

Light scattering enhancement in an aqueous solution of spermine-induced fractal *J*-aggregate composite

Norberto Micali* and Valentina Villari

CNR, Istituto per i Processi Chimico-Fisici, sezione Messina, Via La Farina 237, I-98123 Messina, Italy

Luigi Monsù Scolaro,† Andrea Romeo, and Maria Angela Castriciano

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina Salita Sperone 31, I-98166 Villaggio S. Agata, Messina, Italy

(Received 13 December 2004; revised manuscript received 21 October 2005; published 21 November 2005)

We performed an experimental investigation on the scattering and extinction properties of an aqueous solution of spermine-induced fractal *J* aggregates, constituted by porphyrin molecules. In analogy with nanostructured particle composites, the dipolar moments of different porphyrins, not belonging to the *J* aggregates, are coupled and generate a strong light scattering enhancement. Both the enhanced scattered intensity and the imaginary part of the polarizability of the system obey scaling laws with the optical spectral dimension $d_0=0.3$.

DOI: [10.1103/PhysRevE.72.050401](https://doi.org/10.1103/PhysRevE.72.050401)

PACS number(s): 82.70.-y, 78.35.+c, 78.67.Bf, 78.20.-e

Optical properties of nanostructured and fractal aggregates have been intensively investigated from the theoretical point of view and also under resonance conditions [1–5]. Fluctuations of the local electromagnetic field and consequent enhancement of the linear and nonlinear optical properties are especially pronounced in colloidal aggregates of metal particles and metal nanocomposites [6,7]. In these systems, the optical properties are dramatically different from those observed in bulk: the local field at some nanoparticles differs significantly from the macroscopic one [8,9]. In fractals nanocomposites, which do not have translational invariance (they cannot support propagating waves), excitations are localized in subwavelength regions, called “hot zones.” When the frequency of the illuminating field is close to the frequency of the dipolar eigenmodes of the system a strong scattering enhancement occurs. Several experimental investigations have been carried out on clusters of metal particles (e.g., [10,11]), but only some on organic molecules, regarding essentially metal particles on which some dyes are adsorbed [12,13].

In this study we report on the analogy between the optical properties of an organic fractal structure formed by one-dimensional chains of dyes (known as *J* aggregates) and the properties of more conventional fractal nanoparticle composites. *J* aggregates have attracted a great deal of interest for their applications in nonlinear optical devices, photoelectric cells, recording devices, and as model for the bacterial light harvesting antenna complexes. In general, the optical properties of these structures are described by the Frenkel exciton model [14,15]. For perfectly ordered aggregates, the exciton wave functions are delocalized along all the length of the aggregate. A typical absorption spectrum shows a narrow peak shifted at lower energy with respect to the optical absorption of the isolated molecule. The energy shift corre-

sponds to the nearest-neighbor excitation transfer interaction [16]. In typical *J* aggregates the exciton dipoles are delocalized over about a few tens of molecules; under this condition there is not a pronounced enhancement of the scattering around the *J*-aggregate absorption band. In these *J* aggregates, local field enhancement has been obtained only in the presence of metal tip in near-field optical microscopy (e.g., [17]). A strongly enhanced field is localized at the tip and consists mainly of evanescent components which locally interact with the sample surface and generate the spectroscopic response.

The system under investigation in this paper consists of aqueous solutions of a particular fractal *J* aggregate of tetrakis (4-sulfonatophenyl) porphyrin (TPPS₄), induced by adding a ligand molecule, spermine. An hypothetical model for the structure of the present system can be sketched by considering the formation of an intermolecular network of a porphyrin edge-to-edge arrangement; in such a network spermine induces the branching through interactions between the protonated nitrogen atoms of the spermine and the negatively charged sulfonate end groups of the porphyrin not involved in the porphyrin-porphyrin contacts. In this heterogeneous system, besides the exciton coupling inside the *J* aggregate, the porphyrin molecules (inside the fractal) not involved in the *J* aggregate interact through dipolar coupling, enhancing the Rayleigh scattering. In analogy with fractal composites, the absorption spectrum of the *J* aggregate-spermine system is broad and extends in the long wavelength region well outside the absorption frequency. These fractal *J* aggregates also show an enhancement of the Raman scattering, similar to that observed in molecules adsorbed on the surface of aggregated metal nanoparticles. The enhancement of the optical properties occurs in the presence of the ligand which is directly involved in the formation of the fractal aggregate. The composite is formed when aggregates are seeded into the substrate (matrix) consisting of spermine. On contrary, in typical fractal *J* aggregates obtained under strictly acidic conditions in the absence of spermine, both smaller enhance-

*Electronic address: micali@me.cnr.it

†Electronic address: monsu@chem.unime.it

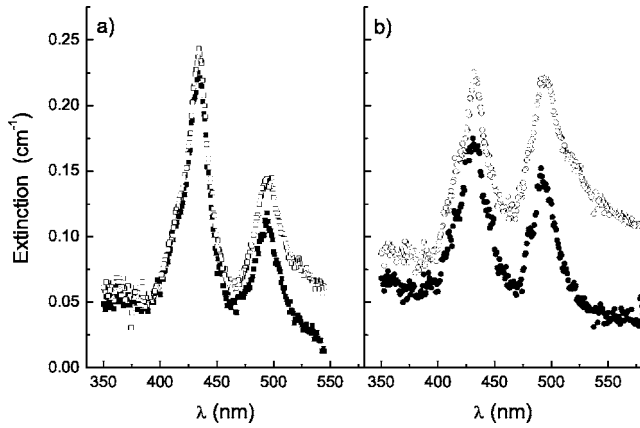


FIG. 1. Extinction (open symbols) and absorption A (closed symbols) spectra of (a) smaller and (b) larger TPPS₄ aggregates in the presence of spermine. Experimental conditions: $c_{TPPS} = 3 \mu\text{M}$, $c_{spermine} = 100 \mu\text{M}$ $\text{pH} = 2.7$, citrate buffer 10 mM.

ment around the J -aggregate band and spectral broadening are observed [18–21].

Figure 1 compares the extinction and the absorption spectra of an aqueous solution of TPPS₄ J aggregate in the presence of spermine for different fractal sizes (larger aggregates are obtained after one week). The absorption and extinction measurements have been carried out using a homemade spectrophotometer. The optical cell (path length 1 mm) was, in the first case, faced to the photomultiplier in order to collect both transmitted and scattered light (up to about 80°) and to obtain the absorption. In the second case, the cell was placed at 50 cm from the photomultiplier; a field aperture selected the transmitted light within 0.5°.

The scattering contribution, $S(\lambda)$, difference between the extinction and absorption spectra [22], increases with the wavelength (Fig. 2) and with the fractal size. On the other hand, the scattering from the acidic solution in the absence of spermine (shown in the inset of Fig. 2) is due to the presence of the J -aggregate resonance peak [23] (the peak at 420 nm is attributable to H aggregates [18]). Therefore, the broadening of the J -aggregate band in the porphyrin-spermine system cannot be attributed to the exciton localization.

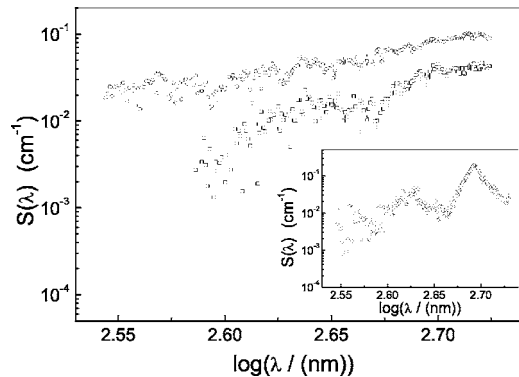


FIG. 2. Scattering contribution for the smaller (squares) and larger (circles) aggregate. In the insert the scattered light from the acidic solution without spermine is reported; experimental conditions: $c_{TPPS} = 3 \mu\text{M}$, $c_{\text{HCl}} = 0.1 \text{ M}$.

According to a purely exciton model, in fact, the energy and the broadening of the band for a J aggregate of N molecules can be obtained by the Frenkel excitation Hamiltonian [14,16]. In particular, the width of the absorption band of the J aggregate, Γ half-width at half maximum (HWHM), centered at $\tilde{\nu}_J$ (which for large N becomes $\tilde{\nu}_0 - 2\beta$, where $\tilde{\nu} = 1/\lambda$, λ being the wavelength in vacuum, and β the nearest-neighbor excitation transfer interaction), is related to the number of molecules of the localized exciton by [14,24]: $N_{del} = (1/1.12) [\sqrt{(3\pi^2|\beta|)/(2\Gamma)} - 2.86]$.

The isolated porphyrin has a Soret band at $\tilde{\nu}_0$, corresponding to $\lambda_o = 434 \text{ nm}$, whose width is $\Gamma_o = 875 \text{ cm}^{-1}$, and the J -aggregate peak is at $\lambda_j = 490 \text{ nm}$ ($\beta = 1275 \text{ cm}^{-1}$) whose width is $\Gamma \approx 100 \text{ cm}^{-1}$.

This theory well describes the J -aggregate absorption spectrum under acidic conditions in the absence of spermine and the resonant band width leads to $N_{del} \approx 10$. By adopting the same approach for the J -aggregate-spermine system, the large spectral width of the J -aggregate resonant peak ($\Gamma \approx 500 \text{ cm}^{-1}$) would correspond to $N_{del} < 3$. This result does not agree with the experimentally measured energy shift $\lambda_j = 490 \text{ nm}$, which, for aggregates with a small number of molecules should be close to that of the two level excitation, $hc\tilde{\nu}_0$ (for $N_{del} = 3$ it is $\lambda_j = 470 \text{ nm}$) [25]. Moreover, the scattering enhancement already appears in the Soret region and increases, according to a power law, well beyond the J -aggregate band.

Experimental data can be rationalized by considering the porphyrin molecules (in the fractal and outside the J aggregate) embedded in the spermine matrix; in analogy with nanocomposites, the dipolar moments induced on monomers by the external electric field are able to interact through dipolar coupling. The dipole-dipole interaction (long range) between different monomers gives rise to the enhancement of the optical properties.

The amplitude of the transition dipole moment d_i at the i th monomer within the fractal is related to the external field E^0 through a light-induced dipolar interaction W (in the limit of monomers smaller than the wavelength of light) [26,27]

$$(Z + W)|d\rangle = |E^0\rangle \quad (1)$$

which represents a coupled-dipole equation, where $Z = -X - i\delta = \alpha_0^{-1}$ (α_0 is the polarizability of the monomer), $|d\rangle$ is the state of the light-induced dipolar moments, $X = -\text{Re}(1/\alpha_0) \propto 1 - \tilde{\nu}_0/\tilde{\nu}$ is the spectral parameter and $\delta = -\text{Im}(1/\alpha_0) \approx \Gamma_0$ the dephasing [1]. The optical properties are easily related to the polarizability χ of the system, that is the average of the polarizability χ_i obtained through the solution of Eq. (1). The eigenvalues w_n of W (with eigenvector $|n\rangle$) contribute to the width of the absorption band. The parameter X has the meaning of a relative frequency detuning and δ determines the resonance width (related to the dissipation within the fractal). When the real part of the polarizability exceeds its imaginary part, the quality factor Q (X/δ) is large, leading to a large enhancement [1].

The optical properties of the system are totally included in χ by means of Z ; moreover, in a fractal system possessing a self-similar structure, any physical quantity F obeys a scaling

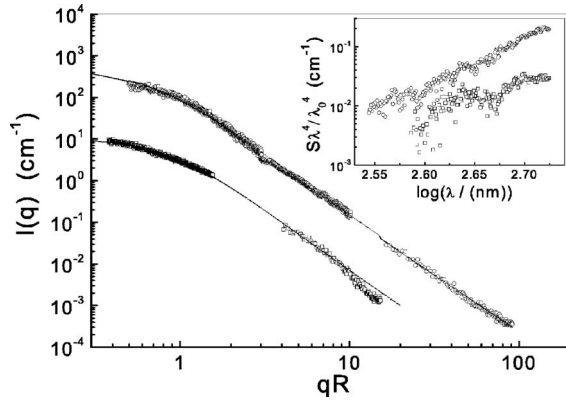


FIG. 3. Small and wide-angle elastic light scattering for smaller (lower data) and larger (upper data) fractal in the presence of spermine. The lines are the best fit according to Eq. (5). The insert displays the scattering from both fractals properly normalized (see text).

law in Z with some scaling index γ [28]. For high quality resonators, for which $Q \gg 1$, such as resonant dipolar modes in a fractal, the local field exceeds the external one. Under this condition physical quantities scale with X . For the absorption, A (which is related to the imaginary part of the polarizability, $\approx k \text{Im} \chi$, where $k = 2\pi/\lambda$) the scaling index becomes $\gamma = d_0 - 1$ [26]

$$A/k \approx \text{Im} \chi(X) \approx |R_0^3 X|^{d_0-1}, \quad (2)$$

whereas for the scattering enhancement F_R (ratio between the scattering from the fractal and that of an equivalent number of noninteracting particles [26] and proportional to $S\tilde{\nu}_0^4/\tilde{\nu}^4$) is $\gamma = d_0 + 1$. The index d_0 ($0 < d_0 < 1$) is the optical spectral dimension, that is the counterpart of the spectral dimension in the case of vibrational excitations, it also characterizes the scaling of the dipolar density of states.

In the case of large fractal clusters (having a size larger than the wavelength of light) F_R can be written as [26]

$$F_R \approx \frac{(kR_0)^{-2}}{R_0^3 \delta} (R_0^3 |X|)^{d_0+1} \quad (D_f > 2), \quad (3)$$

where the prefactor $(kR_0)^{-2}$ (coherence enhancement) takes into account the scattering function of the fractal in the absence of absorption [29]. The resonance character of the scattering dipolar interaction in a fractal is considered in the factor δ^{-1} . For the fractal's size smaller than the wavelength of light, the prefactor becomes unity.

In the case of very large fractals, on the other hand, for which the size parameter $kRn > 20$ (n being the refractive index), the enhanced scattering of Eq. (3) becomes

$$F_R \approx Q_{sc} \pi R^2 \frac{1}{R_0^3 \delta} (R_0^3 |X|)^{d_0+1}, \quad (4)$$

where R is the radius of the fractal and Q_{sc} is the scattering efficiency factor of nonabsorbing spherelike aggregates. For a high value of the size, parameter Q_{sc} reaches a limiting value of 2 [22]. In this case F_R (and $S\tilde{\nu}_0^4/\tilde{\nu}^4$) scales with X according to a power law with index $d_0 + 1$. In order to the

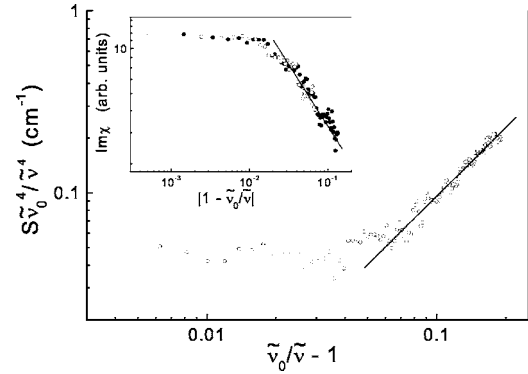


FIG. 4. Enhanced scattering $S\tilde{\nu}_0^4/\tilde{\nu}^4$ for the J -aggregate-spermine sample; the straight line indicates the region having slope $d_0 + 1 = 1.3$. In the inset the imaginary part of the polarizability is reported for both positive and negative values of X ; the straight line indicates the region with slope $d_0 - 1 = -0.7$.

check size and fractal structure of the spermine-induced aggregates of porphyrin and to use the proper coherence enhancement factor, static light-scattering measurements (at $\lambda = 532$ nm) have been performed. The experiment consists in collecting scattered light at small ($q < 4 \mu\text{m}^{-1}$) and wide angle ($q > 4 \mu\text{m}^{-1}$) using two different setups [$q = (4\pi n/\lambda) \sin(\theta/2)$, θ being the scattering angle]. The matching of the two data sets has been performed by normalizing small angle and wide angle scattering experiments through a secondary standard and toluene, respectively.

The fractal structure is evidenced by an inspection of Fig. 3 in which the scattering profile $I(q)$ is well described by the following structure factor [21,30]:

$$I(q) \propto \frac{\sin[(D_f - 1) \arctan(qR)]}{(D_f - 1)qR(1 + q^2R^2)^{(D_f - 1)/2}}, \quad (5)$$

which takes into account both the power law q^{-D_f} of the wide-angle scattering profile and the finite size of the fractal R (indicated by the round off at small q values). The best fit gives the fractal dimension $D_f = 2.5 \pm 0.1$ for both fractals (diffusion limited aggregation) and radii $R = 3 \pm 0.5 \mu\text{m}$ and $R = 0.5 \pm 0.1 \mu\text{m}$. Therefore, for the smaller fractal, for which $kRn \approx 8$, Eq. (3) holds, whereas for the larger fractal ($kRn \approx 45$), Eq. (4) must be applied. As it can be seen from the inset of Fig. 3, the scattering enhancement from both fractals exhibits the same monotonic behavior.

In Fig. 4 the measured enhanced scattering $S\tilde{\nu}_0^4/\tilde{\nu}^4$ for the larger J -aggregate-spermine fractal is shown as a function of the parameter X and a scaling parameter $d_0 + 1 = 1.3$ is obtained. The imaginary part of the polarizability, on the other hand, which is related to the absorption, displays a power law, as a function of X , that agrees with the scaling of Eq. (2) for both positive and negative values of X , with the scaling parameter $d_0 - 1 = -0.7$. The value of the optical spectral dimension agrees with the results from numerical simulations on diffusion limited cluster-cluster fractal aggregates [26]. It is worth noting that in the case of J aggregates under acidic conditions, in the absence of spermine, no scaling law is observed either for scattering or absorption.

In summary, the present work shows that in analogy to metal nanocomposites, the investigated system induces an enhancement of the scattering properties. Whereas under acidic conditions without spermine, the Frenkel excitation model can explain the polarizability behavior satisfactorily; the dipole-dipole interaction between porphyrins (not belonging to the J aggregate) must be considered in order to explain the broadening of the absorption band, the energy shift observed experimentally, and the wavelength depen-

dence of the scattering in the porphyrin-spermine system. Therefore, this system can be regarded as a fractal nanoparticle composite. The correctness of such a model can be based on the fulfillment of both the scattering enhancement and polarizability scaling law with the same optical spectral dimension $d_0=0.3$ as that obtained through numerical simulations on cluster-cluster aggregates of metal nanoparticle composites.

-
- [1] V. M. Shalaev, *Phys. Rep.* **272**, 61 (1996).
 [2] A. K. Sarychev and V. M. Shalaev, *Phys. Rep.* **335**, 275 (2000).
 [3] G. P. Ortiz and W. L. Mochàn, *Phys. Rev. B* **67**, 184204 (2003).
 [4] M. I. Stockman, K. B. Kurlayev, and T. F. George, *Phys. Rev. B* **60**, 17071 (1999).
 [5] M. I. Stockman, L. N. Pandey, L. S. Muratov, and T. F. George, *Phys. Rev. B* **51**, 185 (1995).
 [6] V. A. Markel, V. M. Shalaev, E. B. Stechel, W. Kim, and R. L. Armstrong, *Phys. Rev. B* **53**, 2425 (1996).
 [7] V. M. Shalaev, E. Y. Poliakov, and V. A. Markel, *Phys. Rev. B* **53**, 2437 (1996).
 [8] M. I. Stockman, *Phys. Rev. E* **56**, 6494 (1997).
 [9] M. I. Stockman, L. N. Pandey, and T. F. George, *Phys. Rev. B* **53**, 2183 (1996).
 [10] S. I. Bozhevolnyi, J. Beermann, and V. Coello, *Phys. Rev. Lett.* **90**, 197403 (2003).
 [11] S. I. Bozhevolnyi, V. A. Markel, V. Coello, W. Kim, and V. M. Shalaev, *Phys. Rev. B* **58**, 11441 (1998).
 [12] M. I. Stockman, V. M. Shalaev, M. Moskovits, R. Botet, and T. F. George, *Phys. Rev. B* **46**, 2821 (1992).
 [13] V. P. Drachev, W. T. Kim, V. P. Safonov, V. A. Podolskiy, N. S. Zakovryashin, E. N. Khaliullin, V. M. Shalaev, and R. L. Armstrong, *J. Mod. Opt.* **49**, 645 (2002).
 [14] L. D. Bakalis and J. Knoester, *J. Lumin.* **87-89**, 66 (2000).
 [15] M. Vacha, M. Furuki, L. S. Pu, K. I. Hashizume, and T. Tani, *J. Phys. Chem. B* **105**, 12226 (2001).
 [16] S. S. Lampoura, C. Spitz, S. Daehne, J. Knoester, and K. Duppen, *J. Phys. Chem. B* **106**, 3103 (2002).
 [17] E. J. Sánchez, L. Novotny, and X. S. Xie, *Phys. Rev. Lett.* **82**, 4014 (1999).
 [18] N. Micali, F. Mallamace, A. Romeo, R. Purrello, and L. Monsù Scolaro, *J. Phys. Chem. B* **104**, 5897 (2000).
 [19] M. A. Castriciano, A. Romeo, V. Villari, N. Micali, and L. Monsù Scolaro, *J. Phys. Chem. B* **108**, 9054 (2004).
 [20] F. Mallamace, L. Monsù Scolaro, A. Romeo, and N. Micali, *Phys. Rev. Lett.* **82**, 3480 (1999).
 [21] F. Mallamace, N. Micali, S. Trusso, L. Monsù Scolaro, A. Romeo, A. Terracina, and R. F. Pasternack, *Phys. Rev. Lett.* **76**, 4741 (1996).
 [22] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley and Sons, Inc., New York, 1998).
 [23] R. F. Pasternack and P. J. Collings, *Science* **269**, 935 (1995).
 [24] R. V. Markov, A. I. Plekhanov, V. V. Shelkovnikov, and J. Knoester, *Microelectron. Eng.* **69**, 528 (2003).
 [25] J. Parkash, J. H. Robblee, J. Agnew, E. Gibbs, P. Collings, R. Pasternack, and J. C. de Paula, *Biophys. J.* **74**, 2089 (1998).
 [26] V. M. Shalaev, R. Botet, and R. Jullien, *Phys. Rev. B* **44**, 12216 (1991).
 [27] V. A. Markel, L. S. Muratov, M. I. Stockman, and T. F. George, *Phys. Rev. B* **43**, 8183 (1991).
 [28] M. I. Stockman, L. N. Pandey, and T. F. George, *Nonlinear Optical Material, IMA Volumes in Mathematics and its Applications*, edited by J. V. Moloney (Springer-Verlag, New York, 1998), Vol. 101, p. 225.
 [29] R. A. Dobbins, G. W. Mulholland, and N. P. Bryner, *Atmos. Environ.* **28**, 889 (1994).
 [30] S. H. Chen and J. Teixeira, *Phys. Rev. Lett.* **57**, 2583 (1986).