

Unusual optical properties of porphyrin fractal J-aggregates†

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Received (in Cambridge, UK) 24th January 2005, Accepted 21st April 2005

First published as an Advance Article on the web 6th May 2005

DOI: 10.1039/b501083g

A simple mix and shake procedure in aqueous solution from water-soluble tetrakis(4-sulfonatophenyl)porphyrin and spermine leads to fractal non-covalent supramolecular systems which exhibit unusual large enhancement of resonant light scattering, behaving as metal particles.

Supramolecular assemblies of chromophores have recently gained importance as models for photosynthesis¹ and for their applications in nanooptoelectronics.² In this respect, porphyrin J-aggregates have attracted considerable interest, due to their peculiar structural, kinetic and photophysical properties.^{3–8} The water soluble 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄) has been most investigated, being able to form J-aggregates simply under acidic conditions³ and/or in the presence of cationic templates.⁴ Recent reports have demonstrated the presence in solution of rod-like nanoaggregates,⁵ whose coherence, length and size can be controlled by the nucleating agent⁶ or by exploiting microemulsions as nanoreactors.⁷ On the other hand, porphyrin assemblies structured on a mesoscopic scale in a fractal network have been previously described.⁸ A relevant feature of fractal structures, especially those formed by metal particles, is the occurrence of enhanced Raman and Rayleigh light scattering.⁹ Furthermore, dendritic chromophoric systems have been considered as antennas for light harvesting, owing to their ability to funnel energy.¹⁰

Here we describe a non-covalent approach to obtain almost monodispersed and reproducible fractal J-aggregates of TPPS₄ under mild acidic conditions in the presence of spermine. The resulting porphyrin clusters exhibit very peculiar absorption and scattering features in comparison to the usual rod-like J-aggregates.

When spermine is added to a solution of TPPS₄ at pH 2.5, UV-Vis spectra indicate porphyrin self-aggregation. The B band of the diacid monomeric porphyrin ($pK_a = 4.9$, 434 nm) decreases while a new broad feature appears at 510 nm together with a shoulder at 490 nm (Fig. 1). As a consequence of aggregation, the absorption bands are severely broadened, leading to a non-zero extinction coefficient throughout the visible range, well above 850 nm. The presence of large aggregates, in which porphyrins are strongly coupled, causes an almost complete quenching of fluorescence emission and very intense resonance light scattering (RLS)¹¹ peaks (inset of Fig. 1). Fig. 1 also reports for comparison the UV-Vis and the very sharp (but less intense) RLS spectra of the acid induced

(rod-like) J-aggregates of TPPS₄.⁵ Another relevant difference is the intensity of the resonant signal in the region of the Q-band. In the case of the spermine induced aggregates, the relative intensity of this feature is greater than for the usual J-aggregates. This effect is paralleled by the observed anomalous ratio of intensities between the B and the Q bands and the long tail in the red portion of the extinction spectra.

Optical and scanning electron (SEM) microscopy images of samples evaporated on a glass substrate show almost monodispersed clusters whose internal structure appears to be fractal (Fig. 2 A–B). An analysis of the digitized images using the box-counting method¹² gave a fractal dimension $D = 1.42$. On passing from 2D to 3D space this value can be corrected to 1.75, which is close to the expected value for Diffusion Limited Cluster–Cluster Aggregation (DLCCA).¹² Such a mechanism is operative when the prevalent process in an aggregating system is the interaction between large clusters, the interactions among monomers or small oligomers being of relatively minor importance.

The very intense RLS observed from the solutions is still retained on the evaporated samples. Fig. 2D reports the image of a single cluster adopting a back-scattering configuration. The corresponding RLS profile closely resembles that measured in a liquid phase (Fig. 2C). The aggregates appear to be fairly monodispersed in size (hydrodynamic radii 3–5 μm), in agreement with dynamic light scattering measurements, confirming that these aggregates grow in solution and their morphology is not mediated from the surface. The mixing order of the reagents needs to be

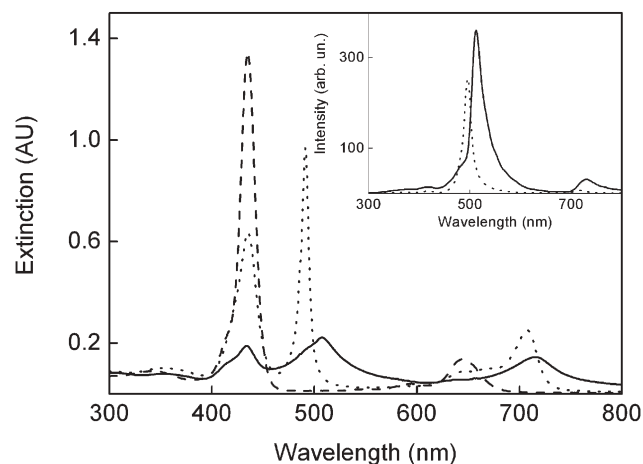


Fig. 1 UV-Vis and RLS (inset) spectra of 3 μM diacid TPPS₄ (dashed line), J-aggregate obtained by adding 0.3 M HCl (dotted line) and J-aggregate obtained by adding 100 μM spermine (solid line) in 20 mM citrate buffer pH 2.5 at 298 K. According to the monomeric nature of this species, RLS spectra of the diacid TPPS₄ are very weak and undetectable on this scale.

† Electronic supplementary information (ESI) available: preparation of the samples, spectroscopic methods and treatment of the data; theoretical treatment and scaling of the polarizability. See <http://www.rsc.org/suppdata/cc/b501083g/>

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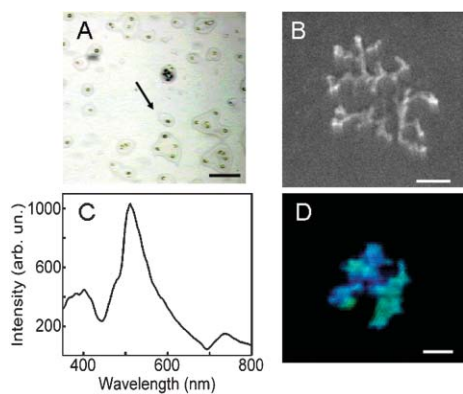


Fig. 2 (A) Optical image of spermine induced TPPS₄ J-aggregates on a glass slide, with the arrow marking a single cluster (bar 50 μm). (B) SEM image of a cluster (bar 1 μm). (C) RLS profile from the sample on a glass substrate. (D) Back-scattering optical image of a cluster illuminated in the spectral region 480–520 nm (bar 2 μm).

noted, because, as for the usual acid triggered J-aggregates, it influences the dynamics of growth and eventually the morphology of the system.⁸

In the present case, an hypothetical model for the supramolecular growth of the spermine induced aggregates can be based on the formation of an intermolecular network mainly stabilized through hydrogen bonds and electrostatic interactions, the basic units being edge-to-edge porphyrin arrangement. Simple molecular models show that in a J-dimer of TPPS₄ the distance between two lateral sulfonate groups is close to 10.5 Å. This value is about the distance between alternate protonated sites in the polyamine. As a consequence, in contrast with the acid induced J-aggregates, further branching in the structure can be easily achieved by interactions between the protonated nitrogen atoms of the polyamine and the negatively charged sulfonate end-groups, which are not involved in the porphyrin–porphyrin contacts (Fig. 3). A series of previous investigations, through a combination of elastic and quasi-elastic light scattering techniques, have shown that the

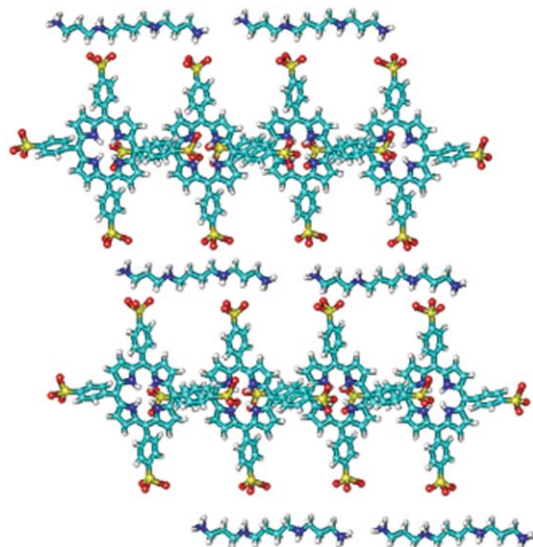


Fig. 3 Molecular model for J-aggregation of TPPS₄ induced by spermine.

first step in the clustering process is the formation of small rod-like aggregates containing up to 20 porphyrin monomers.⁸ These building blocks can be assumed to be the basic particles which on clustering lead to the fractal micrometer-sized structures present in solution. From simple geometrical considerations, taking into account the lower density of a fractal cluster with respect to a compact spherical object having the same hydrodynamic radius,⁸ we can estimate as $\approx 10^5$ the number of porphyrins in a single aggregate.

As a consequence of the fractal or self-similar structure, a power law behavior for the intensity of scattered light I_{RLS} vs. λ can be expected in the present system ($I_{\text{RLS}} \propto \lambda^{D-4}$), and D could be obtained as the slope of a double logarithmic plot from the RLS spectra.⁹ Indeed, apart from the expected Rayleigh contribution (proportional to $1/\lambda^4$) and the marked wells due to photon absorption, a linear behavior of the scattered light is evident in the regions close to the J- and Q-bands (Fig. 4). Anyway, the value of the slope (15.2 ± 0.2) is almost an order of magnitude larger in comparison to what is simply expected for fractal systems with $D = 1.75$, implying the occurrence of enhancement processes.

Theoretical investigations have predicted that fractal structures can exhibit scale invariant resonant enhancement of scattered light.⁹ When individual components of such clusters have a high quality of optical resonance, then very intense, correlated and largely fluctuating local fields can be induced. To the best of our knowledge, these effects have only been experimentally confirmed in the case of metal colloidal particles, such as gold or silver, and are the basis to explain their role in determining very important effects, such as Surface Enhanced Raman Scattering (SERS).⁹ We expect a similar although smaller effect in porphyrin aggregates, where the single unit has a fairly high extinction coefficient and the molecules have strong electronic coupling.

The quality of a molecular oscillator is essentially related to its ability to resonate well beyond its resonance frequency (the absorption band where resonance occurs). Anyway, usually the quality of a molecular oscillator is so low that, outside of the absorption band envelope, no enhancement can be detected, as for the diacid monomeric porphyrin ($\lambda = 434$ nm).

Our experimental RLS and extinction results clearly suggest that the oscillator quality in the present system is rather high. The theory developed for fractal systems indicates that, on irradiating a sample with an electromagnetic field close to the absorption frequency, the electric field is highly localized and consequently

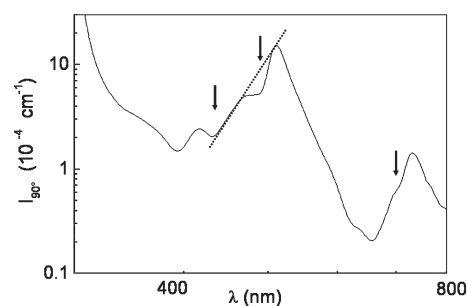


Fig. 4 Double logarithmic plot of absolute RLS intensity vs. wavelength for spermine induced TPPS₄ J-aggregate. The dashed straight lines (slope = 15.2 ± 0.2) indicate the region of the spectra where enhancement is occurring, and the arrows mark the positions of the absorption peaks.

leads to strong collective spatial fluctuations responsible for enhancement of scattered intensity and non-linear effects. These collective oscillations undergo with time a dephasing process, which follows a scaling law, whose characteristic exponent is the density of the excited states of the fractal cluster or optical spectral dimension, d_0 .¹³ Numeric simulations have pointed to a value $d_0 = 0.3 \pm 0.1$ for a DLCCA fractal structure. Our data are in full agreement with such theoretical expectations (see ESI, Figure S11).

In summary, we have reported a very simple method to access supramolecular assemblies of porphyrins having monodispersed sizes, a specific fractal morphology and highly peculiar optical properties. Differing from previous reports, in which self-organization has been achieved in organic solvents,¹⁴ the present example is based on mixing water soluble components in the proper order. Since the spectral properties of the monomeric porphyrins can be finely tuned through chemical changes (*e.g.* by introducing groups with different stereo-electronic properties and/or by metal coordination) or even by changing the counterions (and the corresponding electronic structure can be predicted through Time-Dependent Density Functional Theory),¹⁵ we expect that such clusters can be conveniently exploited in non-linear optical and optoelectronic applications.

This work was supported by CNR and MIUR (COFIN 2002).

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