of the 450 W xenon lamp was measured actinometrically [11, 12] over the 300 - 420 nm range with the assumption that the quantum yield $\Phi_{\text{Fe}^{2+}}$ was 1.2 over this region. Once the absolute emission of the lamp had been obtained in this way, the output at longer wavelengths could be approximated through the use of a photodiode of known response using the formula

$$X = \frac{R_3 - R_2}{R_1} \frac{S_1}{S_2} Y \quad (1)$$

where R_1 is the photodiode reading (300 - 420 nm output), R_2 is the photodiode reading ($\lambda > 700 \text{ nm}^a$ or $\lambda > 800 \text{ nm}^b$ output), R_3 is the photodiode reading ($\lambda > 550 \text{ nm}^a$ or $\lambda > 600 \text{ nm}^b$ output), S_1 is the photodiode sensitivity (centred at $\lambda = 360 \text{ nm}$), S_2 is the photodiode sensitivity (centred at $\lambda = 650 \text{ nm}^a$ or 700 nm^b), Y is the number of photons per second in the

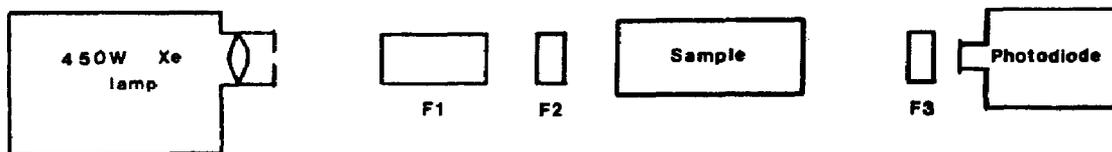


Fig. 2. Steady state irradiation apparatus for the following conditions (F3, neutral density filter).

Actinometry

(1) For the region 300 - 420 nm: F1, 14 g CuSO_4 in 100 ml H_2O (path length, 5 cm); F2, 300 - 420 nm bandpass filter; sample, potassium ferrioxalate solution.

(2)(i) For $\lambda > 550$ nm: F1, H_2O (path length, 5 cm); F2, 540 nm cut-off filter. (ii) For $\lambda > 700$ nm: F1, methylene blue in H_2O (path length, 5 cm); F2, 540 nm cut-off filter.

(3)(i) For $\lambda > 600$ nm: F1, Rhodamine B in H_2O (path length, 5 cm). (ii) For $\lambda > 800$ nm: F1, methylene blue (more concentrated) in H_2O (path length, 5 cm).

Irradiation

(1) Soret bands, as for the actinometry.

(2) Q band (AISP): F1, H_2O ; F2, 540 nm cut-off filter.

(3) Q band (AISN): F1, Rhodamine B solution (path length, 5 cm).

300 - 420 nm region and X is the number of photons per second in the 550 - 700 nm region^a or in the 600 - 800 nm region^b, where superscript a refers to AISP solutions and superscript b refers to AISN solutions.

The photodiode was then used to detect the proportion of light absorbed by the solutions and so, by monitoring the change in optical density of the irradiated solutions at known time intervals, the quantum yield for photodestruction could be estimated.

3. Results

The sulphonated naphthalocyanines were found to be extremely water soluble and, in common with the phthalocyanines, showed a pronounced tendency to aggregate in aqueous solution. This was apparent even for concentrations of AISN as low as 10^{-6} M.

Since both AISN and ZnSN aggregate readily, experiments were carried out in 95vol.%MeOH-5vol.% H_2O mixtures (AISN) or in the presence of 10^{-2} M CTAC (ZnSN), in order to create conditions under which the compounds remain monomeric. The effects of these changes on the absorption spectra of the two compounds are shown in Figs. 3 and 4 (the latter taken from ref. 8). Under these circumstances both AISN and ZnSN obeyed the Beer-Lambert law over the concentration range from 10^{-7} M to 5×10^{-5} M.

The shape of the Q band absorption of both compounds strongly resembles that of the phthalocyanines [13], but the spectral shift induced by the extra conjugation within the molecules is almost 100 nm (about 0.25 eV at these wavelengths). It appears that the Soret (S_2) band remains in practically the same position as for the phthalocyanines. This is in good agreement with a previously published spectrum of zinc(II) unsulphonated 2,3-naphthalocyanine in dimethyl sulphoxide [14], and leads to the unusual observation

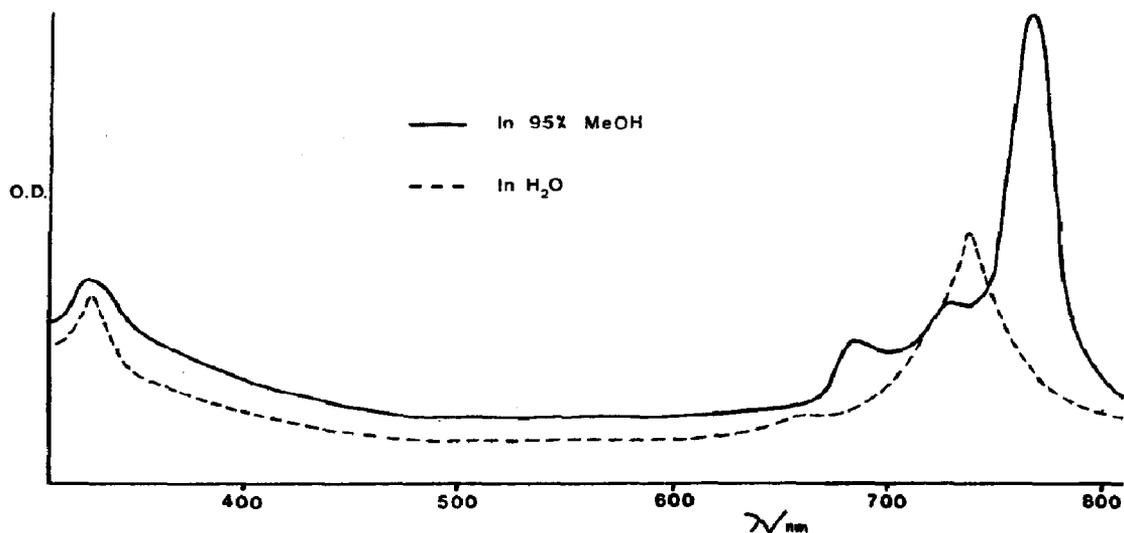


Fig. 3. Absorption spectrum of AlSN.

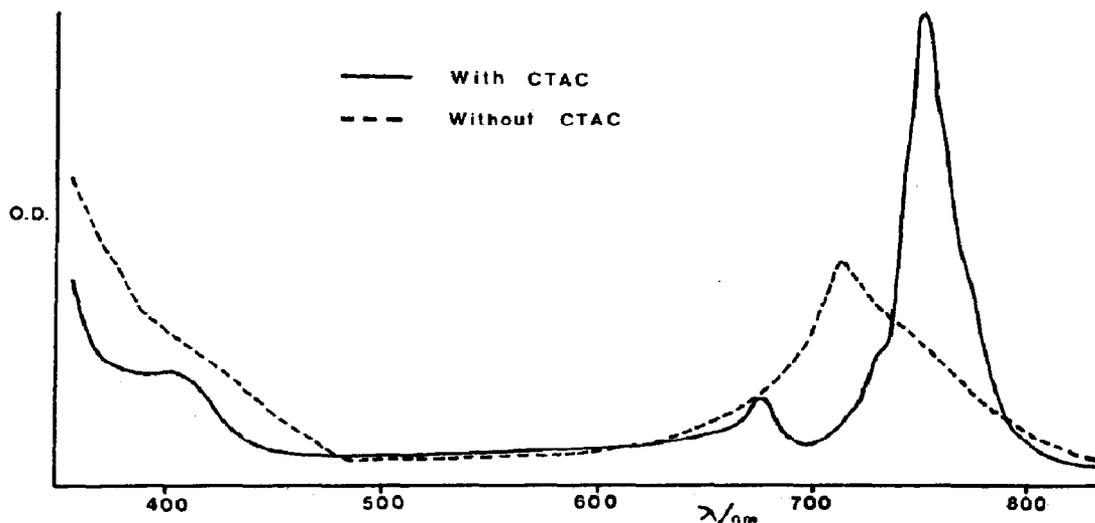


Fig. 4. Effect of CTAC on the absorption spectrum of ZnSN.

of a compound with two widely separated intense absorption bands at opposite ends of the visible absorption spectrum being virtually colourless in solution. The absorption maxima and extinction coefficients for AlSN and ZnSN are shown in Table 1 in comparison with those for AlSP [15] and zinc(II) sulphonated phthalocyanine (ZnSP) [3]. The high intensity of the electronic transitions in phthalocyanines has previously been ascribed to $\pi \rightarrow \pi^*$ ligand bands [16], and we can infer from these results that naphthalocyanines display the same sort of ligand-based absorptions.

Both naphthalocyanines displayed strong fluorescence emission, with only a small Stokes shift relative to the Q band absorption maximum (AlSN emission, $\lambda_{max} = 775$ nm; ZnSN emission, $\lambda_{max} = 768$ nm). In the absence of

TABLE 1

Absorption band	Absorption maxima (nm) ($\epsilon(\text{M}^{-1} \text{cm}^{-1})$) for the following			
	AlSP ^a	ZnSP ^b	AlSN ^c	ZnSN ^b
$S_0 \rightarrow S_1$ (Q band)	675 [15]	690 [3]	769	754
	(1.7×10^5)	(2.9×10^5)	(1.6×10^5)	(1.6×10^5)
	604 [15]		731	732
	(3.2×10^4)		(6.1×10^4)	(6.2×10^4)
		685	684	
		(4.8×10^4)	(4.3×10^4)	
$S_0 \rightarrow S_2$ (Soret band)	345 [15]		330	383
	(6.0×10^4)		(6.9×10^4)	(4.6×10^4)
				329
			(7.1×10^4)	

^aIn H₂O at pH 9.2.

^bIn 10⁻² M CTAC (aqueous).

^cIn 95 vol.% MeOH.

a suitable emission standard in this region of the spectrum, the two compounds' emission yields were simply compared with each other. AlSN was estimated to have a fluorescence intensity approximately twice that of ZnSN under identical conditions, which is similar to the relative fluorescence quantum yields of AlSP [17] (0.58 ± 0.04) and ZnSP [18] (0.32 ± 0.03).

Solutions of ZnSN in H₂O in the absence of CTAC were found to exhibit two fluorescence peaks. One, at 770 nm, corresponded to that observed in CTAC-containing solutions, and the other, a broad weak band centred at 860 nm, disappeared when CTAC was added to the solution. The excitation spectra of the 770 nm emission of the purely aqueous solutions resembled the monomer absorption spectrum (Fig. 4) whereas the excitation spectrum of the 860 nm emission was similar to the aggregate absorption (also see Fig. 4). This suggests that the aggregates of ZnSN may be fluorescent in aqueous solution, an observation that has been made previously for copper porphyrins [19]. Aqueous solutions of AlSN did not display the same phenomenon.

The fluorescence lifetimes τ of AlSN and ZnSN were measured under anaerobic conditions, and are compared with those for AlSP and ZnSP in Table 2. The Group IIIA metallophthalocyanines have previously been found to give reasonable agreement with the Strickler-Berg equation [17], enabling the radiative lifetime τ_0 of AlP (unsulphonated) to be determined as 11.7 ns. Since

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

we can estimate Φ_F for AlSN with the assumption that $\tau_0(\text{AlSN}) \approx \tau_0(\text{AlP})$, so that

TABLE 2

<i>Compound</i>	τ_F (ns)
AlSP	5.0 ± 0.5 [15]
ZnSP	2.9^a [18]
AlSN	2.5 ± 0.3
ZnSN	2.2 ± 0.2

^aMeasured in 5 vol.% pyridine in H₂O.

$$\Phi_F(\text{AlSN}) \approx \frac{\tau_F(\text{AlSN})}{\tau_o(\text{AlP})} = \frac{2.5}{11.7} = 0.2 \quad (3)$$

Microsecond flash photolysis experiments were carried out to probe the triplet states of both AlSN and ZnSN. Table 3 compares triplet lifetimes τ_T , triplet-triplet absorption maxima and extinction coefficients ϵ_T for the T₁-T₂ absorption of these compounds with those for the phthalocyanines, and Fig. 5 shows the difference absorption spectra for the naphthalocyanines. Extinction coefficients were calculated on the assumption that the triplet state absorptions at the singlet state absorption maxima are negligible.

In common with the singlet state lifetimes (Table 2), substitution of zinc for aluminium as the central metal ion within both the phthalocyanines and the naphthalocyanines results in an increase in the deactivation rate of the triplet state (by a factor of about 2). Although not nearly as marked as the effect of paramagnetic metal ions on the excited state lifetimes of phthalocyanines [20], this is an indication that metal substitution within the naphthalocyanines is likely to follow the same photophysical patterns as for the phthalocyanines. The triplet lifetimes of the naphthalocyanines are shorter than those of the corresponding metallophthalocyanines, which, if the triplet (T₁) energies of the naphthalocyanines are lower than those of the latter compounds, is readily understood through an increased opportunity for isoenergetic reverse intersystem crossing to a high vibronic level of S₀.

The T₁-T₂ energy separation for the naphthalocyanines is smaller than that for the phthalocyanines. This is illustrated in Fig. 6 which compares the approximate energy levels of S₁, S₂, T₁ and T₂ as measured by ground and excited state solution phase absorption spectra for AlSP and AlSN (the T₁ energy level of AlSN was estimated to be approximately 0.1 eV below that of AlSP since there is a 0.1 eV difference in S₀-S₁ energy between these

TABLE 3

<i>Compound</i>	τ_T (μ s)	<i>T</i> ₁ absorption maximum (nm)	ϵ_T (M ⁻¹ cm ⁻¹)
AlSP	500 ± 50 [15]	480 [15]	3.2×10^4 [15]
ZnSP	180	—	—
AlSN	240 ± 30	580	4.3×10^4
ZnSN	115 ± 10 [8]	580	2.0×10^4

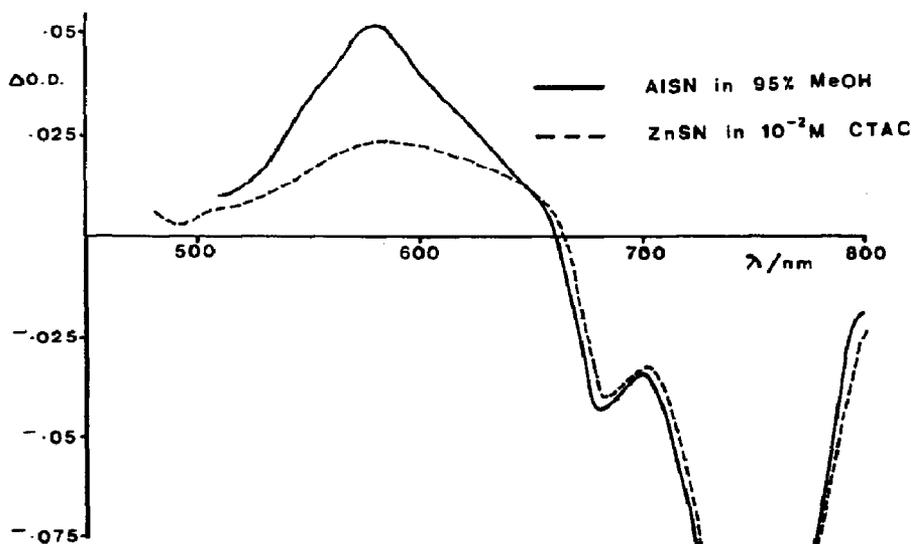


Fig. 5. Difference absorption spectra for the naphthalocyanines.

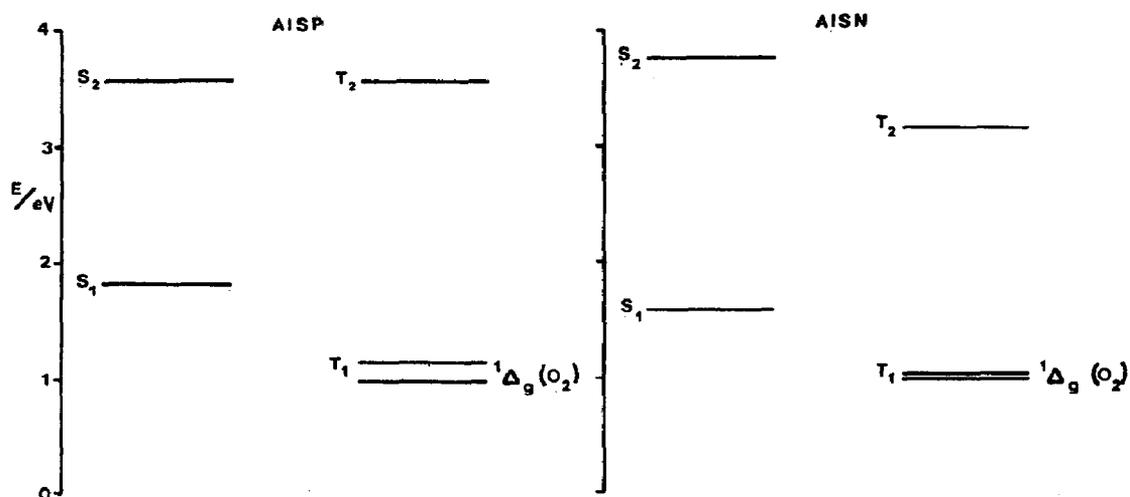


Fig. 6. Energy levels of S_1 , S_2 , T_1 and T_2 states for AlSP and AlSN.

compounds, and the position of T_2 for both compounds was approximated as the point at which the triplet-triplet absorption optical density fell to half its maximum value, as a result of the broadness of the transition in both cases). The triplet-triplet extinction coefficients ϵ_T appear to be in line with previously reported values for unsulphonated phthalocyanines in chloronaphthalene [21].

Measurements are shown in Table 4 of the quantum yields of photo-destruction of both AlSP and AlSN in aerated solution for irradiation into both Q and Soret bands. It is apparent that the increase in ligand size from phthalocyanine to naphthalocyanine has a profound effect on the rate of

TABLE 4

Absorption band	Solvent	Φ_{decomp}	$\Phi_{\text{D}_2\text{O}}/\Phi_{\text{H}_2\text{O}}^a$
<i>AlSP</i>			
Q	H ₂ O	1.7×10^{-6}	8.8
Q	D ₂ O	1.5×10^{-5}	
Soret	H ₂ O	1.2×10^{-6}	15
Soret	D ₂ O	1.8×10^{-5}	
Q	MeOH-H ₂ O	1.1×10^{-6}	
<i>AlSN</i>			
Q(1)	MeOH-H ₂ O	3.0×10^{-3}	
Q(2)	MeOH-H ₂ O	3.1×10^{-3}	
Soret (1)	MeOH-H ₂ O	9.6×10^{-4}	
Soret (2)	MeOH-H ₂ O	1.2×10^{-3}	

^aSee text.

photodecomposition; the latter compound is more than 1000 times less stable to light than the former. That this process is due to photo-oxidation is evidenced by the stability of AlSN in degassed solutions, since no permanent change in optical density takes place during flash photolysis experiments on the naphthalocyanine.

The most likely route for decomposition is through the formation of singlet ($^1\Delta_g$)O₂ by energy transfer from the triplet state (T₁) of these compounds, which may then react with the unsaturated carbon-carbon double bonds of either molecule. For AlSP, this would appear to be more likely than electron transfer from the chromophore to give the superoxide (O₂⁻) radical anion (and subsequent reaction), since (1) the redox potentials for *AlSP(T₁) reacting with O₂ are energetically unfavourable (AlSP^{•+}/*AlSP-(T₁), -0.02 V [22]; O₂/O₂⁻, -0.33 V [23], and (2) the ratios of $\Phi_{\text{D}_2\text{O}}$ to $\Phi_{\text{H}_2\text{O}}$ for AlSP are broadly in agreement with the experimentally observed tenfold difference in the lifetimes of ($^1\Delta_g$)O₂ in D₂O and H₂O [24]. However, it is possible that the greater conjugation of the naphthalocyanine ring could stabilize the radical cation (AlSN^{•+}), thus making the process of electron transfer to oxygen feasible for this compound.

4. Conclusion

Although the photophysical properties of AlSN and ZnSN suggest a suitability for experiments involving photoinduced electron transfer reactions, the susceptibility of this large macrocyclic structure to photo-oxidation may be a substantial drawback for most potential applications.

Acknowledgments

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