Control of coherence length and aggregate size in the *J*-aggregate of porphyrin

A.S.R. Koti, Jharna Taneja, N. Periasamy *

Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400 005, India

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Abstract

The spectroscopic aggregation number (coherence length) and physical size of the *J*-aggregates of anionic *meso*-tetrakis(4-sulphonatophenyl)porphyrin (H_4TPPS^{2-}) are controlled by ammonium ion concentration. The contributions of absorption and scattering are determined using the extinction and resonance light scattering (RLS) spectra of the TPPS *J*-aggregate. The highest spectroscopic aggregation number (12.9) was determined for the *J*-aggregate of hydrodynamic radius of 56 ± 10 nm.

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1. Introduction

Porphyrins and cyanines were found to form *J*-aggregates [1]. Formation of colloidal particles of *J*-aggregates of a water-soluble *meso*-tetrakis-(4-sulphonatophenyl) porphyrin dianion, in acidic solutions under a variety of experimental conditions is reported in several studies [2–7]. The absorption peak of the *J*-aggregate occurs at 490 nm which is relatively narrow compared to the monomer absorption at 433 nm. Ideally, *J*-aggregate is the side-by-side arrangement of monomers and the transition dipoles are collinear with the line joining their centers. In the case of the above porphyrin dianion, the *J*-aggregate is presumed to be formed by oblique stacking of monomers [6].

The spectral width (full-width at half-maximum, FWHM) of the absorption peak of the *J*-aggregate varies with the coherence length as $N^{-1/2}$, where N is the spectroscopic aggregation number [8,9]. The relationship between the growth of molecular aggregates, aggregation number, and their optical properties is an active area of research [10]. In all the preparations of colloidal *J*-aggregates the number of molecules per aggregate is very high. However, the spectroscopic aggregation number determined from the spectral narrowing was typically a few (∼4–6) molecules. On the other hand, nonlinear spectroscopic techniques and ultrafast pump–probe techniques (reviewed in [11]) have identified coherence length as large as 70 monomers [12]. Thus, *J*-aggregates with a largest possible spectroscopic aggregation number as determined by the spectral narrowing is likely to be a very useful material for nonlinear optical applications.

* Corresponding author. Fax: +91-22-2215-2110/2181.
E-mail address: peri@tifr.res.in (N. Periasamy).

We were motivated to prepare a *J*-aggregate in which the spectroscopic aggregation number is maximum so that the coherence length may be comparable to the physical size of the aggregate. In this Letter, we report the realization of such an aggregate.

2. Materials and methods

The sodium salt of *meso*-tetrakis-(4-sulphona-tophenyl) porphyrin (H_2TPPS^{4-} abbreviated as TPPS) was purchased from Strem Chemicals (USA). Purity of TPPS was tested by thin-layer chromatography. The TPPS stock solution was made in deionized water. Concentration of the TPPS in solution was determined using $\varepsilon_{434} = 442\,000$ $M^{-1}cm^{-1}$ at, pH 3 [13]. Absorption studies were done using a spectrophotometer (Shimadzu UV-2100 spectrometer). Resonance light scattering (RLS) spectra of the samples were recorded using a spectrofluorimeter (Spex Fluo-rolog FL111 T-format spectrometer) in right-angle mode by keeping 'excitation' and 'emission' wave-lengths identical and scanning the excitation and emission monochromators simultaneously. Dy-namic light scattering (DLS) experiments were done using a set up that uses laser (826.8 nm, 55 mW) and an APD detector. All the measurements were carried out in an air-saturated aqueous solution of pH 3.0, and at room temperature (25 ± 1 °C).

The extinction spectrum ($OD_m(\lambda)$) measured in the spectrophotometer and RLS spec-trum ($I_{RLS}^m(\lambda)$) measured in the fluorimeter are a sum and product of true absorption and scattering components, respectively (see Eqs. (1) and (2)). In Eqs. (1) and (2), $OD_t(\lambda)$ and $I_{RLS}^t(\lambda)$ are the true absorbance and scattering contributions.

$$OD_m(\lambda) = OD_t(\lambda) + \log\left(\frac{1}{1 - pI_{RLS}^t(\lambda)}\right), \qquad (1)$$

$$I_{RLS}^m(\lambda) = I_{RLS}^t(\lambda) \times 10^{-qOD_t(\lambda)}. \qquad (2)$$

The true absorption and scattering component spectra were obtained by an iterative procedure that adjusts the arbitrary constants, *p* and *q* in Eqs.

(1) and (2). Convergence is obtained in 3 to 4 iterations.

3. Results and discussion

Fig. 1a shows the absorption spectra of TPPS (10 μM, pH 3.0) for different concentrations of ammonium chloride, from 0.05 to 0.5 M. Forma-tion of *J*-aggregate is indicated by a sharp ab-sorption peak at 491 nm. Fig. 1b shows the narrowing of the *J*-peak at 491 nm as the con-centration of NH₄Cl is decreased from 0.5 M. The peak has the narrowest width (FWHM) for 0.1 M
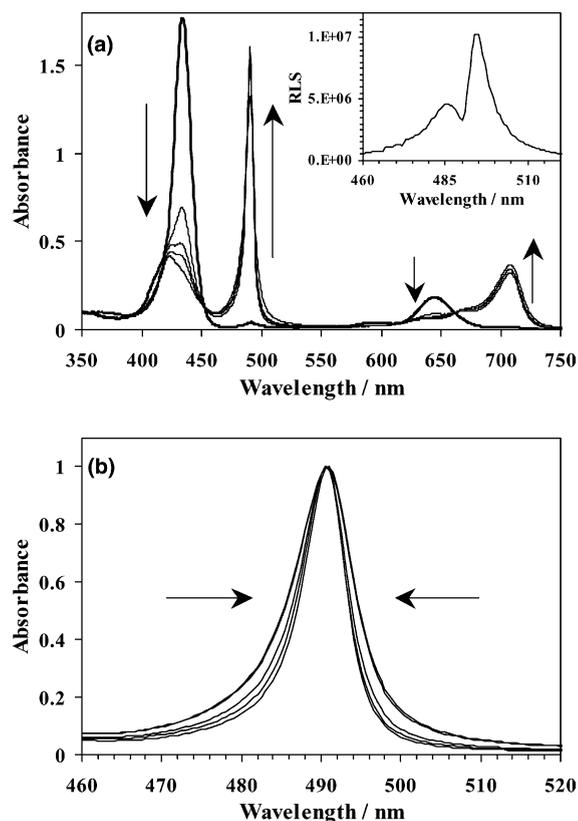

Fig. 1. (a) Absorption (Extinction) spectra of TPPS *J*-aggre-gate formed with NH₄Cl in aqueous solution at pH 3.0. Arrow indicates the change in [NH₄Cl] for, [NH₄Cl] = 0, 0.05, 0.1, 0.2, 0.3, 0.5 M. Inset shows the RLS spectrum in the *J*-band region for [NH₄Cl] = 0.1 M. (b) Normalized extinction spectra of the TPPS *J*-aggregate in the *J*-band region. The arrow indicates the change in [NH₄Cl] for, [NH₄Cl] = 0.5, 0.4, 0.3, 0.2 and 0.1 M.

of NH$_4$Cl. Resonance light scattering (RLS) spectrum of the *J*-aggregate was measured for all the solutions. The RLS in the *J*-peak region for 0.1 M of NH$_4$Cl is intense, which is shown as inset in Fig. 1a. The peak of RLS spectrum is red-shifted by 3.5 nm compared to the absorption peak. The RLS spectrum shows a dip at 491 nm that corresponds to the absorption by *J*-aggregate.

The 'absorption' or extinction band of the *J*-aggregate at 491 nm is a sum of true absorption and scattering. The spectra of the true absorption and scattering components were obtained by an iterative procedure described in Section 2. Fig. 2 shows the extinction, absorption and RLS spectra for the *J*-aggregate obtained for 0.1 M NH$_4$Cl solution. The full-width-at-half-maxima (FWHM) of the three spectra are given in Table 1. The

spectroscopic aggregation number calculated using the spectral width of the absorption spectrum is 12.9. The spectroscopic aggregation numbers for different concentrations of NH$_4$Cl as obtained from the true absorption spectra are given in Table 2.

J-aggregate is a colloidal solution in all the above cases. The hydrodynamic radius of the colloidal particles is measured by dynamic light scattering. Fig. 3 shows the autocorrelation curves for different concentrations of NH$_4$Cl. The hydrodynamic radius of the colloidal particles is determined from the autocorrelation curves. It is implicitly assumed that the shape of the colloidal particle is spherical. Table 2 shows the hydrodynamic radius (R) of the *J*-aggregate measured at different concentrations. Clearly, the hydrodynamic radius is increased with the concentration of NH$_4$Cl.

The geometry and distance between monomers in the *J*-aggregate of porphyrin have not been determined by any experimental method. The exciton theory of *J*-aggregate that explains the spectral red shift and spectral narrowing is well
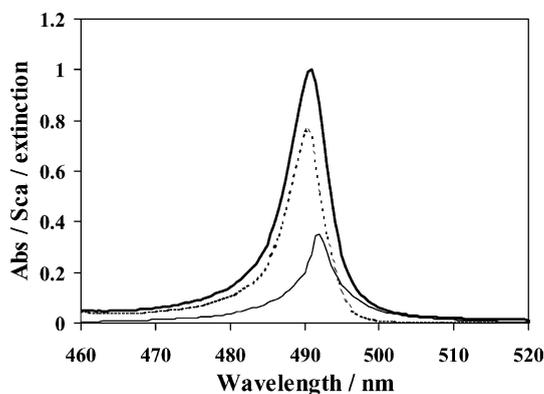

Fig. 2. Absorption (Extinction) spectrum as measured (thick line), and the contributions of absorption (dotted line) and the scattering (thin line) components of the TPPS *J*-aggregate formed with 0.1 M NH$_4$Cl.

Table 1
Spectral width of the *J*-band and the spectroscopic aggregation number (N) obtained after correction of the measured absorption and RLS spectra of TPPS *J*-aggregate formed with 0.1 M NH$_4$Cl

Type	FWHM (cm^{-1})	Aggregation number (N)
Extinction	273	–
Absorption	244	12.9
Scattering	211	–
TPPS monomer	875	–

Table 2
Hydrodynamic radii of TPPS *J*-aggregates obtained from DLS experiments

[NH$_4$Cl] (M)	Aggregation number (N)	Coherence length L (nm)[a]	Hydrodynamic radius R (nm)	Ratio (L/R)
0.05	8.66	9.66	43 ± 13	0.22
0.1	12.90	13.90	56 ± 10	0.25
0.2	10.47	11.47	78 ± 12	0.15
0.3	8.39	9.39	130 ± 20	0.07
0.4	5.49	6.49	250 ± 150	0.03
0.5	5.75	6.75	300 ± 100	0.02

[a] Coherence length, $L = (N + 1)$ times radius of the porphyrin, where N is spectroscopic aggregation number. Radius of the porphyrin is calculated to be ~1 nm.
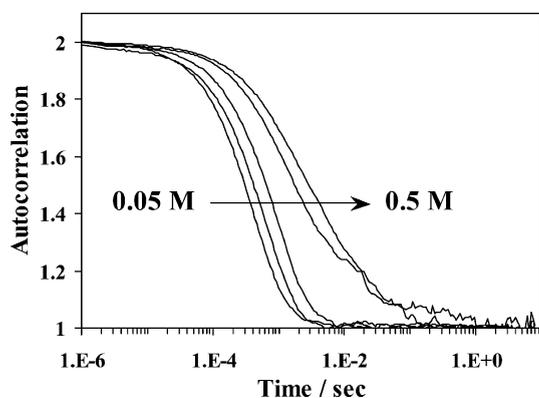
Fig. 3. Autocorrelation data obtained in the DLS experiments for the TPPS *J*-aggregate with different [NH$_4$Cl]. Arrow indicates the change in [NH$_4$Cl] for, [NH$_4$Cl] = 0.05, 0.1, 0.2, 0.4 and 0.5 M.

accepted [14]. The exciton theory is also used to understand nonlinear spectroscopy and ultrafast excited state dynamics of *J*-aggregate [11]. Based on this theory the spectroscopic aggregation number was calculated for the aggregates formed with different hydrodynamic radii (Table 2). The geometric arrangement of monomers in *J*-aggregate is either one or two dimensional [15]. In the case of porphyrin *J*-aggregate the monomer is a dianion and hence two ammonium ions will have to be incorporated in the aggregate for every porphyrin monomer. This suggests a one dimensional arrangement as the most probable one. Assuming side-by-side one dimensional arrangement of monomers in the *J*-aggregate [6], the coherence length (*L*) is calculated as (*N* + 1) times the radius of the porphyrin monomer. The radius of the monomer is calculated to be ~1 nm by geometry optimization using semi-empirical method (PM3 method in HYPERCHEM Version 6.01) program. Table 2 gives the coherence length for the *J*-aggregates thus obtained for different concentrations of NH$_4$Cl. The last column in Table 2 gives the ratio of the coherence length (*L*) to the hydrodynamic radius (*R*).

The results clearly show that the coherence length decreases with increase in the physical size of the *J*-aggregate. The ratio of the coherence length to the hydrodynamic radius is maximum (0.25) for the *J*-aggregate obtained with 0.1 M

NH$_4$Cl. In an ideal *J*-aggregate the coherence length and the physical length are equal and the value of ratio is unity. Such ideal aggregates are difficult to obtain by condensation of monomers from fluid solutions under experimental conditions at room temperature. The porphyrin aggregate in which the coherence length is 25% to that of the hydrodynamic radius is therefore remarkably good.

It may be noted that the spectroscopic aggregation number is calculated using the simplest approach, namely, that the spectral width of the *J*-band is solely due to the motional/exchange narrowing mechanism. This number is not the true estimate of spectroscopic aggregation number because other mechanisms (e.g., temperature and static/dynamic disorder) of line broadening of the *J*-band were not taken into account. If these effects are taken into account it is possible that the spectral width due to exchange narrowing alone is considerably less and therefore the spectroscopic aggregation number and coherence length will be considerably higher than that given in Table 2. We now estimate the coherence length using an alternate set of equations [16] that explicitly includes the thermal effect which is an important mechanism of line broadening.

The energy splitting (ΔE) for an array of N_c molecules (*J*-aggregate) is given by Eq. (3) [16].

$$\Delta E = \Delta E_0 \, \text{Cos}\{\pi/(N_c + 1)\}, \tag{3}$$

where ΔE_0 is the splitting energy as $N \to \infty$. According to the formalism developed by Bakalis and Knoester [16,17], coherence length can be estimated by Eq. (4).

$$N_c = \frac{\sqrt{3\pi^3 \Delta E_0}}{(4\pi\lambda kT)^{1/4}} - 1, \tag{4}$$

where λ is the molecular energy parameter that determines the thermal line broadening. Combining Eqs. (3) and (4), one gets

$$(N_c + 1)^2 \, \text{Cos}\left(\frac{\pi}{N_c + 1}\right) = \frac{3\pi^3}{(4\pi\lambda kT)^{1/2}}\Delta E. \tag{5}$$

ΔE is experimentally measured, which is twice the difference in the transition energy for the monomer and *J*-aggregate. In the case of porphyrin studied

here, the Soret band absorption peaks of monomer and *J*-aggregate occur at 433 and 491 nm, respectively, which gives ΔE to be 2728 cm^{-1}. The Stokes shift in the monomer calculated from the spectral data [6] is 647 cm^{-1}. When we consider a half of the Stokes shift as λ (323.5 cm^{-1}) and $T = 298$ K, Eq. (5) can be solved for N_c. The calculated value for N_c is 15.9. This value for coherence length clearly shows that the estimated coherence length will be larger if thermal line broadening is taken into account.

No simple expressions exist for estimating exciton effects and disorders. If these effects are also correctly taken into account, then the corrected estimate of the coherence length would be even larger. In this context, it is worth noting that nonlinear spectroscopic experiments appear more suited for an accurate estimate of the coherence length in *J*-aggregates. For example, an extended theory of the exchange narrowing mechanism was successfully used to fit the complete line shape of nonlinear absorption spectra of cyanine *J*-aggregate at 1.5 K [18] and room temperature [19].

It may also be noted that the experimental results were interpreted by assuming that the *J*-aggregate is one dimensional but the colloidal particle is three dimensional. It is understood that the one dimensional aggregate is hydrodynamically unstable at room temperature. *J*-aggregate is stabilized by a three dimensional condensation of one dimensional *J*-aggregates with minimal loss of *J*-band structure and spectroscopic features.

The results presented above may be explained by a growth model for the *J*-aggregate in two phases, as follows. In the first phase, the *J*-aggregate grows to a modest size of fixed aggregation number. In the second phase, aggregates of much larger sizes are formed by condensation of smaller aggregates that are formed in the first phase. The condensation process in the second phase does not lead to increase in the conjugation length. The condensation process may result in increase of point defects in the one dimensional chain of monomers, which contribute to a reduction in the coherence length in a large aggregate. Spectroscopically, the *J*-peak of the aggregates formed in the first phase would have narrow spectral width compared to the *J*-peak of the aggregates formed in the second phase. The rate of *J*-aggregate formation in both phases depends upon the concentration of NH$_4$Cl. The rate is slowest in 0.05 and 0.1 M solution of NH$_4$Cl.

Models of aggregation kinetics have been previously examined [10–12]. It is shown by different experiments that a nucleation process is essential for the build up of macroscopic aggregates. The ratio of the coherence length to the hydrodynamics radius is expected to be maximum when the *J*-aggregate is at the nucleation level. The use of ammonium chloride in dilute solution is therefore suitable for the preparation of *J*-aggregates which remain at the nuclear level.

4. Conclusion

Formation of *J*-aggregates with the largest ratio of coherence length to the hydrodynamic radius for the porphyrin TPPS (*meso*-tetrakis-(4-sulphonatophenyl) porphyrin) has been demonstrated. A growth mechanism for the TPPS *J*-aggregation, which explains the correlation between the coherence length and the hydrodynamic radius of the aggregate, has been proposed.

Acknowledgements

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