Controlled J-aggregation of porphyrins by cationic surfactants

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The formation of J-aggregate of tetrakis-(4-sulphonatophenyl) porphine dianion is facilitated by cationic surfactants at extremely low concentrations. The stoichiometric ratio of porphyrin and surfactant in the J-aggregate is 1 : 2. The efficiency of aggregation is controlled by the length of the alkyl chain of the surfactant. The J-aggregate is stable in thin polyvinyl alcohol films.

MOLECULAR aggregates play a very important role in biological systems where they function as energy funnels for solar energy harvesting[1,2]. Aggregates also have significant technological applications as sensitizers in photography industry[3,4], in opto-electronic devices[5], non-linear optics[6], etc. The structure of an aggregate of an organic dye molecule is generally expected to be H-type (ordered arrangement of molecules stacked one above the other) or J-type (molecular planes are parallel, but displaced horizontally) or non-specific (no order in the molecular arrangement)[7]. Aggregation of model porphyrins[8–11] and analogues[12] has attracted significant interest in recent years. Porphyrin aggregates have potential applications in photodynamic therapy of tumours[13]. Suitable control of the size of the aggregates and/or rate of aggregation could result in interesting optical properties useful for applications. It has recently been shown[8,9,15] that tetrakis-(4-sulphonato phenyl) porphine dianion, H_4TPPS^{2-}, (see Figure 1) forms J-aggregate at higher ionic strength or at very low pH. However, high ionic strength may be disadvantageous for various use of the aggregates. We have, for the first time, been able to achieve quantitative, controlled aggregation of the porphyrin in the presence of very low concentration of cationic surfactant with specific porphyrin : surfactant ratio.

H_4TPPS^{2-} exists as a monomer at pH 3.5 (refs. 8, 9). The absorption peaks are at 433, 592 and 644 nm (Figure 2 *a*). In the presence of CTAB (cetyl trimethyl ammonium bromide, < 120 μM), H_4TPPS^{2-} (50 μM) forms aggregate with absorption peaks at 492 nm (hereafter called 490 nm band) and 709 nm (Figure 2 *b*) which are characteristic of the J-aggregate confirmed by several techniques[8,9,15]. The large red shift in the Soret band of J-aggregate has been proposed to arise due to excitonic interactions in the J-aggregate[10]. According to this theory[10], the red shift in the absorption spectra arises due to transitions to lower excited electronic state produced by splitting of the excited energy level in the J-aggregate. The presence of cationic surfactant molecules facilitate the formation of ordered J-aggregate due to the coulombic interaction of the positively charged head group of the surfactant with the porphyrin dianion. Similar aggregation behaviour of H_4TPPS^{2-} was observed[8] in the presence of salts such as KCl. But the concentration of KCl required to bring about the aggregation is high by several orders to that of the porphyrin. The fact that the surfactant concentration required for similar aggregation was four orders less suggests that the alkyl chain of the surfactant does play a key role in the aggregation process. Aggregation of H_4TPPS^{2-} was also observed with other cationic surfactants with shorter alkyl chains such as TTAB (tetradecyl trimethyl ammonium bromide), DTAB (dodecyl trimethyl ammonium bromide) and organic cation TMAB (tetramethyl ammonium bromide). The cationic head group for CTAB, TTAB, DTAB and

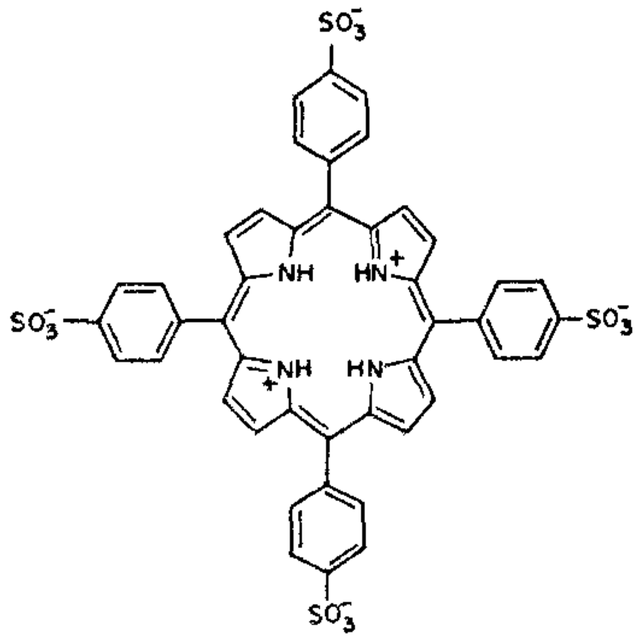

Figure 1. Structure of the dianion of tetrakis-(4-sulphonatophenyl) porphine, H_4TPPS^{2-}.

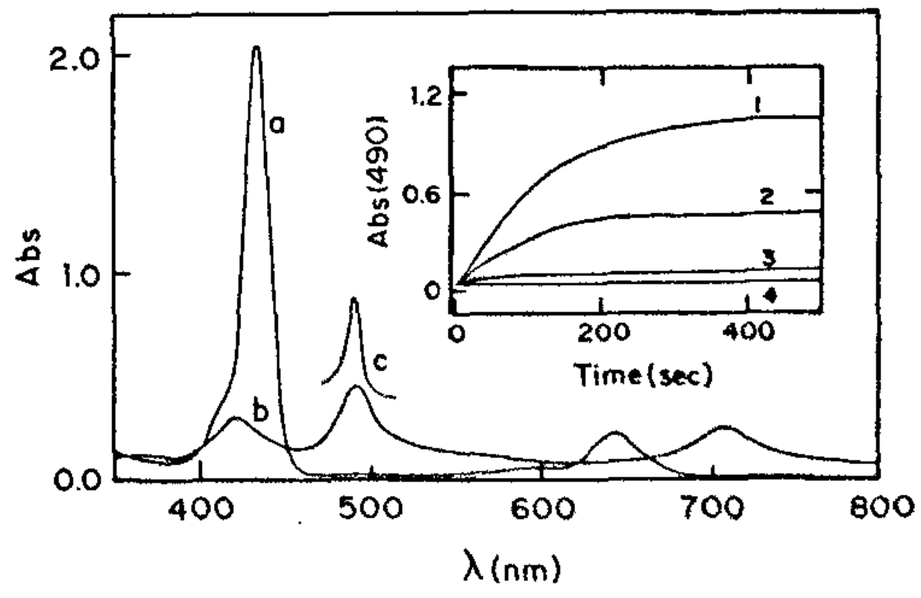

Figure 2. Absorption spectra of TPPS monomer and J-aggregate at pH 3.5, (0.002 M sodium acetate buffer). $[H_4TPPS^{2-}] = 50$ μM: (a) monomer dianion, (b) J-aggregate in the presence of CTAB (100 μM) and (c) CTAB-induced J-aggregate immobilized in polyvinyl alcohol film (~ 0.5 mm); the 490 band is displaced vertically for clarity. Inset: Growth curves of J-aggregate (absorbance at 490 nm) in different media. pH 3.5 (0.01 M sodium acetate buffer), [TPPS] = 25 μM, path length = 1 cm: (1) [CTAB] = 50 μM, (2) [TTAB] = 50 μM, (3) [DTAB] = 50 μM, (4) [KCl] = 50 μM.

TMAB is the same ($-NMe_3^+Br^-$) but the amount of surfactant required to cause maximum J-aggregation of H_4TPPS^{2-} was found to increase with decreasing chain length of the surfactant. This clearly shows that the length of the alkyl chain of the surfactant molecule plays an important role in J-aggregation.

The spectroscopic data including linewidths ($\Delta\nu$) of the 490 nm band of J-aggregates formed in the presence of various surfactants and cations are given in Table 1. The linewidths of the J-aggregate in solution were found to be large in long chain surfactants (CTAB, TTAB and DTAB) compared to that in the presence of TMAB or KCl. However, the optical spectra of a thin film of CTAB-induced J-aggregate immobilized in polyvinyl alcohol showed sharp peak at ~ 490 nm (Figure 2 *c*) comparable to that of K^+ or TMAB-induced J-aggregate.

The kinetics of the formation of aggregates was monitored by stopped flow method (using HI-TECH SF61MX stopped flow instrument). Figure 2 (inset) shows the plots of increase in absorbance at 490 nm with time in the presence of CTAB, TTAB, DTAB and KCl. The rate of aggregation is several orders faster in the presence of CTAB. Among surfactants, the rate was found to decrease with decrease in the chain length of the surfactant. Moreover, the optimal concentration of the surfactant required for maximum conversion of monomer to aggregate formation was found to be ~ 2, ~ 2.2 and ~ 5 times that of H_4TPPS^{2-} for CTAB, TTAB and DTAB, respectively, while ~ 10,000-fold excess of TMAB or KCl was required to achieve a similar conversion of monomer to J-aggregate. The presence of anionic surfactant, e.g. sodium dodecyl sulphate (SDS) or neutral surfactant, e.g. Triton X-100 did not cause J-aggregation of H_4TPPS^{2-}, indicating that the charge of the surfactant was primarily responsible for the formation of J-aggregate of the porphyrin.

Steady state fluorescence was measured using a Shimadzu RF540 spectrofluorimeter and time-resolved fluorescence studies were performed using the tunable picosecond dye-laser pulse, from a synchronously pumped cavity-dumped dye (Rhodamine 6G or Pyridine-1) laser system described elsewhere[14,16]. Fluorescence decay profiles were collected using a time-correlated single photon counting set-up coupled to a microchannel plate photomultiplier. The plots of fluorescence decay profiles for the J-aggregate (trace a) and the monomeric H_4TPPS^{2-} (trace b) are shown in Figure 3. The steady state fluorescence emission spectrum of the J-aggregate is shown in the inset of Figure 3. The fluorescence peak and lifetime (τ_f) of the aggregate in the presence of CTAB were 720 nm and 62 ps respectively. Monomeric porphyrin dianion (H_4TPPS^{2-}) showed fluorescence maximum at 672 nm and the fluorescence lifetime[8] was 3.87 ns. The contribution of the monomer (< 1%) in the emission spectrum gives rise to a prominent shoulder at ~ 672 nm because of its long lifetime and high quantum yield compared to the J-aggregate. A sharp decrease in the lifetime (Table 1) of the J-aggregate is characteristic of the excitonic interaction in the J-aggregate.

Figure 4 shows that the formation of J-aggregate is controlled in an optimal concentration range of CTAB. The plot shows the absorbance of the monomer at 433 nm, the absorbance of the J-aggregate at 490 nm and the absorbance at 418 nm due to a new species which shows up at higher concentrations of CTAB. The absorbance of monomer (concentration, 20 μM) at 433 nm decreases sharply with increasing concentration of CTAB with a corresponding quantitative increase in the absorbance of the J-aggregate at 490 nm. The conversion of monomer to J-aggregate is maximum when the concentration of CTAB is 50–60 μM. The extrapolation of the sharp decrease of A_{433} gives 40 ± 2 μM as the concentration of CTAB at which A_{433} is zero. The porphyrin : CTAB ratio is 1 : 2. The ratio remains constant when the porphyrin concentration was as low as 5 μM. Similar concentration ratios for J-aggregation with other

Table 1. Spectroscopic properties of monomer and J-aggregate of H_4TPPS^{2-} ($T = 24 \pm 1$°C)

Cations	$[H_4TPPS^{2-}]$: [Cation][a]	λ_{abs} (nm)	$\Delta\nu_{490}$ (cm^{-1})	λ_{em} (nm)	τ_f (ns)
Buffer	–	433,592,644	904	672	3.87 ± 0.01
CTAB	1 : 2	492,709	993	720	0.062 ± 0.01
CTAB[b]	1 : 2	490,707	400	718	–
TTAB	1 : 2.2	491,710	934	716	–
DTAB	1 : 5	491,710	883	716	–
TMAB	1 : 10000	489,706	393	715	–
KCl	1 : 12000	490,706	400	714	0.05 ± 0.01

[a] $H_4TPPS^{2-} = 50$ μM, pH 3.5 (0.002 mM sodium acetate buffer).
[b] J-aggregate with CTAB in polyvinyl alcohol film.

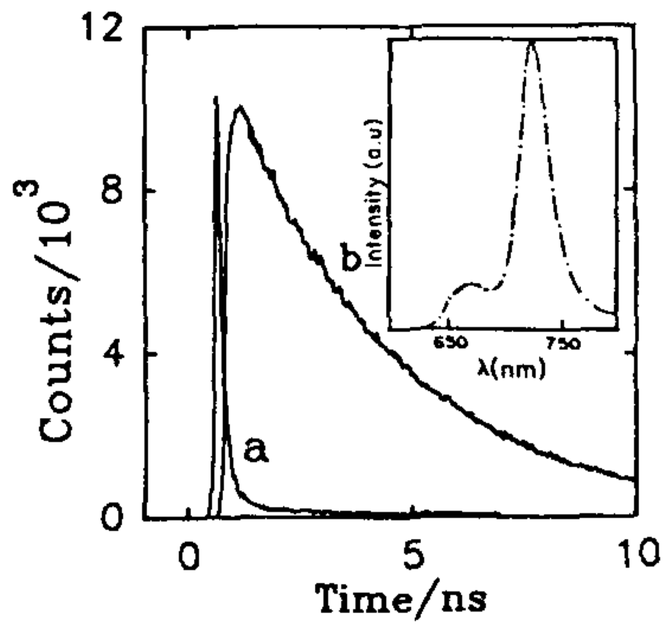

Figure 3. Fluorescence decay of CTAB-induced J-aggregate and monomer of H_4TPPS^{2-} at pH 3.5 (sodium acetate buffer, 0.02 M). (a) J-aggregate; $\lambda_{ex} = 692$ and $\lambda_{em} = 725$ nm, time per channel 0.037 ns (b) Monomer; $\lambda_{ex} = 630$ and $\lambda_{em} = 672$ nm. Time per channel 0.037 ns. Inset: Fluorescence emission spectrum of CTAB induced J-aggregate. $\lambda_{ex} = 490$ nm.

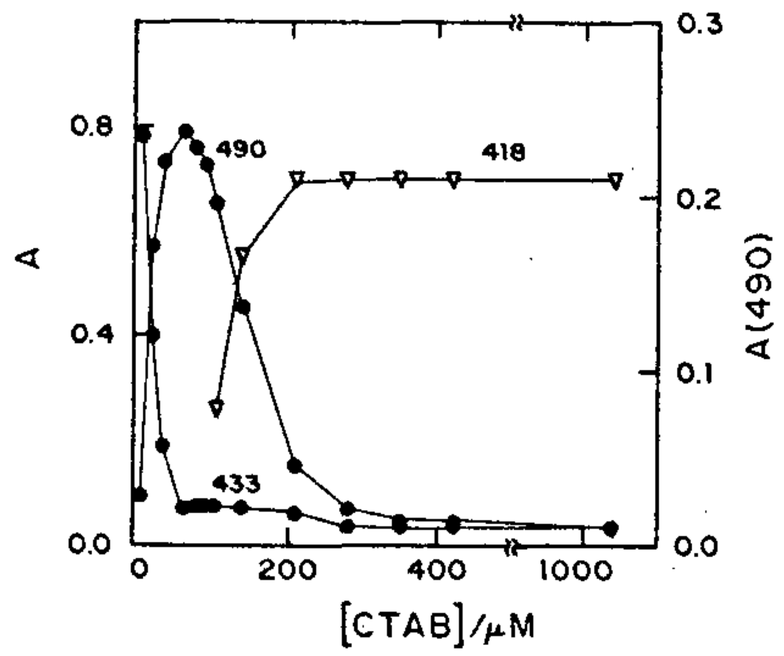

Figure 4. Variation of the concentration (absorbance) of monomer and aggregates of H_4TPPS^{2-} (20 μM) with CTAB at pH 3.5 (0.002 M sodium acetate buffer). A_{433} (monomeric dianion) decreases and A_{490} (J-aggregate) increases for $0 < [CTAB] < 60$ μM. A_{418} (monomer tetraanion) is formed in the region of [CTAB] > 0.2 mM, including the micellar region of CTAB > 0.9 mM. There is evidence for a H^- or nonspecific aggregate of porphyrin in the region 0.06 mM < [CTAB] < 0.02 mM (see text).

surfactants and cations are given in Table 1. As the concentration of CTAB is increased further, the J-aggregate becomes unstable, leading to the formation of a new species absorbing at 418 nm. Spectroscopic evidence (absorption and fluorescence spectra, fluorescence lifetime, fluorescence anisotropy and resonance light scattering) indicates (data not shown) that the species formed at CTAB concentration above its critical micellar concentration (> 0.9 mM) is unambiguously the monomer tetra anion, H_4TPPS^{2-}, intercalated in micelles with an absorption peak at 418 nm. However, in the pre-micellar concentration region 0.08 mM < [CTAB] < 0.2 mM, an aggregate of H- or non-specific type (absorption peak at 400 nm, results not shown) is formed, similar to other dye aggregates formed in pre-micellar concentration[10], and references therein[10]. The structure and spectroscopic properties (results to be published) of this aggregate in this concentration regime are different from those of the J-aggregate and monomer in micelle.

The spectral widths of the absorption peaks of the monomer (Soret band at 433 nm) and the J-aggregate (490 nm band) under different conditions are given in Table 1. Theory[17,18] predicts that the spectral width of the J-aggregate ought to be narrower ($\Delta\nu_{agg} \alpha N_{agg}^{-1/2} \Delta\nu_{monomer}$). Spectral narrowing was however, not observed for the J-aggregate in surfactant solutions. Surprisingly, the spectral width was broader than even that of the monomer. It was shown[8] that the 490 nm band of the KCl-induced aggregate is indeed a mixture of J-aggregates and the observed spectral width is mainly due to the inhomogeneous broadening. The broader spectral width of the J-aggregate in surfactants may also be due to inhomogeneous broadening. It is interesting to note that the spectral width of CTAB-induced J-aggregate becomes narrower when immobilized in polyvinyl alcohol films. This spectral width narrowing is comparable to KCl or TMAB-induced J-aggregate.

We have suggested earlier[8] that the formation of J-aggregate requires two cations per porphyrin to neutralize the charge of the dianion, H_4TPPS^{2-}. This stoichiometric ratio is confirmed in this study. If the formation of J-aggregate is thermodynamically and kinetically most favourable, then aggregation is quantitatively complete when the porphyrin : surfactant concentration ratio is 1 : 2. The present study has shown that the cationic surfactant CTAB leads to quantitative formation of J-aggregate at the lowest concentration, giving a stoichiometric ratio of 1 : 2 for the porphyrin : CTAB in J-aggregate. The fact that the ratio is 1 : 5 in DTAB shows that the alkyl chain of the surfactant plays a unique role in stabilizing and facilitating the quantitative formation of the J-aggregate. The J-aggregate of CTAB-porphyrin complex remains stable as thin films or when incorporated in polymeric films. The spectroscopic characteristics of the J-aggregate in thin films are being investigated.

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Received 13 March 1996; revised accepted 2 May 1996