Aggregation in Water Solutions of Tetrasodium Diprotonated *meso*-Tetrakis(4-sulfonatophenyl)porphyrin

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The title porphyrin shows non ideal cmc with formation of J-aggregates, due to the formation of intermolecularly stabilized zwitterions, which at high concentration also results in H-aggregates.

The association in acid medium of water soluble tetrasodium 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS^{4-}), which was detected by UV–VIS some years ago,[1] has not been studied. In acidic media below pH *ca.* 2.5 it has been described that new species appear with absorptions at 491 and 706 nm. This behaviour in the acidic region has even been described as very complicated.[1c,d]

At very low porphyrin concentrations, when both H_2TPPS^{4-}- and $H_4{}^{2+}TPPS^{4-}$ are in monomeric non-aggregated form, it is possible to obtain isosbestic points in the spectrometric titration $H_2TPPS^{4-} \rightleftharpoons H_4{}^{2+}TPPS^{4-}$.† In $H_4{}^{2+}TPPS^{4-}$ solutions by increasing the ionic strength or the porphyrin concentration new species appear (Table 1). Figs. 1 and 2 show the UV–VIS changes by the effect of the substrate concentration at pH = 3.5 and constant ionic strength. For concentration values higher than 5×10^{-5} mol l^{-1} a new species appears with red-shifted B- and Q-bands (Beer-law is no longer observed above 3×10^{-5} mol l^{-1}, *i.e.* non ideal cmc behaviour is observed). For concentration values above 1×10^{-4} mol l^{-1} other species appear with blue-shifted B- and Q-bands. The formation of this second species entails the extinction of the bands corresponding to the monomeric $H_4{}^{2+}TPPS^{4-}$ together with an ε decrease and a widening ($\Delta W_{1/2}$ *ca.* 4 nm) of the red-shifted B-band. At very high concentration (> 2.5×10^{-3} mol l^{-1}) the B-band at 422 nm leads to blue-shifted bands towards 400 nm and a gel-like rheologic behaviour; the presence of optical dispersion effect is detected. These results can be explained through the formation of an associated species of $H_4{}^{2+}TPPS^{4-}$ increasing in size with $H_4{}^{2+}TPPS^{4-}$ concentration, and the aggregation of these species giving a new type of associated species.‡

The energy shift of porphyrin B-band has been interpreted through exciton theory.[2,3] According to this model the first association of $H_4{}^{2+}TPPS^{4-}$ (B-band = 489 nm) must result from an edge-to-edge interaction (J-aggregates) and the second association (422 nm) could be explained through a face-to-face aggregation (H-aggregates) of the former associates. Although the UV–VIS spectra only afford information about the type of association but not on the size of the aggregate, the narrow band at 489 nm suggests a small number of associated porphyrins whereas the colloidal behaviour at higher concentrations coincidental with the formation of the B-band at 422 nm, suggests the formation of bigger aggregates.§

Table 1 UV–VIS absorption spectral data of H_2TPPS^{4-} and diprotonated H_2TPPS^{4-} ($H_4{}^{2+}TPPS^{4-}$) (pH = 3.5 : acetic acid–sodium acetate 0.1 mol l^{-1}): in parenthesis ε or relative intensities (Fig. 1)

	B-band	Q-bands
$H_2TPPS^{4-}(Na^+)_4$[a]	412 (355 000)	515, 551, 579, 633 (130 : 4.5 : 1.9 : 1)
$H_4{}^{2+}TPPS^{4-}$ (non-aggregated)	433 (357 000)	550, 594, 644 (140 : 1 : 3 : 14)
$H_4{}^{2+}TPPS^{4-}$ (first aggregate)	489; $W_{1/2}$ = 8 nm	668,707 (*ca.* 30 : 2 : 7)
$H_4{}^{2+}TPPS^{4-}$ (second aggregate)	422; $W_{1/2}$ = 25 nm	575, 625 ± 5 (*ca.* 20 : 1 : 3)

[a] 3.5×10^{-6} mol l^{-1}; pH = 7.7 (acetic acid–sodium acetate 0.1 mol l^{-1}).

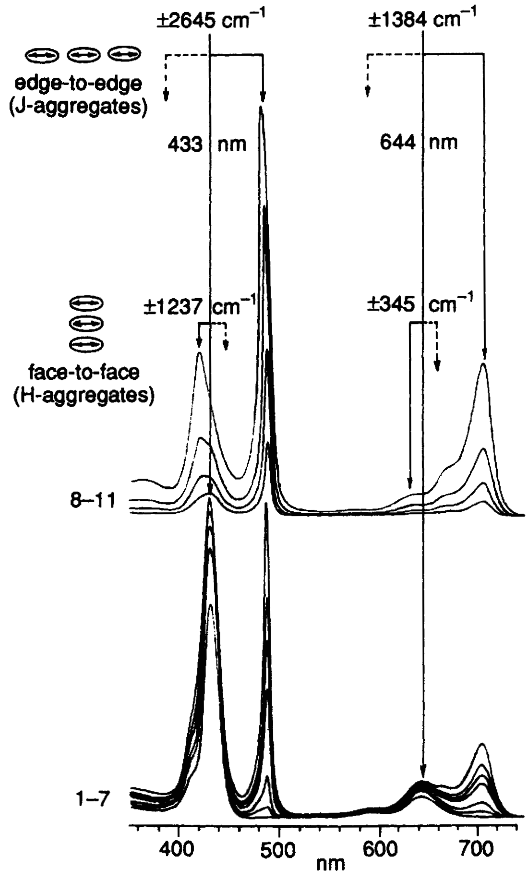

Fig. 1 UV–VIS spectra in water at pH = 3.5 (acetic acid–sodium acetate 0.1 mol l^{-1}) of tetrasodium 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS^{4-}) at several concentrations. **1–7**: cell path = 0.1 cm; 4, 5, 6, 7, 8, 9 and 10 ($\times 10^{-5}$) mol l^{-1}. **8–11**: cell path = 0.01 cm; 1.25, 2.5, 5 and 10 ($\times 10^{-4}$) mol l^{-1}.

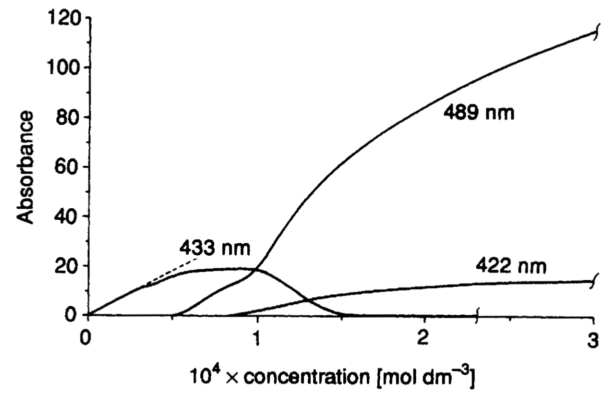

Fig. 2 Change of absorbance with substrate concentration of the B-bands of $H_4{}^{2+}TPPS^{4-}$ (433 nm), and its first (489 nm) and second (422 nm) aggregated forms (changes were followed to absorbance values of about 250)

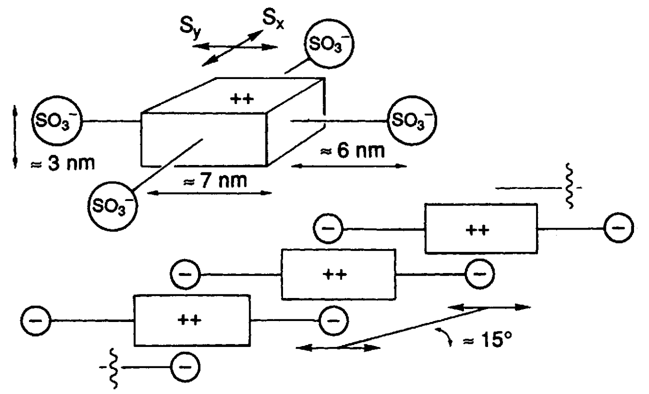

Fig. 3 Edge-to-edge aggregation (J-aggregates) model of $H_4^{2+}TPPS^{4-}$ through intermolecularly stabilized zwitterions. Geometries are extracted from ref.[3g,4]

For the first associated form the large shift and narrowing of the B-band, the strong decrease of luminescence and the red-shift of the Q-bands, a fact not normally observed, point towards an association due to stronger effects than the simple hydrophobic interaction between π systems. Diprotonated *meso*-tetraphenylporphyrin, although it shows a deformed macrocycle (each pair of confronted rings show their N–H bonds out of plane) is a more planar structure than the corresponding free base because in the former compound the phenyl rings are almost planar to the porphyrin ring,[4] *i.e.* it allows association between molecules.¶ The formation of intermolecularly stabilized aggregated zwitterions (Fig. 3) could justify the results reported here (out-of-plane NH could also contribute to association by intermolecular hydrogen bonding with the negatively charged sulfonate groups). Size increases of these zwitterionic aggregates would allow the association between 'chains' forming the second aggregated species (face-to-face), which show a blue-shifted allowed exciton coupling band. The formation of zwitterions implies the segregation of sodium salts, which we have detected by SEM-EDX (presence of NaCl crystals in the residue from the evaporation of HCl acidified concentrate solutions).

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Footnotes

† 3.5×10^{-6} mol l^{-1} substrate, acetic acid–sodium acetate buffers at constant ionic strength: 0.1 mol l^{-1}: $pK_a = 4.65 \pm 0.05$.

‡ The exchange between these forms is relatively fast as inferred from the ^1H NMR spectra. ^1H NMR spectra, recorded at concentrations corresponding to mixtures of both aggregated species, show broad bands *i.e.* the protonated species have molecular size outside extreme narrowing conditions, and the observed signals correspond to the exchange between the different forms present in the solution.

§ From the evaporation of the colloidal solutions ribbon-like anisotropic structures can be obtained.

¶ We have studied the chemical behaviour of other water soluble sulphonated tetraarylporphyrins but *ortho*-disubstituted (dichloro, dimethyl and difluoro *ortho*-substituted). Nevertheless, in these compounds the *ortho*-disubstitution prevents an aggregation behaviour similar to that of $H_4^{2+}TPPS^{4-}$.

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