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EXCITONS IN TWO-DIMENSIONAL ORGANIC DYE AGGREGATE

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Abstract Excitons in monolayer dye aggregates have been studied using linear optical spectroscopy. Through the analysis of the spectra aided by a simple numerical simulation, we found that the system is characterized by rather large static disorder.

INTRODUCTION

It has been more than fifty years since the drastic change in the optical properties of organic dyes was first noted when they form aggregates, the so-called J-aggregates.[1,2] Through intensive efforts, it is now recognized that the outstanding optical properties of these aggregates are well described in terms of molecular (Frenkel) excitons, in which the correlated excited states of individual molecules are the eigenstates of the system.[3] Main interest in them lies in understanding the coherence effects that are expected to show up in the optical properties, e.g. enhanced nonlinearity and superradiance. Large volume of studies that has been accumulated in the past has been mainly on pseudo-isocyanines (PICs) in the form of precipitates in glass, typically in the water/ethylene glycol mixture. The reference would be too vast to quote, but most notably the relevant works are due to the group of Wiersma.[4]

It is worthwhile to point out, however, that in these works on PICs, the aggregates are considered to be one-dimensional (1D) even in the case in which the dyes are assembled in the Langmuir-Blodgett (LB) monolayers.[5] It is well known that there are two types of molecular arrangement in J-aggregate, the 'brickstone' type and the 'herringbone' type. From the study of the oriented aggregate, it is likely that J-aggregate of PICs is of the latter type.[6] In the herringbone arrangement, the transfer energy (see below) is negative in one direction but is positive in another making the effective interaction pertinent to the appearance of the J-band quasi one-dimensional. Whether a dye aggregate falls into a particular type or not is a subtle question. For example, in one case, a dye adsorbed to LB monolayers forms a clear herringbone arrangement shown by

electron diffraction[7], while there are other cases in which the brickstone arrangement was inferred from the optical measurements.[8]

On the other hand, it is natural to expect that the coherence of the excitons would be much stronger in two- or three-dimensions (2D or 3D). The conectivity in 1D can be seriously disturbed by a single disorder in the system but in 2D, for example, molecules can still interact bypassing the disorder. We therefore have investigated into the possibility of realizing an ideal 2D system suitable for the study of excitons and found that a cyanine dye (1,3,1',3'-Tetraethyl-5,6,5',6'-tetrachloro-2,2'-imidacarbocyanine) adsorbed on mica can be a candidate. The choice of this particular dye was motivated by the x-ray crystallographic study that shows a clear brickstone arrangement.[9] We have performed absorption and emission measurements on monomolecular form of the dye. Since the bulk body of the results will appear elsewhere[10] we will concentrate here on the discussions about the disorder that seems to be the dominant factor determining the spectra.

EXPERIMENTAL

The cyanine dye (the molecular structure shown in Fig. 1) was purchased from Japan Research Institute for Photosensitizing Dyes Co., Ltd. and was used as received. A piece of mica was immersed in a saturated solution of the dye in boiling water for a couple of minutes. During this period, the dyes are adsorbed onto the mica. No quantitative understanding of the adsorption process is available at present but AFM observation shows that the sample is made of polycrystalline patches mostly of monolayer or bilayer thickness.

The sample was placed in a continuous-flow cryostat where the cryogen cools the sample directly, an important feature since the thermal conductivity in mica is poor.

THEORETICAL BACKGROUND

The Frenkel exciton is described by the following hamiltonian,

$$H = \sum_n E_n |n\rangle\langle n| + \sum_n \sum_{n \neq m} V_{nm} |n\rangle\langle m|, \qquad (1)$$

where E_n is the excitation energy of the n-th molecule, $|n\rangle$ is the state in which only the n-th molecule is excited and all others in the ground state, and V_{nm} is the transfer energy of the excitation from m-th molecule to the n-th molecule. In a perfect crystal, both E_n (=E) and V_{nm} (=V) are constants. The solution for the one-exciton state is the linear combination,

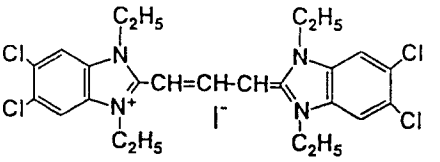

Fig. 1 Molecular structure of the cyanine dye.

$$|k\rangle = \frac{1}{\sqrt{N}} \exp(i\mathbf{k}\cdot\mathbf{r}_n)|n\rangle, \tag{2}$$

where N is the number of molecules, with the energy,

$$E_k = E + 2V\cos(k). \tag{3}$$

Since the optically allowed transition from the ground state is $|k=0\rangle$, the absorption spectrum consists of a sharp line at $\hbar\omega = E + 2V$. In J-aggregate, this is the bottom of the band, i.e. V is negative.

In a real crystal, however, there are various kinds of disorder to cause E_n and V_{nm} deviate from the ideal values: phonons and imperfections to name a few. The disorder has profound effects in the energy spectrum of strongly interacting molecules, which has been one of the most studied subject in solid state physics.[11] Main feature in the optical properties caused by the disorder is that the absorption spectrum is no longer a sharp line but is composed of Lorentzian on the high energy side and an exponential tail on the low energy side (the so-called Urbach tail). The Lorentzian is caused by the scattering of the $k=0$ state into other upper ($k \neq 0$) states by the disorder and the exponential tail is due to the distribution of low energy sites. The low energy sites also serve as the trap into which the excitons at higher energy fall. The emission spectrum is, therefore, most significantly governed by these states.

In order to illustrate this physical picture, we have performed a simple numerical study. In the hamiltonian (1), we took the disorder into account by assuming a gaussian random distribution of the site energy,

$$P(E_n) \propto \exp(-E_n^2/2D^2), \tag{4}$$

where D is the standard deviation of the degree of disorder and the origin of the energy is shifted so that the average site energy is taken to be zero. We furthermore assumed that the transfer energy is constant, V = -1, with which energy is scaled: the relevant parameter to describe the disorder is thus $|D/V|$. The resulting hamiltonian was numerically diagonalized. We tried 2D systems whose size ranged from 16x16 to 38x38 molecules. It turns out that the largest system is needed to avoid the effect of the boundary condition. However, for qualitative discussions below, results with the system of 16x16 molecules are also used.

RESULTS AND DISCUSSIONS

Absorption and emission spectra are shown in Fig. 2. The absorption peak of the aggregate is shifted from the monomer absorption maximum by 2200 cm^{-1}, an indication of strong intermolecular interaction V. However, the peak width is rather broad and the Stokes shift is clearly seen in the emission. These features are in marked contrast to the case of PICs[4].

It is of interest to consider the difference between our system and the PICs in glass matrix. The latter is formed by the precipitation from solution and the precipitates should be essentially crystallites. Therefore they must be bulk-like and basically stress-free. (This point seems to be further augmented by the recent analysis.[12]) However, in our sample, molecules are attached to a solid surface (mica) and exposed to another environment on the other side. That a slight change in the environment affects the state of aggregation quite a bit is evidenced in Fig. 3. When the sample was exposed to He gas, the absorption spectrum suffered strong broadening. The role of the gas molecule, which must be very inert in naive sense, is not cleat at the moment.

Results of a simple simulation to gain insight into the phenomena are also shown in Fig. 3. The spectra for the sample in vacuum is well fitted by a calculation with $|D/V|$ = 1 whereas for that in He gas a good fit was obtained with $|D/V|$=1.2. The two calculations were done with all other parameters held the same. One might expect that the gas molecules enter into the interstitial site of the crystal effectively severing the transfer V. However, a simulation with this model, in which the transfer energy was weakened at random yielded rather poor agreement with the experiment. This scenario is thus unlikely. Although, it is not clear how the gas molecules can shift the site energy so much by simply 'attaching' to the dye molecules, this incidence shows the sensitivity of the optical spectra

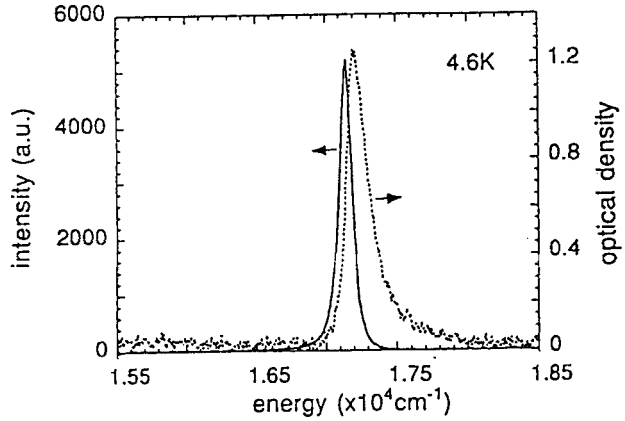

Fig. 2. Absorption (dotted curve) and emission (solid curve) spectra of 2D aggregate at 4.6 K.

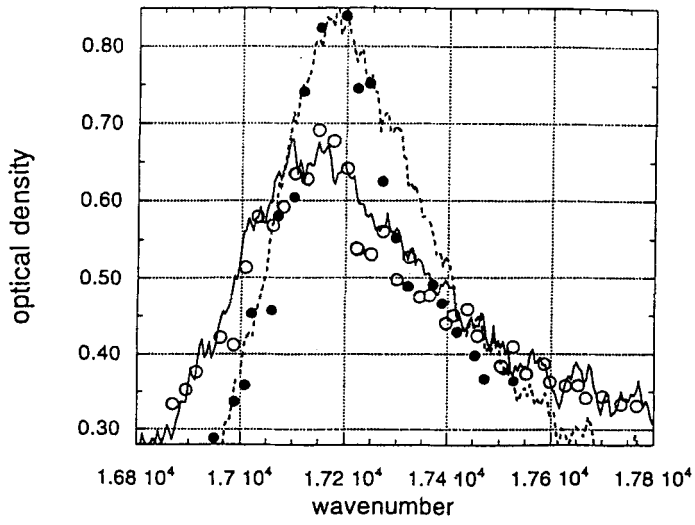

Fig. 3. The effect of He gas to the absorption spectrum (at room temperature). In vacuum (dotted curve) and after He gas was introduced (solid curve). The circles are fit using a simple simulation.

to the environment.

At the lowest temperature (4.6K), the absorption spectrum was well fitted with a simulation using $|D/V|$=0.9, a still large disorder. At this temperature, the effect of static disorder is found to be much larger than the effect of phonons. The large disorder implies that the low-lying states are localized. This is well illustrated in Fig. 4, which shows the probability distribution (i.e. the square of absolute value of the eigenfunction) of the lowest 9 states in a simulation for a 38x38 system. Contrary to these low-lying states, the higher states are more delocalized which can be judged from the 'degree of delocalization'.[13] : at the absorption peak it is more than 100.

It is expected that after the photon energy is deposited into the higher exciton states, they relax to lower states. In fact, the Stokes shift of the emission spectrum can be quantitatively explained if we assume that the excitons all fall down to the several lowest states from which they emit photons. Within this model, the molecules belonging to these states stay in the excited state for the longest period; thus the best chance to undergo photo-degradation if it is possible. This is indeed the case as shown in Fig. 5, where the sample was left under room light for a period and the successive change of the absorption spectrum was recorded. The photo-degradation is probably oxidation of the excited molecule. In the absence of either light or oxygen, the process is severely suppressed.

If the aggregate is extremely small so that the extent of localization due to the site energy disorder still exceeds the size of the sample, then the exciton migration to the

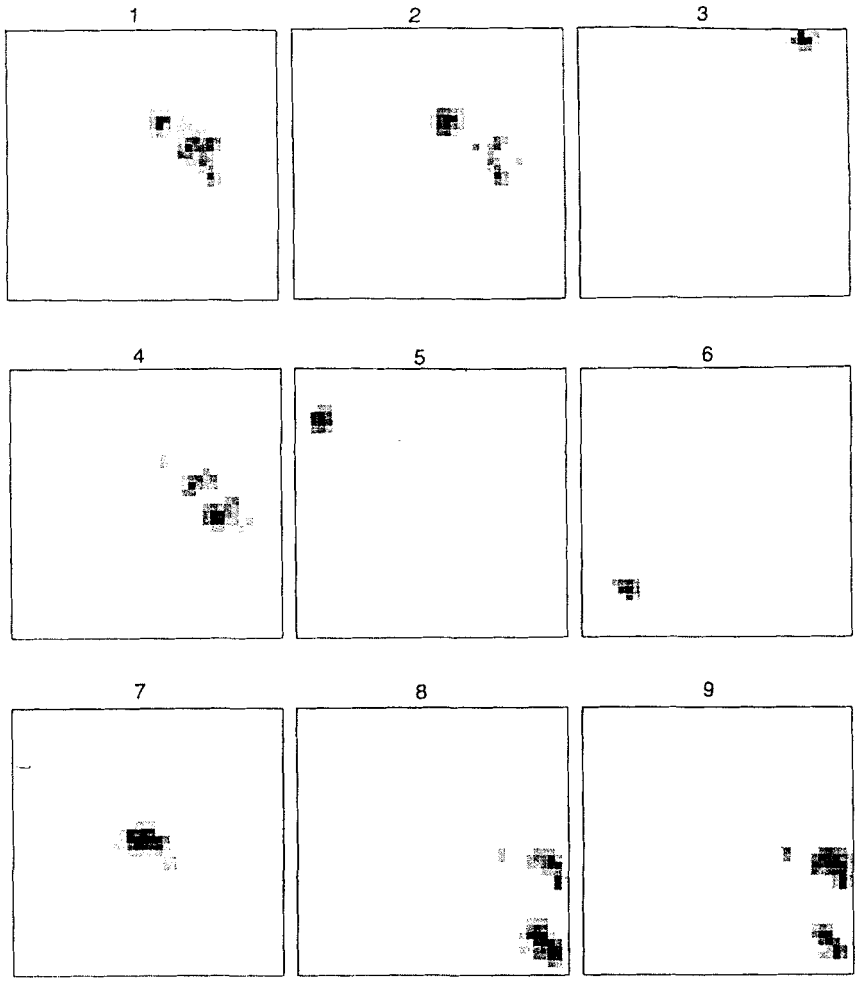

Fig. 4. The shape of the wave function of the lowest 9 states in a numerical simulation of a 38x38 lattice. The square of absolute amplitude is plotted. The strength of the gaussian disorder is $|D/V| = 0.9$. Note the similarity in states 1, 2, and 4, and 8 and 9. These are localized around deep site-energy minima. Since all states are orthogonal to each other, the states 1 and 2, for example, resemble even and odd states in a 'square well' potential, respectively. Therefore, the oscillator strengths of these state differ markedly.

lower-lying states described above does not occur. One then expects that the Stokes shift is much smaller and the photo-degradation occurs uniformly. That this is indeed the case is shown in Fig. 6, clearly substantiating our picture. The peak width is still rather wide. The inhomogeneity, however, shold be resolvable by the site-selective spectroscopy at

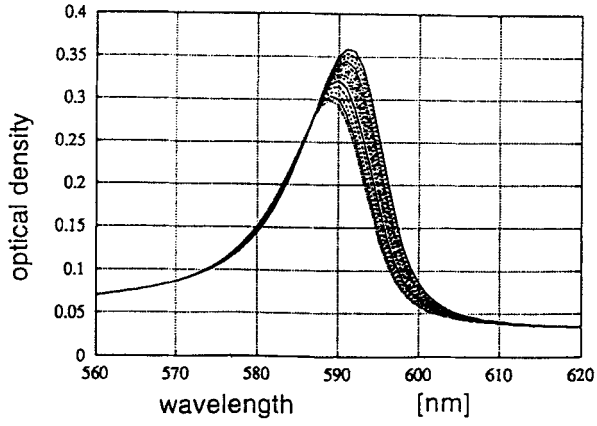

Fig. 5. The absorption spectral change due to photo-degradation of 2D aggregate. The sample was left under room light and the spectra were taken every 1.5 min. The bleaching occurs from the low energy edge of the spectra.

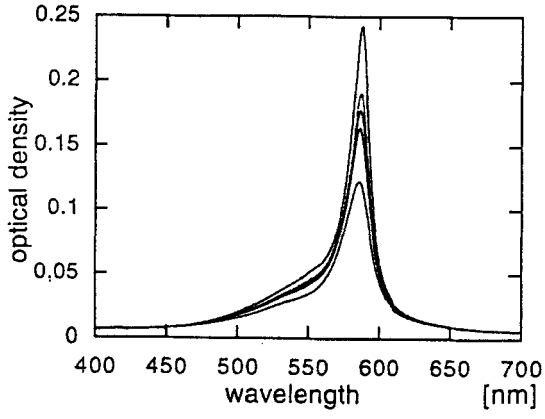

Fig. 6. The absorption spectral change due to photo-degradation of very small aggregates ('0D' aggregates). Note that the photo-bleaching occurs uniformly, in strong contrast with Fig. 5.

low temperature. Also, the nonlinear properties of these system are naturally of interest. Experiments along this line are underway.

CONCLUSION

We have demonstrated through the linear optical spectroscopy, that the dye aggregate studied here shows 2D nature which can be semi-quantitatively understood in terms of the exciton migration toward lower-lying states. The large site-energy disorder seems to be characteristic of a 2D system. By reducing the size of the system, the effect of

disorder is reduced. Comparison of both linear and nonlinear optical properties of 2D and 0D systems will elucidate the structure of the excited states in molecular aggregates.

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