The Proton-controlled Fluorescence of Aminomethyltetraphenylporphyrin–Tin(IV) Derivatives[1]

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The fluorescence quantum yield of the aminomethyltetraphenylporphyrin–tin(IV) compound, **1a–h** is strongly influenced by pH in a bimodal manner owing to photoinduced electron transfer and axial ligand exchange processes.

Ion-controlled fluorescence in the visible region, especially 'on–off' switching, is of interest not only for ion sensing in the life sciences,[2] but also for the construction of molecular optoelectronic devices.[3] The use of porphyrin derivatives in photodynamic therapy[4] and their intracellular location by fluorescence imaging,[5] combined with the fact that intracellular pH is significantly different in normal and tumour cells,[6] provided the impetus to the present work.

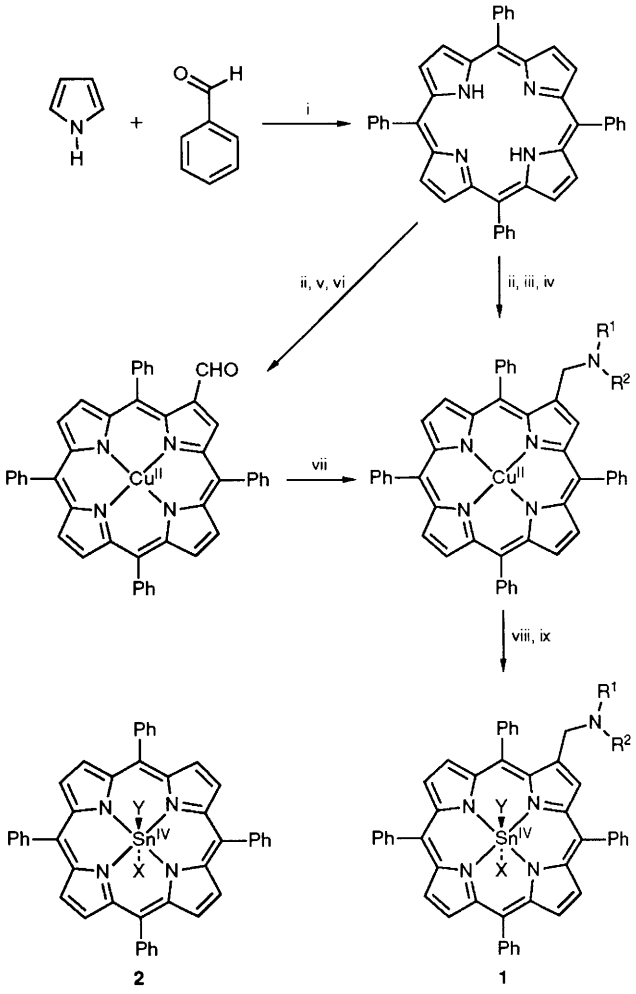
The aminomethyltetraphenylporphyrin–tin(IV) series **1** was designed so that photoinduced electron transfer[7] would take place from the amino group to the porphyrin moiety, resulting in fluorescence quenching. However, when the amino group is protonated fluorescence becomes an important deexcitation pathway. A related intermolecular situation is known.[8] Application of the Weller equation[9] shows that the photoinduced electron transfer process is thermodynamically feasible (Table 1). The syntheses of **1a–h** are summarised in Scheme 1.

The fluorescence quantum yield (ϕ)–pH profiles (Fig. 1) of **1** are bimodal, being composed of two sigmoidal curves of opposite gradients, and are due to two separate processes. The segment with the negative gradient is assignable to the photoinduced electron transfer process. The other is attributed to an axial ligand exchange process on the tin(IV) centre. The results (Table 1, Fig. 1) show that significant proton-induced fluorescence changes are exhibited by all members of the series **1a–h** without alteration of fluorescence band position or vibrational fine structure of fluorescence. The pK_{a2} values determined by fluorescence titration and the use of eqn. (1) on the sigmoidal segment of the ϕ–pH profile with negative gradient correlate well with the $pK_{a,model}$ values for the corresponding 'parent' methylamines, as demonstrated by the constant ΔpK_a values in Table 1. Thus the sigmoidal segment results from protonation equilibria of the amino group in **1a–h**. Furthermore, this correlation suggests a constant steric hindrance to solvation[16] of the protonated amino group by the bulky porphyrin moiety across the series. It is also notable that the pK_{a2} values determined fluorimetrically are in close agreement with those obtained by the analysis, *via* eqn. (2), of the small pH-dependent alterations of the UV–VIS absorption spectrum for each member of series **1**. This demonstrates the unusual result that the pK_{a2} values obtained by excited state experiments are thermodynamic (equilibrated) values.[17] This arises from the spatial isolation of the amino group from the photoantenna porphyrin moiety by the methylene spacer unit. The ϕ_{max} values are essentially constant across the series **1a–h** and are identical to the value for the parent compound **2**. The ϕ_{min2} values correlate with the thermodynamic driving force for photoinduced electron transfer in the series **1a–h**, which is supporting evidence for the validity of the design principle employed.

$$\log[(\phi_{max} - \phi)/(\phi - \phi_{min})] = pH - pK_a \quad (1)$$

$$\log[(A_{max} - A)/(A - A_{min})] = pH - pK_a \quad (2)$$

The axial coordination sites of the tin(IV) centre are occupied by hydroxide ions or H_2O depending on the pH of the solution. At neutral or weakly acidic pH values the axial ligands will be hydroxide ions whereas at low pH values the sites will be occupied by water ligands. This results in a significant perturbation of the fluorescence quantum yield of **1a–h**. Confirmatory evidence is that the parent metalloporphyrin **2** displays similar pH effects in its unimodal ϕ-pH profile with a sigmoidal curve and a positive gradient. The pK_{a1} values associated with this axial ligand exchange process can be determined *via* eqn. (1) and are essentially identical for all members of series **1a–g** except for **1e** which has a value close



Scheme 1 *Reagents and conditions*: i, $EtCO_2H$, reflux; ii, $CuSO_4$, $CHCl_3$, MeOH; iii, $POCl_3$, R^1R^2NCHO, CH_2ClCH_2Cl, reflux, 18 h; iv, $NaBH_3CN$, MeOH, room temp., 30 min; v, $POCl_3$, dimethylformamide (DMF), CH_2ClCH_2Cl, 18 h; vi, NaOAc, room temp., 1 h; vii, R^1R^2NH, MeOH, CH_2Cl_2, $NaBH_3CN$ (for **1f** and **1g**); viii, $CHCL_3$ HCl(g); ix, $SnCl_2$, NaOAc, HOAc (for **1a–b**, **d–g**) (these conditions lead to mixed axial ligand compounds), $SnCl_2$, pyridine (for **1c** and **1h**)

a; $R^1 = R^2 = Me$
b; $R^1 = R^2 = Et$
c; $R^1R^2 = -CH_2[CH_2]_2CH_2-$
d; $R^1R^2 = -CH_2[CH_2]_3CH_2-$
e; $R^1R^2 = -CH_2CH_2OCH_2CH_2-$
f; $R^1R^2 = -CH_2[CH_2]_4CH_2-$
g; $R^1R^2 = -CH_2[CH_2]_5CH_2-$
h; $R^1 = Me$, $R^2 = Ph$

For **2** and **1a–b**, **d–g**, X = Y = Cl, OH, OAc or X = Cl, Y = OAc, OH; for **1c** and **1h**, X = Y = Cl

Table 1 Fluorescence and pK_a data for the porphyrin–tin derivatives **1a–h**[a]

Compound	pK_{a1}		pK_{a2}		pK_a[b] (model)	ΔpK_a[c]	ϕ_{min1}	ϕ_{max}	ϕ_{min2}	$-\Delta G$[d]/eV
	Fl.	Abs.	Fl.	Abs.						
2	6.1	5.9	—	—	—	—	0.014	0.021	—	—
1a	4.9	5.1	7.5	7.8	9.8	2.3	0.015	0.020	0.013	0.33
1b	4.9	5.2	8.0	7.9	10.3	2.3	0.015	0.021	0.007	0.49
1c	5.0	5.1	8.0	8.0	10.5	2.5	0.015	0.021	0.011	—
1d	4.9	5.0	7.9	7.7	10.1	2.2	0.015	0.020	0.011	0.35
1e	6.3	6.4	4.6	4.0	7.4	2.8[e]	0.015[f]	0.013[f]	0.016[f]	—
1f	4.9	5.0	8.0	7.9	10.3	2.3	0.015	0.020	0.005	—
1g	4.8	5.1	7.8	7.8	10.2	2.4	0.016	0.021	0.003	—
1h	—	5.7	2.1	—	5.1	3.0[e]	—	0.014	0.001	0.68

[a] 50% v/v aqueous methanol (10^{-7} mol dm^{-3}). For absorbance studies *ca.* 10^{-6} mol dm^{-3} solutions were used. pH range 0–12; 25 °C; μ = 0.01 mol dm^{-3}.[10] λ_{ex} = 423 nm; 32 nm slits. Data analysis (least squares): average gradient 0.9–1; correlation coefficient 0.9–1; no. of points 10. Quantum yield for tetraphenylporphyrin–zinc in benzene.[11] [b] Ref. 12. [c] $\Delta pK_a = pK_{a,model} - pK_{a2,Fl}$). [d] Calculated from the Weller equation $\Delta G = -E_s + E_{ox,amine} - E_{red,porph.} - E_{i.p.}$ with singlet energy (E_s) calculated taking the 0,0 band as 596 nm. Amine oxidation potentials ($E_{ox.amines}$) are from ref. 13, porphyrin reduction potential ($E_{red,porph.}$) from ref. 14, and ion pairing energy (0.1 eV; $E_{i.p.}$) from ref. 15. [e] These values are larger than average because, in contrast to the other cases, the amine protonation occurs at lower pH than axial ligand exchange. [f] This is a local minimum bounded by two plateaux.

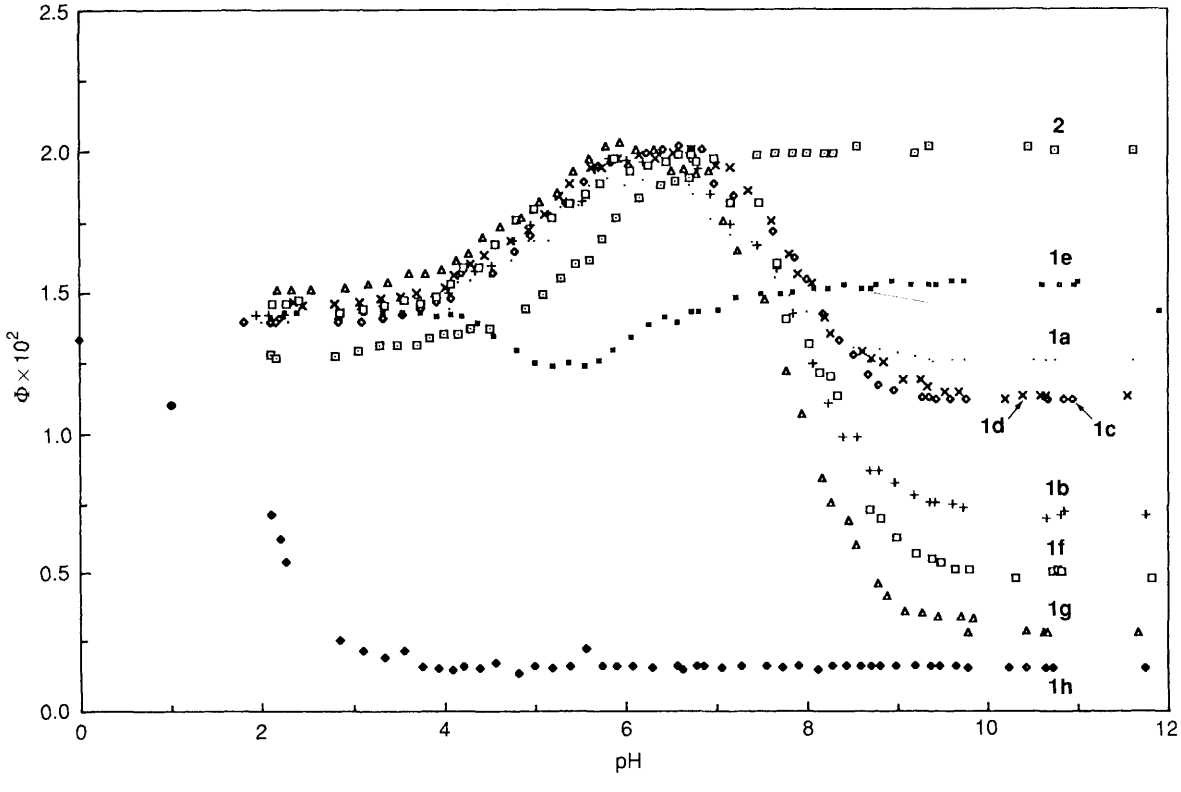


Fig. 1 pH *vs.* fluorescence quantum yield (ϕ) profiles of **2** and **1a–h** in methanol–water (1 : 1)

to that for the parent compound **2**. In the case of **1e** axial ligand exchange occurs while the amino group in unprotonated owing to its lower basicity whilst **2** lacks a protonatable amino group. Again the pK_{a1} values determined fluorimetrically are in agreement with those obtained by analysis of the small pH-dependent changes in the UV–VIS absorption spectra (Table 1). The ϕ–pH profiles for **1a–h** and **2** converge to an essentially common curve at limiting low pH values (Fig. 1).

In conclusion, the series **1a–h** provides the first examples of

fluorophores based on metal complexes whose fluorescence can be sensitively enhanced by ion binding to an unconjugated group.

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