

The first genuine observation of fluorescent mononuclear phthalocyanine aggregates

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An initial photophysical study of a tetra-solketal-substituted zinc phthalocyanine is reported; at low temperature this compound exhibits very strong aggregation, and a new red shifted emission peak is observed, $\lambda_{\text{max}} \approx 750$ nm, attributed to a fluorescent phthalocyanine dimer.

Phthalocyanines (Pcs) have a rich and diverse chemistry,¹ and their propensity to form aggregates is well known. The spectroscopic behaviour of Pc dimers and higher aggregates is of considerable interest both as a study of the fundamental spectroscopy of the compounds and from an industrial point of view, where aggregation can lead to changes in the colour/appearance of a dyestuff.

Theory predicts that the spectroscopic behaviour of the aggregates depends strongly upon the relative geometry of the macrocycles,² and hence a wide range of behaviour is to be expected. The most commonly encountered interaction is when the two adjacent Pcs are in a slipped cofacial conformation, where, depending upon the degree of slippage, such an aggregate can exhibit blue or red shifted absorption. Most aggregates described to date are of the blue shifted type, and selection rules are such that these species are non-fluorescent. Another possible geometry is the clamshell arrangement, whereby the Pc molecules are no longer parallel. The selection rules are relaxed for such aggregates and both red and blue shifted absorption bands are predicted, and emission (red shifted) is not categorically excluded. Calculations on binuclear aluminium Pcs having this clamshell arrangement have been reported, but these systems are non-fluorescent.³ Actual examples of fluorescent Pc dimers (or small oligomers) are exceedingly rare.

Most initial reports of fluorescent dimers have since been demonstrated to arise from artefacts. For example, we and others have demonstrated that the effects of re-absorption⁴ and Pc ring protonation⁵ can lead to perturbed absorption and emission spectra which have been erroneously attributed to fluorescent dimers by other researchers.

The tetra-(\pm)-2,2-dimethyl-1,3-dioxane-4-methanol (solketal) substituted phthalocyanine species, **1** (Fig. 1), (prepared by standard condensation procedures[†]) shows a strong susceptibility to aggregation, and at room temperature deviates from the Beer-Lambert equation throughout the concentration range 10^{-4} – 10^{-7} mol dm⁻³. Phthalocyanine **1** is emissive, with quantum yield and lifetime comparable with values of other zinc Pcs (Table 1). On cooling, the extent of aggregation

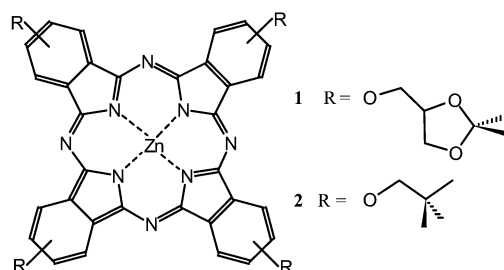


Fig. 1 Structures of **1** and **2**.

Table 1 Photophysical data for compounds **1** and **2**

	Φ_f^e	$\tau_f^{\pm b}$ /ns	$\lambda_{\text{max}}(\text{abs})^a/\text{nm}$	$\lambda_{\text{max}}(\text{em})^a/\text{nm}$
1	0.28	3.5 ^{c,e} 3.5 ^{c,f} 3.6 ^{d,e} 4.0 ^{d,f}	680	685
2	0.30	3.1 ^{c,e}	682	696

^a In dichloromethane, 293 K; error $\pm 10\%$. ^b 5:5:2 v/v/v diethyl ether–2-methylbutane–ethanol, $\lambda_{\text{ex}} = 635$ nm; error ± 0.1 ns. ^c At 293 K. ^d At 77 K. ^e $\lambda_{\text{em}} = 680$ nm. ^f $\lambda_{\text{em}} = 750$ nm.

increases greatly, as evidenced by the reduction of monomeric Q-band absorption at 675 nm and concomitant growth of a new absorption at 625 nm (Fig. 2A). Below the freezing point of the solution (~ 175 K) little further change to the spectrum is observed, except slight sharpening of the bands.

At room temperature **1** shows the characteristic emission spectrum of a metallo-Pc. As the temperature is lowered, the emission intensity centred at 685 nm decreases, and below 175 K a new red shifted peak is observed, $\lambda_{\text{max}} \approx 750$ nm, its intensity continuing to grow as the temperature is decreased to 77 K (Fig. 2B). Excitation spectra for these two bands obtained with $\lambda_{\text{em}} = 850$ nm and $\lambda_{\text{em}} = 710$ nm, respectively, show strong differences, the latter typical of monomeric phthalocya-

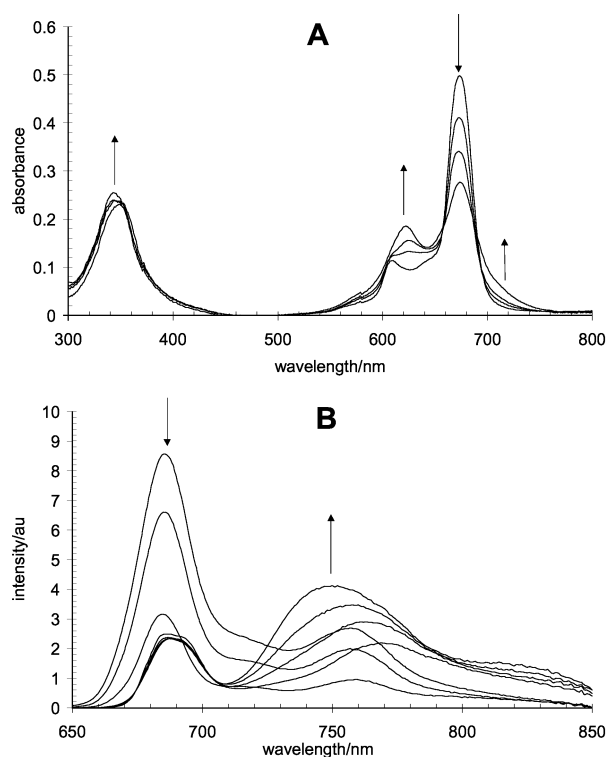


Fig. 2 Absorption (A) and emission (B) spectra of **1**.§ Arrows indicate changes in absorbance/intensity in the direction 293 \rightarrow 77 K.

nine, whilst the former shows broadening and also a strong absorbance at 625 nm.

At room temperature a dilute solution (5×10^{-8} mol dm $^{-3}$) of **1** shows an absorption spectrum typical of a monomeric Pc. It is possible to determine the absorption spectrum of the aggregate by subtraction of a fraction of this spectrum from the observed low temperature spectrum. The spectrum obtained in this fashion correlates well with the excitation spectrum of the red shifted emission band, $\lambda_{em} = 850$ nm (Fig. 3).

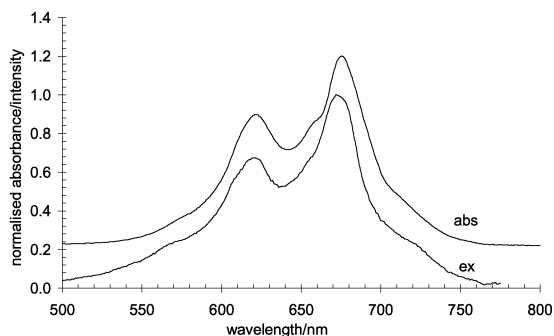


Fig. 3 Absorption (offset for clarity) and excitation spectra of **1** at 77 K.

Lifetimes of the monomeric (3.6 ns) and dimeric (4.0 ns) species ($\lambda_{em} = 680$ nm and $\lambda_{em} = 750$ nm, respectively, at 77 K) show a small but distinct change, that of the dimer being slightly increased (Table 1).

The tetra-nepentoxy zinc Pc reference compound, **2**, (prepared as previously reported⁶) is not dissimilar to **1**, substituents on both compounds including a linking OCH $_2$ unit, and peripheral CH $_3$ groups. Table 1 shows that at room temperature **2** possesses similar photophysical properties to compound **1**. However, as seen in the absorption spectrum (Fig. 4A), cooling of a solution containing **2** results in no apparent aggregation, the expected sharpening of band profiles representing the only change. Such sharpening is also observed in the emission spectrum (Fig. 4B), but the lack of any red shifted emission at 77 K is notable. Despite the superficial structural similarities of **1** and **2**, there is clearly a substantial difference in aggregation behaviour.

Leznoff and Lever have investigated the synthesis and spectroscopic properties of metal free tethered binuclear Pcs, and have reported⁷ that one such compound, linked by a -OCH $_2$ C(Me)(Et)CH $_2$ O- unit, displayed red shifted emission (centred at ~ 750 nm) at 77 K. The similarity between this spectrum and those reported here is obvious. The reason for the reported red shifted emission was hypothesised to be due to intramolecular interaction. Our more detailed, ongoing spectroscopic study of this phenomenon concurs with this explanation, and leads us to believe that **1** provides the first genuine example of a fluorescent mononuclear Pc aggregate. Whilst zinc Pcs usually form slipped cofacial, non-fluorescent dimers, we suggest that the present results are due to the peripheral substituents of **1** forcing the macrocycles into a different (possibly clamshell) conformation.

Interestingly, preliminary studies indicate that some other Pc derivatives show similar aggregate fluorescence in low temperature solutions, and we are currently synthesising further compounds in order that we may more fully understand the nature and structure of the aggregates. Results from this work will be reported in the near future.

In this work we demonstrate for the first time a new fluorescent species attributed to either a dimer or higher order

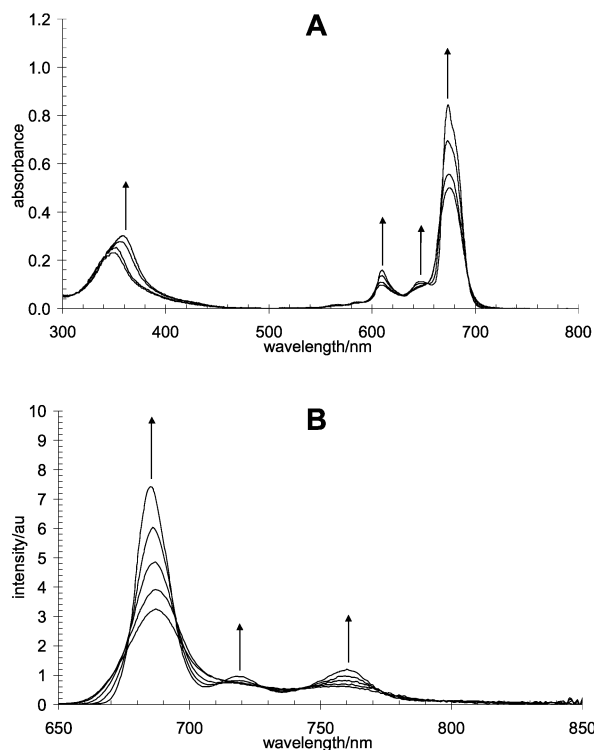


Fig. 4 Absorption (A) and emission (B) spectra of **2**. Arrows indicate changes in absorbance/intensity in the direction 293 \rightarrow 77 K.

aggregates formed upon cooling a solution of a mononuclear Pc. This new species shows red shifted emission, and the excitation spectrum of this matches the absorption spectrum.

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Notes and references

† Zinc acetate templated cyclisation⁶ of the 4-solketal-substituted 1,2-dicyanobenzene in DMF at 160 $^{\circ}$ C for 5 h gave **1** as a dark green solid (38%) after column chromatography over silica gel (eluent 95:5 CH $_2$ Cl $_2$ -MeOH). Selected data for **1**: mp > 300 $^{\circ}$ C, (electrospray MS, found: [M+H] $^+$, m/z 1097.3386; C $_{56}$ H $_{56}$ N $_8$ O $_{12}$ Zn requires [M+H] $^+$, 1097.3387, error of < 0.1 ppm); δ_H (400 MHz, CDCl $_3$) 1.3–1.7 (6H, br m, CH $_3$), 3.5–4.5 (5H, br m, CHO, CH $_2$ O), 7.2–8.7 (3H, br m, PcH).

‡ Fluorescence lifetimes were recorded by time-correlated single photon counting using equipment described elsewhere.⁵

§ Solutions used for fluorescence measurements had maximum absorbances of < 0.25 in order to eliminate reabsorption effects.⁴ Solvent: 5:5:2 v/v/v diethyl ether–2-methylbutane–ethanol.

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