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Luminescence of Porphrins and Metalloporphyrins

Part 6.—Luminescence of Aluminium(III) Tetraphenylporphine and its μ -Oxo Dimer

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Aluminium(III) tetraphenylporphine possesses a tightly bound axial ligand, the nature of which influences the photophysical properties. As the spin-orbital coupling character of the ligand increases (OH⁻ < OOCCH₃ < F⁻ < Cl⁻ < Br⁻ < I⁻), the singlet excited state lifetime and the fluorescence quantum yield decrease whilst the quantum yield for formation of the excited triplet state increases. The observations can be interpreted in terms of an internal heavy-atom enhanced intersystem-crossing mechanism, and for these compounds internal conversion is unimportant. However, for the μ -oxo dimer internal conversion accounts for some 46% of the decay route for the excited singlet state although there is little evidence to suggest pronounced exciton coupling between the two porphyrin rings.

The primary electron donor in both bacterial and green-plant photosynthetic processes is believed to be some kind of metalloporphyrin dimer. This understanding has led to considerable investigation into the possible role of metalloporphyrin dimers in photoinduced electron-transfer processes, using both *in-vivo* and *in-vitro* systems. Often, the dimers possess small red shifts in their absorption and fluorescence spectra relative to the monomers which facilitate excitation-energy trapping by the dimer when it is present as an impurity within an array of monomer molecules. There is, however, little or no clear evidence to show that the dimer may or may not be a better electron-transferring agent than the monomer; in fact, the photophysical properties of the dimers depend very much upon the actual structure of the dimer.¹⁻⁶ For example, dimers and higher-order aggregates of chlorophyll-a, formed in non-polar solvents, appear to be non-fluorescent,⁷ whereas chlorophyll-a, as observed in polar solvents, has a fluorescence quantum yield of ca. 0.32.8 In contrast, many synthetic dimers in which two porphyrin head groups are linked by covalent bonds exhibit fluorescence quantum yields identical or very similar to those of the monomers.⁴⁻⁶ Thus there is a need to increase our research effort in this area; in particular, it would be of interest to identify a synthetic metalloporphyrin dimer that shows a significant fluorescence-quenching effect relative to the monomer. This paper describes the photophysical properties of a few aluminium(III) porphyrins (I) and it shows that there is a substantial fluorescence quenching for the aluminium porphyrin μ -oxo dimer (II). The fluorescence-quenching pathway appears to involve internal conversion from the first excited singlet state to the ground state, a process which is relatively unimportant in the monomer.

In previous work⁹ we reported that the photophysical properties of chloroaluminium(III) tetraphenylporphine (ClAITPP) were typical of those expected for a simple

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diamagnetic metalloporphyrin. However, the presence of a strongly coordinated axial ligand may cause a few problems, especially if the ligand possesses strong spin-orbital coupling properties, and so here we describe the effect of the axial ligand upon the fluorescence and triplet formation yields. Few other reports have been concerned with the luminescence (or absorption) characteristics of aluminium porphyrins, although Buchler¹⁰ has described the preparation and chemical properties of several such compounds. It was also reported¹¹ that the hydroxyaluminium(III) porphyrins could be converted into μ -oxo dimers by dehydration at modest temperatures; this method provides a facile route for synthesis of a face-to-face dimer. Similar μ -oxo dimers are formed for many other metalloporphyrins, especially ones in which the central metal ion has a formal valency of +3 or higher, and Gouterman et al.¹² have reported on the luminescence properties of scandium(III) porphyrin μ -oxo dimers. Although there were observable adsorption-band shifts, the fluorescence yields and lifetimes of the μ -oxo dimer and the monomer were similar. The experimental results were explained in terms of a weak exciton-coupling model;¹² however, with aluminium(III) porphyrins we have found that the fluorescence from the μ -oxo dimer is considerably less than that of the monomer. Thus in this system there is a quite strong interaction between the two porphyrin head groups.

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EXPERIMENTAL

MATERIALS

Chloroform (spectroscopic grade) was refluxed over basic-grade molecular sieves to remove any acidic impurities and redistilled from basic molecular sieves prior to use. Mesotetraphenylporphine (chlorin-free) was obtained from Aldrich Chemicals. Chloroaluminium(III) tetraphenylporphine was prepared as follows. Meso-tetraphenylporphine (0.3 g) in CS₂ (100 cm³) was purged continuously with a stream of N₂ gas and the outlet was protected with a CaCl₂ tube. After 1 h stirring, AlCl₃ (2 g) was added in three aliquots over a 10 min period and the mixture was stirred, under N₂, for 48 h. The solution was evaporated to dryness under reduced pressure and the residue was treated cautiously with cold water and then extracted with a large volume of CHCl₃. The organic layer was dried and evaporated to low volume before being chromatographed on alumina with CHCl₃ as eluant. The material so isolated was rechromatographed to remove an impurity with absorption maximum at 618 nm and the final yield of material in a typical preparation was 7%. Found: C = 78.28; H = 4.20; N = 8.13; Cl = 5.13. Calculated for C₄₄H₂₈N₄AlCl: C = 78.27; H = 4.18; N = 8.30; Cl = 5.25%.

The above chloride complex was converted into the corresponding hydroxide complex by stirring for 8 h with a dilute NaOH solution (*ca.* 1 mol dm⁻³). After removal of the aqueous phase the residue was dried and chromatographed on basic grade alumina using a 2:1 mixture of benzene and tetrahydrofuran as eluant. Found: C = 80.78; H = 4.60; N = 8.42. Calculated for $C_{44}H_{29}N_4AIO$: C = 80.47; H = 4.45; N = 8.53%.

The hydroxide complex was heated at 220 °C under vacuum (10^{-2} Torr*) for 36 h and the resultant μ -oxo dimer was chromatographed twice on basic grade alumina using CHCl₃ as eluant. Found: C = 81.42; H = 4.52; N = 8.55. Calculated for C₈₈H₅₆N₈Al₂O: C = 81.59; H = 4.36; N = 8.65%.

The other axially coordinated aluminium porphyrins were obtained by shaking a chloroform solution of the μ -oxo dimer with an aqueous solution of the appropriate acid (*e.g.* acetic acid). After 4 h shaking, the chloroform layer was isolated, dried and evaporated to dryness under reduced pressure. The residue was chromatographed on basic grade alumina using a 2:1 mixture of benzene and tetrahydrofuran as eluant and, with the exception of the iodide complex, satisfactory elemental analyses were obtained. There was no difference in the photophysical properties of the chloride complex obtained by direct synthesis and that prepared by treatment of the μ -oxo dimer with dilute HCl. In order to obtain a satisfactory elemental analysis for the iodide complex it was necessary to purify the material by preparative-scale thin-layer chromatography. Found: C = 69.14; H = 3.82; N = 7.11; I = 16.18. Calculated for C₄₄H₂₈N₄AlI: C = 68.93; H = 3.68; N = 7.31; I = 16.55%.

METHODS

Absorption spectra were recorded with a Perkin-Elmer 554 spectrophotometer and all luminescence spectra were recorded with a Perkin-Elmer MPF 4 spectrofluorimeter equipped with fully corrected spectral attachments. The luminescence properties of the metalloporphyrins in dilute CHCl₃ solution were measured as described in previous papers in this series.^{9,13} Fluorescence quantum yields were estimated relative to ZnTPP ($\phi_F = 0.03$).

Singlet excited-state lifetimes were measured either by a single-shot Nd glass laser/streak camera system (pulse duration 6 ps, excitation wavelength 530 nm, maximum energy 50 mJ) or by a single-photon counting system (pulse duration *ca*. 500 ps, excitation wavelength 580 nm, maximum energy 0.01 mJ). Triplet excited-state lifetimes were measured with a frequency-doubled Nd laser (pulse duration 15 ns) using N₂-purged solutions. This latter system was used also to determine the quantum yields for formation of the triplet excited state using the method described by Bensasson¹⁴ with bipy₃Ru²⁺ and ZnTPP as standards. The errors associated with each of these measurements are given in the tables.

* 1 Torr \equiv 101 325/760 Pa.

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RESULTS AND DISCUSSION

Hydroxyaluminium(III) tetraphenylporphine exhibits an absorption spectrum typical of a diamagnetic metalloporphyrin.¹⁵ As shown in fig. 1, there are moderately intense Q bands at 546 and 590 nm and an intense B band at 415 nm. Replacement of the axially coordinated hydroxide ion with an acetate or halide ion has little effect upon the absorption spectrum. Similarly, the μ -oxo dimer shows near identical absorption spectral features (fig. 1) except that the Q bands are shifted slightly to the red (*ca.* 200 cm⁻¹) whilst the B band is broader and seems to possess a low-energy tail. This lack of significant absorption spectral changes suggests that there is little exciton coupling in the dimer molecule.



FIG. 1.—Absorption spectra for HOAITPP (—) and the μ -oxo dimer (----) in CHCl₃ solution.

Again, HOAITPP shows a normal¹³ fluorescence spectrum which has a small Stokes shift (*ca.* 70 cm⁻¹), good mirror symmetry with the lowest-energy absorption bands and a good correlation between ground-state absorption spectrum and corrected excitation spectrum. The aluminium porphyrins with different axial ligands show almost identical fluorescence spectra and there is no obvious systematic variation in fluorescence (or absorption) maxima. The fluorescence spectrum observed for the μ -oxo dimer is slightly red-shifted relative to the monomers at both 77 and 300 K, but otherwise in qualitative terms the spectral features of the momomers and μ -oxo dimer are identical.

Low-temperature (77 K) phosphorescence was observed for all the aluminium porphyrins, with a maximum at 780 ± 5 nm; however, because CHCl₃ forms an ice rather than a glass upon freezing, phosphorescence yields or lifetimes could not be measured with any real significance. Qualitatively there appeared to be no changes

in spectral distribution for any of the compounds, but the rather wide bandpasses used for the excitation and emission monochromators preclude too much meaning being attached to such observations. Instead, we can only comment that, under such conditions, the triplet excited state is populated for all the compounds studied here.

The lowest-energy Q bands show good mirror symmetry with the fluorescence profile, and the absorption transitions are relatively strong. Thus the aluminium porphyrins might be expected to exhibit Strickler-Berg behaviour, and from the integrated absorption spectrum the rate constants for radiative decay from the first excited singlet state (k_F) were calculated¹⁵ to be *ca.* 10⁷ s⁻¹ (table 1). There seems to be no significant dependence upon the nature of the axial ligand.

compound	$\phi_{ m F}$	$\tau_{\rm S}/{\rm ns}$	$\phi_{\mathrm{T}}{}^a$	$k_{\rm F}/10^{-7}~{ m s}^{-1}$	$k_{\rm isc}/10^{-8}~{ m s}^{-1}$	ζ/cm^{-1}
HOAITPP	0.14 ± 0.01	9.0 ± 1.0	0.82	1.6	0.91	150
AcOAITPP	0.14 ± 0.01	8.2 ± 0.8	0.82	1.7	1.00	180
FAITPP	0.12 ± 0.01	6.7 ± 0.8	0.85	1.8	1.27	269
CIAITPP	0.10 ± 0.01	5.6 ± 0.3	0.85	1.7	1.52	587
BrAITPP	0.069 + 0.007	3.9 + 0.4	0.91	1.8	2.33	2460
IAITPP	0.023 + 0.005	1.9 + 0.4	0.95	1.8	5.00	5070
μ -oxo dimer	0.077 ± 0.01	4.0 ± 0.5	0.46	1.6	1.15	_

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SOLUTION											

$a \pm 0.06$.

In contrast, the excited-singlet-state lifetimes (τ_s) and the fluorescence quantum yields (ϕ_F) do depend upon the nature of the axial ligand. There is a progressive decrease in both τ_s and ϕ_F as the axial ligand acquires more spin-orbital coupling character (table 1). Certainly, with bromide and iodide ligands there is substantially less fluorescence observed than for the corresponding hydroxide and acetate compounds. From measurements of the quantum yield for formation of the triplet excited state (ϕ_T) it is clear that this quenching phenomenon involves intersystem crossing to the triplet manifold. In all cases studied the sum of the fluorescence and triplet formation quantum yields lies close to unity (within experimental error), and the introduction of ligands with good spin-orbital coupling properties enhances triplet-state formation at the expense of fluorescence. This situation can be seen clearly by considering the rate constant for intersystem crossing (k_{isc}) , as obtained from the following equations:

$$\phi_{\rm F} = k_{\rm F} \tau_{\rm s} \tag{1}$$

$$\tau_{\rm s}^{-1} = k_{\rm F} + k_{\rm isc} + k_{\rm ic} \tag{2}$$

$$\phi_{\rm F} = k_{\rm isc} \,\tau_{\rm s} \tag{3}$$

where k_{ic} refers to the rate constant for internal conversion from the first excited singlet state to the ground state.

Previously, Gouterman *et al.*¹⁶ reported upon the influence of the axial ligand upon the deactivation processes of singlet and triplet excited states of Group IV metalloporphyrins and it was found that axial ligands with strong spin-orbital coupling properties (*e.g.* iodide) catalysed non-radiative processes. Following their work¹⁶ and that described for internal heavy-atom effects in aryl hydrocarbons¹⁷ and metalloporphyrins¹⁸ we can express our results in the form

$$k_{\rm isc} = A k_{\rm isc}^{\rm o} Z^2 \tag{4}$$

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where A is a constant common to all members of the series, k_{isc}° refers to the rate constant for intersystem crossing in the absence of any spin-orbital coupling effects associated with either the central metal ion or the axial ligand and Z is a spin-orbital coupling factor. The term Z can be expressed in the form

$$Z = -C_{\rm M}^2 \zeta_{\rm M} - C_{\rm L}^2 \zeta_{\rm L} \tag{5}$$

where C refers to the relevant atomic-orbital coefficient and ζ is the spin-orbital coupling constant for the central metal ion (M) or the axial ligand (L). In previous work¹⁶ it has been demonstrated that the most pronounced spin-orbital coupling effects are associated with the axial ligand: since we are concerned only with aluminium(III) porphyrins, we can raise the approximation

$$C_{\rm M}^2 \zeta_{\rm M} \ll C_{\rm L}^2 \zeta_{\rm L} \tag{6}$$

and consequently we can include the first term in the constant A. Thus

$$k_{\rm ise} = Bk_{\rm ise}^{\rm o} (-C_{\rm L}^2 \zeta_{\rm L})^2 \tag{7}$$

where

$$B = A(-C_{\rm M}^2 \zeta_{\rm M})^2. \tag{8}$$

Now for the axial ligands used in this study the spin-orbital coupling constants ($\zeta_{\rm L}$) are collected in table 1 whilst the atomic-orbital coefficients ($C_{\rm L}$) can be obtained from extended Hückel calculations. Such coefficients have been calculated previously for several diamagnetic¹⁹ and paramagnetic²⁰ metalloporphyrins but we have not been able to make such calculations (at least for the time being). Therefore we are restricted to looking at the effect of $\zeta_{\rm L}$ on the rate constant for intersystem crossing; the findings are shown in fig. 2 in the form of a double logarithm plot. Qualitatively there is quite a good correlation between $k_{\rm isc}$ and $\zeta_{\rm L}^2$, although without some knowledge of the $C_{\rm L}$ terms it is not possible to take this argument any further.





Overall, the effect of the axial ligands can be explained rather simply, in terms of internal heavy-atom-enhanced intersystem crossing to the triplet manifold. Similar photophysical properties were measured for the μ -oxo dimer and the derived values are collected in table 1, together with those of the hydroxide complex for easy comparison. Triplet-state formation is relatively inefficient in the dimer and the sum of the quantum yields for fluorescence and triplet-state formation does not approach

unity, even allowing for experimental limitations. Thus internal conversion is important in the dimer whereas it has little, if any, importance in the monomer. In fact in the dimer internal conversion accounts for some 46% of the total deactivation pathways but in the monomer it is 5%.

In the dimer molecule the two porphyrin head groups must come into quite close proximity. The angle between the two rings is not known, but it must be around $(170 \pm 5)^{\circ}$ based upon other metalloporphyrin μ -oxo dimers. Presumably this close interaction is sufficient for exciton coupling to occur and this provides an extra pathway for non-radiative decay of the excited singlet state. Note that the room-temperature excited-triplet-state lifetime of the dimer is less than half that of the hydroxide complex.

Forming the μ -oxo dimer affects the B region of the absorption spectrum as follows: (i) the B band is broadened but the maximum remains at the same wavelength; (ii) the maximum extinction coefficient is decreased but the total oscillator strength remains the same; (iii) a low-energy tail appears which stretches out as far as 480 nm and (iv) the vibrational band, located at *ca*. 390 nm, appears more as a shoulder than as the clear vibrational overtone found in the monomer. These effects suggest that, for the second excited singlet state, any exciton coupling in the dimer is minimal. In the Q region of the absorption spectrum the effects associated with formation of the μ -oxo dimer are as follows: (i) there is a red shift of 200 cm⁻¹; (ii) there is broadening of the bands (the halfwidth of the monomer is *ca*. 950 cm⁻¹ and for the μ -oxo dimer it is *ca*. 1100 cm⁻¹) and (iii) the oscillator strength for the overall transition remains the same. Because the Q transition is not very intense (*cf*. the B band), exciton-coupling effects may be masked by the inhomogeneous solvent broadening since, using a treatment described previously,²¹ we have calculated that the exciton-coupling term for the μ -oxo dimer (*V*) must be in the range

$$50 < V/cm^{-1} < 150$$
 (9)

assuming an interplanar distance of ca. 0.5 nm. If we accept that exciton coupling in the B region of the spectrum should be about ten times as strong as in the Q region (based upon the molar extinction coefficients) then we might not expect to see any real shift in wavelength of the B band. This is because the shift (Δ) accompanying dimer formation can be expressed in the form²¹

$$\Delta = V - D \tag{10}$$

where D is a term reflecting the solvent effect due to the dimer environment. Since D has a very approximate value¹² of ca. 1000 cm⁻¹ the overall value expected for Δ is close to zero (this is a gross approximation).

Even accepting that the magnitude of exciton coupling in the μ -oxo dimer may be ca. 1000 cm⁻¹, this is a very low value relative to other metalloporphyrin dimers. The poor coupling between the two porphyrin rings may be due to steric hindrance between the phenyl rings,¹² which are tilted out of the plane of the porphyrin rings. Such a steric effect may force the two porphyrin head groups to adopt a configuration closer to a parallel head-to-head dimer than to the tilted structure expected for a 'normal' μ -oxo dimer.

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