

Electronic Supporting Information

for

Unusual Optical Properties of Porphyrin Fractal J-Aggregates

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Experimental section

Sample preparation. The porphyrin 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS₄) was obtained from Aldrich Co. as tetrasodium salt, and spermine (1,12-diamino-4,9-diazadodecane) was purchased from Sigma. Aqueous concentrated solutions of this porphyrin ($1\text{-}2\times 10^{-4}$ M) were prepared in dust-free Millipore water, stored in the dark and used within a day of preparation.

The concentration of the porphyrin samples was measured spectrophotometrically using $\varepsilon_{412} = 5.33 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ in water. Purity of samples was checked by electrophoresis.

Samples of J-aggregated diacid TPPS₄ were prepared by adding a known volume of a concentrated stock solution of spermine (100 μM) to a solution of porphyrin (3 μM) in 20 mM citrate buffer at pH 2.5. Milli-Q water was used throughout.

Methods. UV/Vis spectra were obtained on a Hewlett-Packard mod. 8453 diode array spectrophotometer using 1 cm pathlength quartz cells. Resonance light scattering (RLS) experiments were performed on a Jasco mod. FP-750 spectrofluorimeter, adopting a

synchronous scan protocol with right angle geometry (R. F. Pasternack, P. J. Collings, *Science* **1995**, *269*, 935.). RLS spectra were corrected for the absorption of the samples. In all the cases, a microcell (Hellma, 0.3 cm) was used to minimize this contribution. The absolute value for RLS reported in Figure 4 was obtained from the raw RLS data by dividing for the scattered intensity of toluene and by multiplying for the absolute value of toluene scattering from the literature at each wavelength. The F_R ratio reported in the inset of Figure S11 has been evaluated by dividing the previously obtained absolute scattering for the expected theoretical scattered intensity for the monomer ($\propto 1 / \lambda^4$).

Quasi-elastic light scattering measurements (QELS) were performed on a Malvern 4700 submicron particle analyzer. The exciting light source was a 17 mW polarized HeNe laser (632.8 nm).

Glass microscope slides were used as substrates. They were cleaned prior to use by immersion into a 1:1 mixture of concentrated NH_3 solution and 30+ % H_2O_2 (Caution! This mixture is highly corrosive and should be handle with care under a ventilated hood and avoiding skin contact), then rinsed with Millipore-Q water and dried under a N_2 stream. 25 μL of solution containing J-aggregated porphyrin were deposited on the cover slides and evaporated at room temperature under a gentle N_2 stream. An optical microscope Zeiss Axiovert S100 equipped with a CCD camera was used to acquire the images. The RLS images were acquired adopting a back-scattering configuration and illuminating the sample with a band-pass filter (Corion S40-500; 480-520 nm).

The samples for the SEM imaging were treated by graphite-coating and were visualized on a LEO S420 Cambridge instrument operating with an accelerating potential of 20 kV.

Theoretical treatment and analysis of spectroscopic data

We assume our system as formed by clusters of particles having resonance frequency ω_0 . In the case of a cluster having a size R_0 greater than the wavelength of the incident field, the enhancement factor F_R for scattering is given by the following equation (valid for $D < 2$) (V. M. Shalaev, *Phys. Rep.* **1996**, 272, 61):

$$F_R \approx \frac{(kR_0)^{-D}}{R_0^3 \delta} (R_0^3 |X|)^{d_0+1}$$

This factor is controlled for coherence by the fractality of the structure, through the term $(kR_0)^{-D}$ (where k is the wavevector of the incident light), and by the density of the excited states. It exhibits also an inverse dependence on a decay parameter δ , which is proportional to the particle absorption bandwidth and related with the quality of the oscillator. At the same time, the absorption data (more precisely the quantity $A \times \lambda$, which is related to the imaginary part of the polarizability $Im(\alpha)$) obeys to a power law with a characteristic exponent, i.e. $d_0 - 1$. The spectral variable X has been theoretically introduced to make the treatment independent on the wavelength dependence of polarizability. In the present case, assuming only dipolar excitations, X is proportional to the energy distance (X') with the resonance.

The inset of Figure SI1 reports the ratio between the corrected RLS intensities for the aggregated and the monomeric species, which can be related to the F_R factor. An accurate analysis of its scaling behavior is partially prevented by the presence of the modulation introduced by the absorption features. After being properly re-scaled for the “trivial” enhancement for coherence, $(kR_0)^{-D}$ these data give a reasonable power law behavior as function of X' , with a scaling exponent $d_0 = 0.3$. A much better agreement between our experimental data and the theoretical model is shown by the absorption

data analysis, which evidence a power law behavior with a slope -0.7 , pointing once again to the expected value $d_0 = 0.3$. (V. A. Markel, L. S. Muratov, M. I. Stockman, T. F. George, *Phys. Rev. B* **1991**, *43*, 8183.)

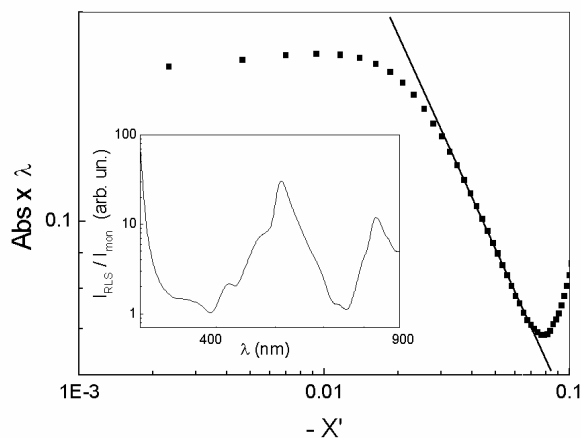


Figure S11. Imaginary part of polarizability (from the absorption data) for a sample of J-aggregated TPPS₄ as function of the spectral variable X' . The solid line represents a power law with an exponent $d_0 - 1 = -0.7$ (see text) The inset shows the enhancement factor reported as RLS intensity normalized for the intensity of the monomer for a sample of J-aggregated TPPS₄ as function of wavelength.