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Giant static dipole moment in pseudoisocyanine J-aggregate with a hierarchical structure

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A new model of hierarchical structure in J-aggregates, *mesoaggregates* and *macroaggregates*, is proposed on the basis of the linear and nonlinear optical properties of the oriented J-aggregates prepared by a novel vertical spin-coating method. The concentration dependence of dichroic spectra, wavelength dependence of hole-burning efficiency, and polarization dependence of electroabsorption are studied. The mesoaggregate is characterized by coherent exciton delocalized over the mesoscopic size, while the macroaggregate can be oriented by macroscopic centrifugal force of solvent flow. The macroaggregate is constituted by an incoherent ensemble of the mesoaggregates alternately stacked.

Keywords; J-aggregate, mesoaggregate, macroaggregate, electroabsorption, static dipole moment, exciton

1. Introduction

J-aggregates of cyanine dyes are attracting interest of many scientists as a model material for one-dimensional molecular excitons [1-4]. J-aggregates exhibit a characteristic sharp absorption peak, so-called the J-band, below the monomer transition band [1, 2]. The J-band is due to the transition of excitons delocalized over an aggregate by intermolecular dipole interaction. A simple model of N identical molecules aligned in a one-dimensional chain has been proposed to explain the optical

spectrum of the J-aggregates [4-6], and it seemed to be successfully reproduced. However, one-dimensional model is too simple to explain the optical properties of J-aggregates, and the detailed structure is still open to question. The main interesting problem in J-aggregates is the complete assignment of the excitonic bands including the J-band, related with the molecular arrangement.

Structure of J-aggregates has been discussed by many scientists after the discovery of J-aggregates. Kuhn *et al.* calculated the spectral shift due to the aggregation. The experimental value of the shift was explained assuming a brick stone work structure instead of a ladder or staircase [7, 8] In their calculation, they applied extended dipole model, where molecules are replaced by dipoles of a length l and a charge pair +e and −e. Daltrozzo *et al.* measured circular dichroism of J-aggregates induced by optically active agents and considered non-planarity of the PIC molecule [9]. They concluded the crystal is built up by helical columns of quasi-one-dimensional threads of dye molecules. The helical structure is the result of the brick stone work made of non-planar dye molecules [10]. Kopainsky et al. investigated the dimerizaiton process as the first step for aggregation by measuring the concentration dependence of the absorption spectrum. In these studies mentioned above, anisotoropy due to the one-dimensional structure has not been observed. One dimensionality was only included as a model in the calculations of isotropic spectra. In order to understand how the excitonic bands are characterized by the structure of the J-aggregates, it is important to make oriented aggregates and to observe the dimensionality directly. Highly oriented J-aggregates was prepared for the first time in a

polyvinylalcohol (PVA) film by a novel method, named "vertical spin-coating", which has been developed by the authors [11].

In the present article, we propose a hierarchic structure of J-aggregate; mesoaggregate and macroaggregate, on the basis of concentration dependence of dichroic spectra, and wavelength dependence of hole-burning efficiency in the J-band of the oriented J-aggregates.

2. Linear Dichroism

2.1. Concentration dependence of the absorption spectrum

Dichroic absorption spectra of the samples of several dye concentrations in PVA were measured, the results being shown in Fig. 1. From the concentration dependence, it can be concluded that the randomly oriented aggregates and the oriented ones are different in size; the formers are smaller, while the latters larger than some critical size needed to be aligned by the solvent flow introduced by the centrifugal force. A remarkable finding is that the J-aggregates become isotropically dispersed around a weight ratio of 3/80. The outstanding sharp J-band indicates that the J-aggregates in this sample are smaller than the critical size, but large enough for exciton delocalization.

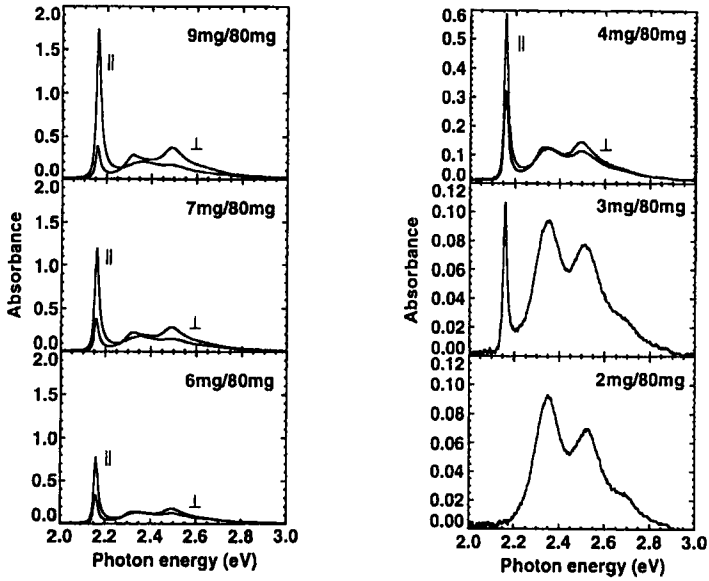

Fig. 1 : Concentration dependence of dichroic spectra

2 .3. Extracted spectra

We separated the dichroic absorption spectra of the oriented J-aggregates into two. One component is sharp and nearly isotropic, while the other is broad and strongly dichroic. They correspond to small-size coherent aggregates dispersed isotropically in the sample and large scale rod-shaped aggregates with wel -aligned configuration. The former is called *mesoaggregate*, which is characterized by coherent exciton delocalized over the mesoscopic size, while the latter *macroaggregate*, which can be oriented by macroscopic centrifugal force of fluid-dynamical flows. The separated absorpion spectra of the two different types of aggregates are shown in Fig.2.

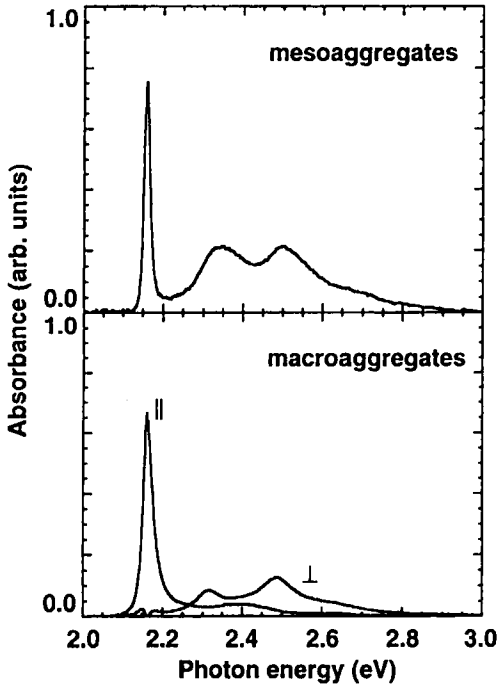

Fig. 2 : Extracted spectra of the mesoaggregates and macroaggregates

3. Hole-burning

Figure 3 shows the hole spectra of the oriented J-aggregate at a 8/80 weight ratio burnt at 570.1 and 571.0 nm with the parallel polarization pump to the orientation axis after 6-min irradiation. The accuracy of the burning wavelength is limited within about 0.05 nm by the grating resettability of the monochromator. The burning intensities at 570.1 and 571.0 nm were 0.26 and 0.34 mW/cm^2, respectively. The hole-burning process was reversible at an elevated temperature. When the tempe

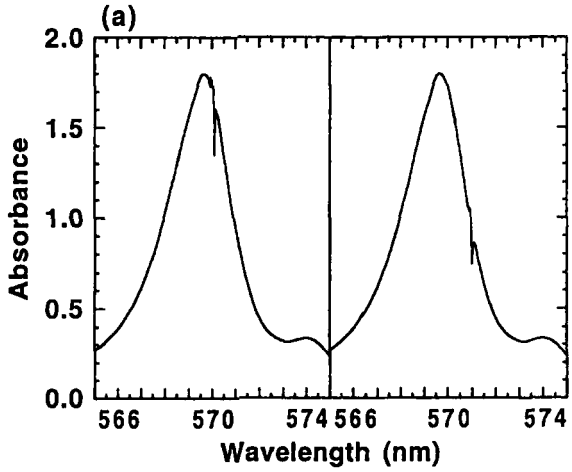

Fig. 3 : Typical hole spectra burnt at 570.1 and 571.0 nm with parallel excitation to the orientation axis of the J-aggregates, (a) whole J-band spectra and (b) magnified spectra around the holes.

Figure 4 shows the quantum efficiency obtained for pallarel and perpendicular polarizations at several burning wavelengths. We calculated the efficiency under the assumption that the absorption cross section of a homogeneous aggregate is constant over the J-band. The cross section used for the calculation was previously determined to be 2×10^{-14} cm^2 by absorption saturation measurement [12].

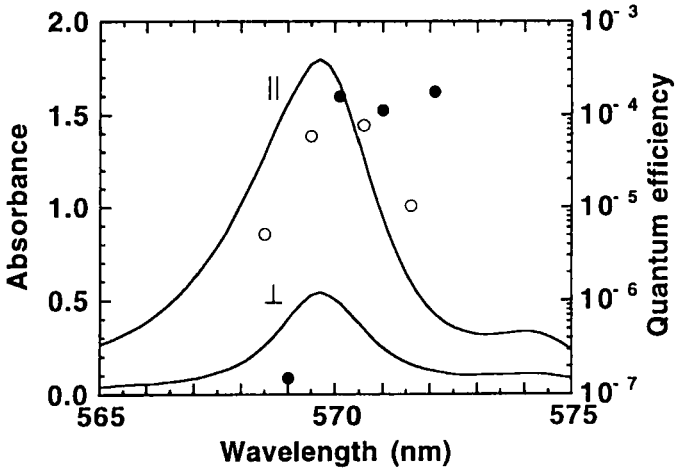

Fig. 4 : Wavelength dependence of the quantum efficiency of hole-burning for parallel (●) and perpendicular (○) polarization to the orientation axis. Solid curves represent the absorption spectra with parallel (||) and perpendicular (⊥) polarizations. The closed circle at 569 nm represents the detection limit of
the present measurement.

The spectral holes could be burnt more efficiently on the lower-energy side of the J-band for parallel polarization. In this wavelength region, the burning efficiency and hole width are almost independent of wavelength. On the contrary, no hole including satellites was observed on the higher-energy side for parallel polarization. Even when the excitation intensity was increased by two orders of magnitude, the hole could not be detected.The lowest efficiency of 10^{-7} is obtained on the assumption that the homogeneous width of the J-aggregates with higher transition energy is equal to that at lower energy side. If we take

the lifetime broadening into account, the efficiency of the higher energy side is calculated to be 1/30 as follows. Comparing the apparent efficiency of 10^{-7} with 10^{-4}, the hole depth ΔA is observed to be $\Delta A/1000$. Let us assume the lifetime of the excited state in the macroaggregates becomes n times as fast as that of the mesoaggregates. In this case, the hole width Γ becomes $n\Gamma$ due to the lifetime broadening. The quantum efficiency should be evaluated by the hole area. Since the efficiency is inversely proportional to the lifetime, the efficiency of the shoter - wavelength components is estimated to be $1/\sqrt{1000} \approx 1/30$ of that of longer-wavelength components.

Holes could be burnt in the shorter-wavelength region for perpendicular polarization. The width of the hole burnt at 568.4 nm with 1.9 mW/cm^2 for 6 min is measured to be 4.8 cm^{-1}, which is about three times as broad as that on the lower-energy side. The effective efficiency is also three times as low as that at the lower energy side as shown in Fig. 4. This is consisent with the above consideration on the effective efficiency. The quantum efficiency is still about one order of magnitude higher than that for parallel polarization on the higher-energy side.

4 .Hierarchical structure

In the final chapter, we propose a hierarchical structure in the oriented J-aggregates on the basis of the experimental results described in the preceding chapters. From the concentration dependence of the dichroic spectra, the J-aggregates are classified

into two species; isotropicly dispersed aggregates and rod-shaped oriented aggregates. The former and the latter are named as *mesoaggregates* and *macroaggregates*, respectively. The linear absorption spectrum at any degree of orientation can be expressed by a sum of these spectra. The size of the mesoaggregates has been determined to be about 100 by several spectroscopic measurements. The molecular arrangement in a mesoaggregate is still open to question, and a new technique to align the mesoaggregates is being developed by us.

The hierarchical structure proposed in Fig. 5 describes that a macroaggregates is composed of an incoherent ensemble of the mesoaggregates. This is deduced from the concentration dependence of the absorption spectra, and wavelength and polarization dependence of the hole-burning efficiency supports the idea. The efficiency at the higher energy side of the J-band, which is specific for the macroaggregates, is determined by the exciton lifetime due to the bi-excitonic annihilation[13]. When shorter pulse than a few hundeart fs was used two-exciton staes are observed before the bi-excitonic quenching takes place[14-16] This annihilation is an incoherent relaxation process, and the mesoaggregates should be packed close to each other for efficient energy transfer. This annihilation process has been observed in the femtosecond and picosecond nonlinear absorption measurements, and the lifetime of the excitons determined by the annihilation is in very good agreement with the homogeneous width and relaxation rate estimated from the hole-burning measurement[17]. Hence, the closely packed mesoaggregates are concluded to form a macroaggregate. Our model is recently

verified by a microscopic observation of J-aggregates using a near-field scanning optical microscope [18].

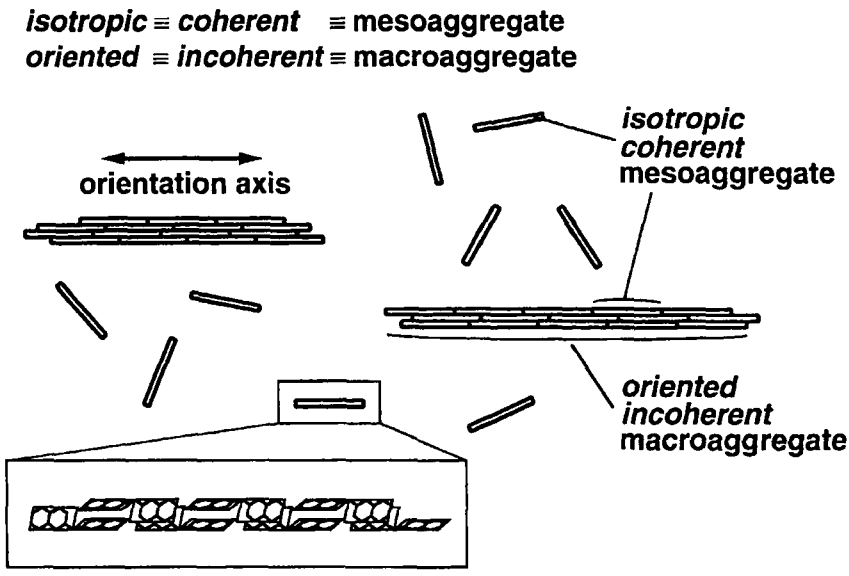

Fig. 5 : Schematic diagram of hierarchical structure of J-aggregates

Unexpectedly large static dipole moment was observed in the mesoaggregates by the electroabsorption measurement[19]. This is also a key to the microscopic structure of the mesoaggregates, where the counter-anions take an important role. On the contrary, the static dipole in the macroaggregates is not quite enhanced compared with the mesoaggregates. This implies that the mesoaggregates are alternatively stacked in a macroaggregate. The static dipole moment is not constructively superposed in a

macroaggregate, where the coupling of excitons is incoherent among different constituent mesoaggregates.

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