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**ABSORPTION AND LUMINESCENCE SPECTRA OF
TETRA(3-PYRIDYL)PORPHYRAZINE: A CONVERGENT
SPECTROSCOPIC METHOD FOR THE ELUCIDATION
OF ASSOCIATION REACTIONS IN SOLUTION**

Key words: Porphyrazine spectra, molecular association, luminescence

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ABSTRACT

Tetra(3-pyridyl)porphyrazine is soluble in trifluoroethanol yielding intense blue solutions. The electronic spectra exhibit the characteristic Soret and Q bands around 330 and 610 nm, respectively; however, the absorption profile is strongly dependent on the concentration, reflecting the occurrence of an association process. The system has been elucidated by solving the equilibrium and the absorbance-concentration equations for all the wavelengths in the spectral range, according to a variational procedure. In this way the consistent spectra of the individual species have been generated. The study has also been extended to the luminescence properties of the porphyrazine molecule, and discussed in terms of the ground state association and the exciplex formation involving the monomeric species.

INTRODUCTION

The spectral properties of the porphyrins and related species have been a subject of great interest, because of their relevance to biological systems, photodynamic therapy and supramolecular chemistry¹⁻⁹. In general, this class of compounds exhibits strong tendency to form aggregates^{6,8,10,11} and the neutral species are insoluble in most of the conventional organic solvents. As a consequence, most of the studies in solution has been restricted to the protonated or functionalized species. In the last few years, we have been surprised by the unusual solvent properties of trifluoroethanol. This has shown to be a particularly efficient and mild solvent for the porphyrin type of compounds, facilitating the synthesis of new supramolecular species¹² and making possible studies in solution, which were otherwise precluded by the lack of solubility. Here we report on the association behavior of the tetra(3-pyridyl)porphyrazine compound (1) in trifluoroethanol solutions. We also describe a versatile approach to evaluate the equilibrium constants and the spectrum of all species involved in the equilibria, based on a spectral convergence method. The structure of compound 1 is shown in Fig. 1.

EXPERIMENTAL

The free-base porphyrazine was synthesized and purified as previously reported in the literature¹³. Elemental analysis for $C_{28}H_{20}N_{12}O_3$ exp. (calc.): C = 59.4 (58.7), H = 3.6 (3.5), N = 28.1 (29.3).

The electronic and luminescence spectra were obtained by means of a Hewlett Packard 8453A diode array spectrophotometer or a Photon Technology Inc. LS100 spectrofluorimeter, respectively. Trifluoroethanol solutions of porphyrazine, in the 0.3 to 80 $\mu\text{mol dm}^{-3}$ concentration range, were used in the experiments. These solutions were purged with argon for 30 minutes, just before the luminescence measurements, in order to minimize the luminescence quenching by dioxygen. All the measurements were carried out employing a triangular quartz cell.

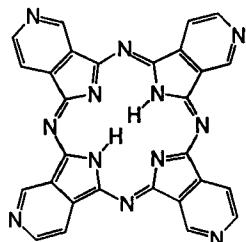


Fig.1. Structure of the free-base tetra(3-pyridyl)porphyrazine.

RESULTS AND DISCUSSION

The tetra(3-pyridyl)porphyrazine (TPyPz) compound has been isolated in the free-base form as a black solid, insoluble in almost all solvents, in analogy with the porphyrins and phthalocyanines. As a consequence, studies in solution have only been performed for the N-methylated species¹³⁻¹⁶, or in the presence of acids, which convert the porphyrazine into the soluble N-protonated species. In the last few years, we have observed that, in contrast with the conventional solvents, trifluoroethanol is particularly effective in dissolving the porphyrazine species, yielding stable, bright blue solutions, suitable for spectroscopic work.

The electronic spectra of trifluoroethanol solutions of TPyPz, from 0.86 to 61 $\mu\text{mol dm}^{-3}$, are shown in Fig. 2. Two broad absorption envelopes can be seen at 330 nm and 610-670 nm, ascribed to the Soret and the Q transitions, respectively. At higher concentrations, the Q bands envelope is dominated by a broad absorption at 610 nm, but the narrow band at 675 nm becomes more and more prominent as the concentration is lowered. This type of spectral dependence on concentration is characteristic of an association process involving the soluble porphyrins or phthalocyanines. Nevertheless, the association reactions involving the neutral species have not been investigated because of the solubility constraint.

In general, the monomer and the associated species are present in equilibrium even at very low concentrations (e.g. $10^{-7} \text{ mol dm}^{-3}$). Furthermore, the spectral analysis can be complicated by the strong superimposition of the

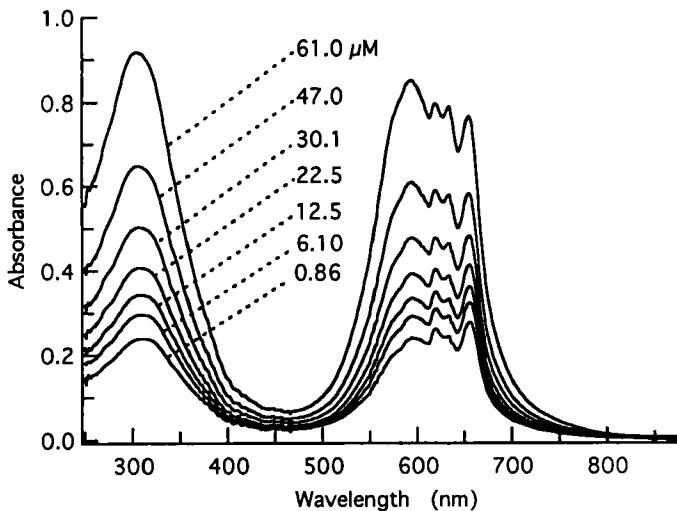


Fig. 2. Spectra of the TPYpZ in trifluoroethanol solution, in the 0.86×10^{-6} to 61×10^{-6} mol dm $^{-3}$ concentration range.

absorption bands and the absence of isosbestic points¹¹. This is the case for the porphyrazine species here investigated (see Fig. 2), precluding the use of direct methods to calculate the association constants.

In the present case, a well behaved trend was observed in the Q band profile, in the 10^{-5} to 10^{-7} mol dm $^{-3}$ concentration range, suggesting the occurrence of a monomer-dimer equilibrium, $2M \rightleftharpoons D$, where $K_D = [D]/[M]^2$

From the total concentration $[C_0] = [M] + 2[D]$, it follows that

$$[D] = \{[C_0] - [M]\}/2 \text{ and } K_D = \{[C_0] - [M]\}/2[M]^2.$$

For a given value of $[C_0]$, K_D can be readily obtained from the corresponding values of $[M]$ and $[D]$ in equilibrium. In this case, however, the absorption spectrum of the monomer and the dimer species should be previously known.

In order to circumvent the problem, one can try a variational procedure, starting from the measured absorbances at a wavelength λ , $\text{Abs}(\lambda)$, for two or more different concentrations (e.g., 1 and 2), as expressed by

$$\text{Abs}_1(\lambda) = [M]_1 \varepsilon_M(\lambda) + [D]_1 \varepsilon_D(\lambda) \quad \text{eq. 1}$$

$$\text{Abs}_2(\lambda) = [M]_2 \varepsilon_M(\lambda) + [D]_2 \varepsilon_D(\lambda) \quad \text{eq. 2}$$

where ε_M and ε_D are the absorptivities (per mol) of the monomer and the dimer species, respectively. By combining Eq. 1 and eq. 2, the following expression can be obtained for $\varepsilon_M(\lambda)$:

$$\varepsilon_M(\lambda) = \frac{[D]_1 \text{Abs}_2(\lambda) - [D]_2 \text{Abs}_1(\lambda)}{[D]_1[M]_2 - [D]_2[M]_1} \quad \text{eq. 3}$$

Therefore, by assuming an equilibrium constant K_D , one can calculate the hypothetical spectrum of the monomer (and of the dimer) from the absorbance measurements at the several wavelengths. As a consequence, every distinct value of K_D should lead to a different spectrum for the several concentrations employed, except when K_D approaches or coincides with the real value. In this case, all the calculated spectra should converge and match, since K_D expresses the true equilibrium constant for the system. The spectral convergence criterion not only allows the determination of K_D but also provides an effective way of deducing the correct spectra of the species in equilibrium. In addition, it can also be employed to exclude the existence of aggregate species other than the dimer, since in this case, the calculated spectra would not converge.

A simple way to perform the calculations is by using a worksheet containing the digitalized spectra and the complete cross referenced data, in such a way that the only variable is K_D . Thus, the value of the equilibrium constant can be varied as in a self-consistent process, ending up with the convergence of the calculated spectra for the dimer and monomer species. The convergence method was successfully applied in this work, leading to the calculated spectra of the monomer and the dimer, shown in Fig. 3, and $K_D = 4 (\pm 1) \times 10^5 \text{ mol}^{-1} \text{ dm}^3$. This

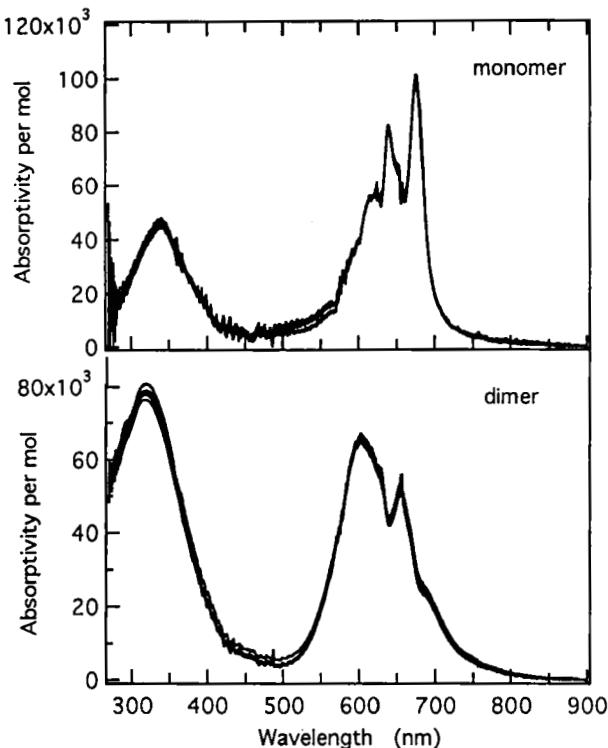


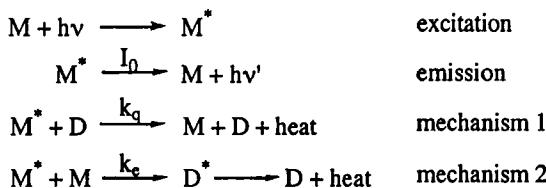
Fig. 3. Convergence of the calculated spectra of the monomer (top) and the dimer (bottom), for nine different combinations of the experimentally measured spectra, shown in Fig. 2.

value is lower than the one found by Yang et al.¹¹ for the tetrasulfonated cobalt phthalocyanine in aqueous solution ($K = 2 \times 10^6 \text{ mol}^2 \cdot \text{L}^{-2}$), or by Kobayashi et al.^{6,17} for the crown ether substituted phthalocyanines dimerization induced by cations ($K = 5 \times 10^9 \text{ mol}^2 \cdot \text{L}^{-2}$, for K^+). In the last case, the constant tends to be much higher because of the extra stability gained by the dimer as a consequence of the formation of crown ether/ K^+ complexes.

The calculated spectrum for the monomer bears some similarity with those reported for the protonated or methylated species¹⁴, exhibiting the Soret band at 349 and the four Q bands at 597, 613, 642 and 676 nm. The dimer exhibits the Soret band at 323 nm and the Q bands at 607 (broad) and 655 nm (narrow). These two components can be observed in the absorption spectrum of the concentrated solutions (Fig. 2), at the corresponding wavelengths, superimposed to the bands of the monomer species.

Luminescence Study

The TPyPz species in solution exhibits a sharp and intense fluorescence band at 684 nm, when excited in the Soret and Q bands. The corresponding excitation spectrum has a profile similar to the monomer absorption spectrum, as can be seen in Fig. 4, indicating that the emission comes from this species and not from the dimer. However, the luminescence intensity was not a linear function of the concentration of the monomeric species, for $[C_0] = 0.34-82 \times 10^{-6}$ mol dm⁻³, suggesting the occurrence of quenching mechanisms. Accordingly, two possible mechanisms were examined:



Mechanism 1 involves the hypothetical collisional quenching of the monomer excited state emission by the dimer species. Mechanism 2 corresponds to the formation of a non emitting exciplex species, *via* the interaction of M^* with the ground state M molecules.

Both mechanisms can be included in the corrected Stern-Volmer equation,

$$\frac{I_0 [M]}{I [M_0]} = 1 + k_q[D] + k_e[M] \quad \text{eq. 4}$$

where, I_0 = integrated luminescence intensity of the more dilute solution, I =

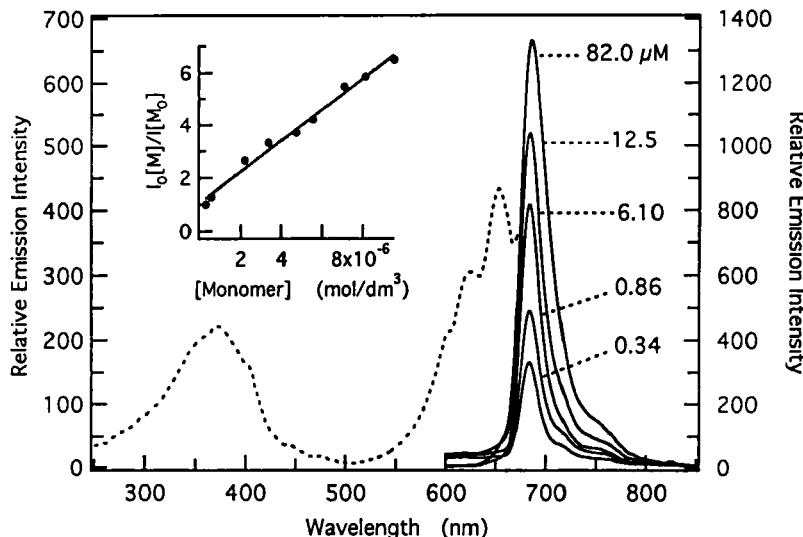


Fig. 4. Emission spectra of TPyPz in trifluoroethanol solutions, in the 0.34 to 82×10^{-6} mol.dm $^{-3}$ concentration range (full lines, $\lambda_{\text{exc}}=340$ nm) and a typical excitation spectrum (dotted line, $\lambda_{\text{em}}=710$ nm). Inset: Stern-Volmer plot of $I_0[M]/I[M_0]$ as a function of the calculated monomer concentration.

integrated luminescence of the solutions, $[M_0]$ = monomer concentration in the more dilute solution, $[M]$ and $[D]$ = calculated monomer and dimer concentrations, respectively.

The best fit of the experimental data was obtained by neglecting completely the mechanism 1, as can be seen in the linear plot of $I_0[M]/I[M_0]$ versus $[M]$ (Fig. 4, inset). The plot exhibits a linear coefficient of 1.06 and a slope equal to 5.9×10^5 mol d m^{-3} s $^{-1}$, with a correlation parameter better than 0.99.

Therefore, from the Stern-Volmer results, one can conclude that the quenching of the fluorescence emission of the monomeric species occurs solely *via* the formation of the non-emitting exciplex species, and that the dimer species does not emit either.

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