# Origin of the Long Wavelength Fluorescence Band in Some Preparations of J-Aggregates: Low-Temperature Fluorescence and Hole Burning Study

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A broad fluorescence band red-shifted from the absorption line of J-aggregate of pseudoisocyanine chloride in thin films of poly(vinyl sulfate) has been investigated. The fluorescence originates from traps populated by energy transfer from the excitonic band of the J-aggregate. The shift of the fluorescence maxima and the decrease of its intensity with increasing temperature have been explained by interaction of the trap with a 39 $cm^{-1}$ phonon mode. Spectral hole burning study shows that the traps are functionally associated with the whole J-aggregate fiber rather than with individual coherently coupled segments of the aggregate.

## 1. Introduction

Molecular aggregates play an important role in many biological processes, e.g., photosynthesis. Artificial aggregates, on the other hand, have a great potential in technological applications. In particular, the J-aggregates of pseudoisocyanine (PIC) dyes[1,2] have attracted attention because of their application as sensitizers in silver halide photographic films.[3] Another promising field of applications arises from the large third-order optical nonlinearity theoretically predicted[4] and recently discovered in PIC J-aggregates.[5]

The characteristic spectral feature of J-aggregate is the appearance of a strong narrow absorption line (the so-called J-band) red-shifted from the monomer band. It has been shown that the J-band originates from Frenkel-type excitonic transitions on a linear chain.[6] The narrow width of the J-band is the result of motional narrowing that averages structural disorder within the chain.[7,8]

Fluorescence spectra of the self-assembled PIC J-aggregates in low-temperature ethylene glycol/water glasses consist basically of narrow intense lines which are counterparts of the absorption J-bands.[9,10] On the other hand, it has been found that in PIC J-aggregates formed on AgBr microcrystals the fluorescence J-band is accompanied by a broad band shifted to the red from the J-band.[11] The broad band was most intense at 90 K but was still discernible at 270 K. Red-shifted intense fluorescence has been observed also for PIC J-aggregates in Langmuir−Blodgett monolayers at 77 K,[12] as well as for J-aggregates grown in poly(vinyl sulfate) (PVS) thin films[13] and aqueous PVS solution[14] at room temperature. While the existence of the long wavelength fluorescence band has been confirmed for various sample preparations, there is still little understanding of the origin of the band.

In this paper we examine the phenomenon in greater detail. As samples we use J-aggregates of PIC chloride prepared by spin-coating in thin films of PVS. We study fluorescence spectra in the temperature range between 4.6 K and room temperature. Further information is obtained from the comparison of spectral hole burning in the low-temperature absorption and excitation spectra of the J-band.

## 2. Materials and Methods

In the preparation of the samples we basically followed the method of refs 13 and 15. A 30 mg sample of potassium poly(vinyl sulfate) (PVS, purchased from Wako Pure Chemical Ind.) was dissolved in 4 mL of bidistilled water at 80−90 °C. Separately, a 10 mM solution of PIC−Cl (Nippon Kankoh Shikiso Kenkyusho) in methanol was prepared. A 0.4 mL aliquot of the PIC−Cl solution was added to the polymer solution, the resulting solution was mixed, and after a short waiting time (seconds to minutes) a drop of the mixture was transferred on a cover glass (thickness 0.12−0.17 mm) and spin-coated for 20 s at 3000 rpm. The cover glass is placed eccentrically with respect to the rotation axis of the spin coater, which ensures that the J-aggregates are uniformally oriented throughout the whole sample. Room-temperature absorption spectra of the samples have a typical optical density of about 0.05 at the maximum of the J-band. The samples were checked with an optical fluorescence microscope (Olympus IX70, oil immersion 100× objective lens MPlan 100). The microscope well resolves threadlike structures, or fibers, that are tens of microns long and have a submicron diameter. In contrast to ref 13, most of the fibers are stretched and oriented in one direction (perpendicular to the tangent of the spin-coating rotation).

Fluorescence and excitation spectra were measured on a conventional fluorescence spectrometer (Hitachi 850, maximum spectral resolution 1 Å). Absorption and absorption hole burning spectra were taken by scanning a double-pass 1.5 m monochromator (Jobin-Yvon THR1500, resolution 0.03 $cm^{-1}$). In both cases the samples are cooled in a He gas flow cryostat (Oxford CF1204). The holes were burned with a single-mode dye laser (Coherent 699-29 Autoscan, Rhodamine 6G, jitter $<2-3$ MHz).

## 3. Results and Discussion

Basic spectral characteristics of two different sample preparations are presented in Figure 1. The difference between the two sample preparations is in the waiting time between mixing

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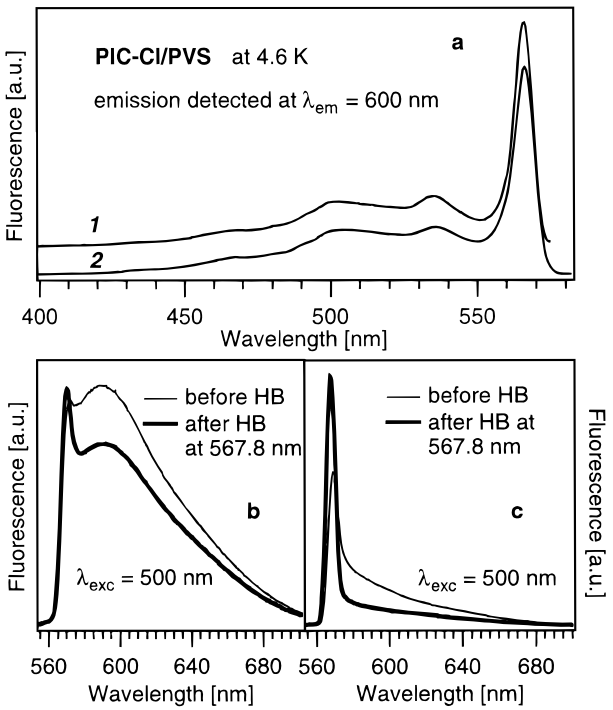


**Figure 1.** (a) Excitation spectra of two different sample preparations detected near the maximum of the broad fluorescence band at 600 nm. (b) Fluorescence spectrum of the sample 1 of (a) excited at 500 nm. The thin line is before and the thick line after laser irradiation (hole burning) of the sample at the maximum of the J-band. (c) Fluorescence spectrum of sample 2 of (a) excited at 500 nm. The meaning of the thin and thick lines is same as in (a).

the PIC dye solution with the polymer solution and spin-coating the mixture on a cover glass. The waiting time for the sample in Figure 1b was minimum, and that for Figure 1c was several minutes. We can readily see the effect on the fluorescence spectra: the intensity of the red-shifted broad band rapidly decreases with the waiting time. On the other hand, excitation spectra of both samples detected at 600 nm (Figure 1a) are almost identical and resemble other presented spectra of PIC/PVS J-aggregates.[13,14] They consist of the J-band with a maximum at 567.4 nm and width of 6.0 nm and of vibronic and higher aggregate bands. Thus, the spectral features of the J-aggregates themselves are independent of the amount of the red-shifted fluorescence. Further in Figure 1b,c are fluorescence spectra measured after an extensive laser irradiation of the J-band (with tens of mW/cm$^2$ for several minutes). We can see that while the intensity of the red-shifted fluorescence drops the intensity of the J-band actually increases! This is a direct evidence that the species emitting to the red from the J-band are of different origin from the J-aggregate. As suggested before,[11,12] the species are probably trapping states populated very efficiently by excited energy transfer from the J-band—as the amount of traps decreases, the excitations are more likely to be emitted from the J-band itself, the intensity of which increases. The trapping species are photochemically highly unstable even when excited nonresonantly by the energy transfer.

We attempted to identify the photoproduct states of the trapping species by measuring excitation spectra (detected at 600 nm) of the sample of Figure 1c before and after the irradiation at 567.8 nm. The resulting difference spectrum (normalized at 560 nm) is shown in Figure 2 as the bottom trace. For comparison, the top trace shows the corresponding part of the excitation spectrum before irradiation. The shape

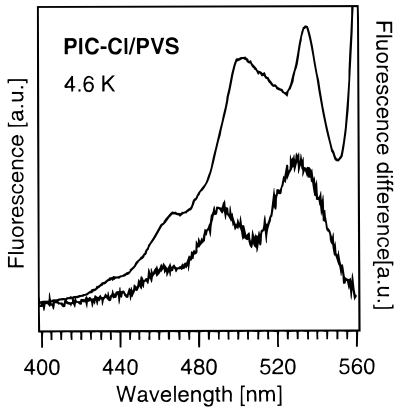


**Figure 2.** Bottom: difference excitation spectrum of sample 2 of Figure 1a obtained by subtracting the spectrum before irradiation from the one after irradiation at 567.8 nm. The spectra were normalized at 560 nm. Top: corresponding part of the excitation spectrum of the J-aggregate before irradiation.

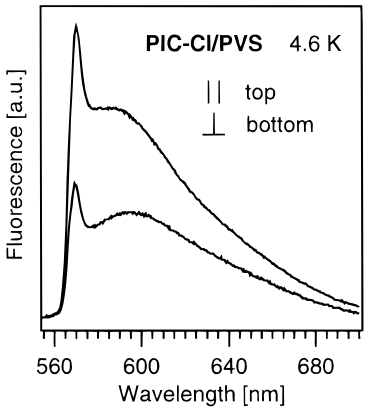


**Figure 3.** Polarization fluorescence spectra excited at 500 nm. The symbols correspond to parallel (top) and perpendicular (bottom) orientation of the analyzer.

and maxima positions of the difference spectrum correspond to those of a dilute solution of PIC monomer quenched to 4.7 K.[16]

Figure 3 shows the polarization dependence of the fluorescence spectra excited at 500 nm where negligible dependence of fluorescence intensity on the polarization of the exciting light is expected.[15] In Figure 3 the analyzer in front of the detector is oriented parallel with the direction of the J-aggregates in the top spectrum and perpendicular in the bottom spectrum. It is evident from the high degree of polarization that the fibers of J-aggregates are well oriented. Fluorescence both from the J-band and from the traps is polarized in the direction of the fibers. However, the ratio of the parallel-to-perpendicular intensity is somewhat higher for the J-band: 2.2 at 567.5 nm compared to 1.8 at 600 nm.

The intensity of the emission from the traps is strongly temperature dependent. In Figure 4, we studied the temperature dependence of the fluorescence spectra (excited at 500 nm and normalized at the J-band maxima) between 4.6 and 300 K. With increasing temperature we observe a shift (denoted as $\Delta$) of the broad fluorescence from 591 nm at 4.6 K to about 620 nm at room temperature and a relative decrease of the intensity of the band. The J-band shows a similar red shift with temperature except for the region between 4.6 and 51.5 K where blue shift is observed. The anomalous blue shift is caused by the overlap with the broad band at low temperature. Figure 4b shows the shift $\Delta$ as a function of inverse temperature $1/T$. The data were obtained from several experiments on different samples. The

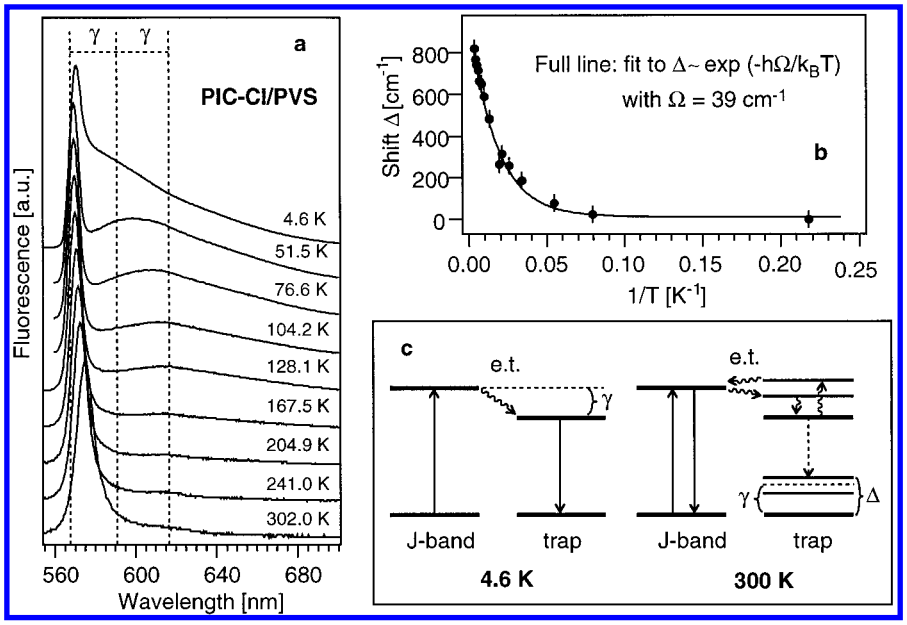


**Figure 4.** (a) Temperature dependence of the fluorescence spectra excited at 500 nm. The vertical dotted lines are markers (from the left) at the position of the J-band absorption maximum at 4.6 K and at the broad-band fluorescence maximum at 4.6 K. (b) Relative shift Δ of the fluorescence maximum with respect to the 4.6 K value, plotted as a function of inverse temperature 1/*T*. (c) Schematic explanation of the temperature behavior of the fluorescence.

experimental points are well fit with a single exponential $\Delta \sim \exp(-h\Omega/k_BT)$, where the fitting parameter $\Omega = 39$ cm$^{-1}$. This indicates that the shift is caused by a single thermally activated phonon mode. This could be either a local or pseudolocal mode associated with the trap or a low-frequency mode commonly found in polymers. The interaction of the trap with the phonon mode can also explain the radiationless deactivation at room temperature (Figure 4c). At 4.6 K there is a large gap $\gamma$ (704 cm$^{-1}$) between the lowest level of the excitonic J-band and the excited state of the trap. At this temperature the excitations are transferred from the J-band to the trap where the energy is emitted as fluorescence. As the temperature increases, vibronic levels of both ground and excited states of the trap are being increasingly populated. The population of the ground-state vibronic levels is manifested by the red shift of the trap fluorescence. We may reasonably expect that analogue vibronic levels of the excited state will be populated as well. When the population of these vibronic levels compensates the gap $\gamma$ (in other words when $\Delta$ approaches $\gamma$), the backward excited energy transfer from the trap vibronic levels to the J-band becomes increasingly likely. $\Delta = \gamma$ at approximately 150 K, and we can see from Figure 4a that the intensity of the trap fluorescence at and above 167.5 K almost does not change. This kinetic scheme also implies that the excited-state lifetime of the trap must be relatively long compared to the energy-transfer rates and the J-aggregate exciton lifetime.

Further information on the nature of the traps can be obtained from spectral hole burning in the J-band. In Figure 5 we compare the effect of laser irradiation near the maximum of the J-band in absorption (Figure 5a, measured by monochromator) and excitation (Figure 5b, detected at 600 nm) spectra. The burning conditions (laser power and burning time) are identical in both cases. In absorption the difference spectrum shows a narrow resonant hole at the position of the burning laser and a sign of antihole to the blue of the resonant hole. The excitation difference spectrum shows homogeneous decrease of the whole spectral band. The observation of the resonant hole means that the homogeneous line width of the J-aggregate excitonic transition is narrow. The narrowest hole that we were able to detect had a width of 4.1 cm$^{-1}$, which is

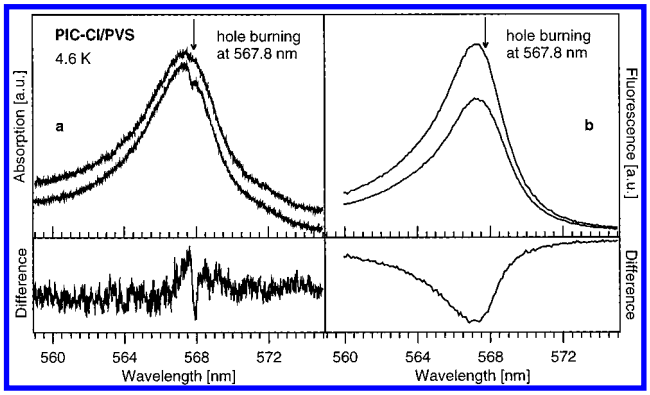


**Figure 5.** (a) Top: absorption spectra of the J-band before and after hole burning near the band maximum. For clarity, the spectra are offset. Bottom: difference of the above two spectra exhibiting a resonant hole at the position of the laser and an antihole shifted to the blue. (b) Top: excitation spectra of the J-band before and after hole burning near the band maximum detected at 600 nm. Bottom: difference of the above two spectra. Hole burning causes a homogeneous decrease of the whole excitation J-band.

about 1 order of magnitude larger than in J-aggregates of PIC in ethylene glycol/water glasses[17−19] and about 3 times larger than in PIC/poly(vinyl alcohol) films.[20] While the larger hole width may partly reflect different exciton dynamics in PVS, it can be also an experimental artifact caused by the low value of the peak optical density in the J-band.

The difference between the hole burning results in absorption and excitation spectra reflects the different hole burning mechanisms. In absorption spectra we probe directly the homogeneous excitonic transitions of the coherently coupled segments of the J-aggregate fibers. Those segments that absorb at the burning light wavelength themselves undergo a photoinduced change that shifts the position of the excitonic line to the blue. On the other hand, in excitation we monitor the spectra by observing the fluorescence from the traps. During the hole burning process the energy is absorbed again by a coherent segment of the aggregate, and then it is very efficiently transferred to a trap that subsequently undergoes a photochemical change. The fact that the spectral selectivity is lost (that is,

that we observe a homogeneous decrease of the whole band instead of a narrow hole) means that the trap which has been burned out by exciting the coherent segment at the burning wavelength is common to all other segments that make up for the inhomogeneously broadened J-band. Thus, the traps are not associated with individual segments of the J-aggregate fiber but are located in positions where they can be efficiently populated by energy transfer from any J-aggregate part. The fact that we did not observe any resonant hole in the excitation hole burning also indicates that the efficiency of energy transfer between the coherent segments and to the trap and the efficiency of the photodissociation of the trap are orders of magnitude higher than the hole burning efficiency of the coherent segment itself.

As suggested earlier,[11,12] the trapping species may be a PIC dimer that has a formally allowed blue-shifted transition and a formally forbidden red-shifted transition with respect to the PIC monomer. The red-shifted transition would be the trapping state. The possible origins of the PIC dimers include the following:

*1. Remains from the Aggregation Procedure.* PIC J-aggregates are formed in the solution by electrostatic interaction between the dye and the negative $SO^{3-}$ groups on the polymer chain. Dimerization is most likely the first step of the aggregation. Depending on the sample preparation procedure, different amounts of the unbound dimers can be homogeneously distributed in the PVS film. The dimers that are located close to the J-aggregate fibers with their transition dipoles parallel to the J-band would serve as traps.

*2. Off-Diagonal Energy Disorder.* It has been shown by a numerical study[21] that a distribution in the intermolecular distances on the aggregate chain can lead to the formation of strongly interacting dimers within the chain. These dimers would be easily accessible from any part of the J-aggregate fiber and would act as traps.

Without excluding any of the above possibilities, we favor the former one as it, in our view, more readily explains the dependence of the amount of traps on the sample preparation procedure, the polarization properties, and the dissociation of the traps.

## 4. Conclusions

Our results are consistent with the hypothesis that the trapping species are PIC dimers. We have shown that the traps are located close to the J-aggregate fibers and their transition dipoles are oriented along with the aggregate transitions. The trapping states are populated by energy transfer from the lowest level of the aggregate excitonic band. Thermal excitation of the trap phonon states at room temperature probably enables backward energy transfer to the J-aggregate and quenches the luminescence. The traps are highly photochemically unstable even under nonresonant excitation with the product states exhibiting PIC monomer-like absorption spectra.

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