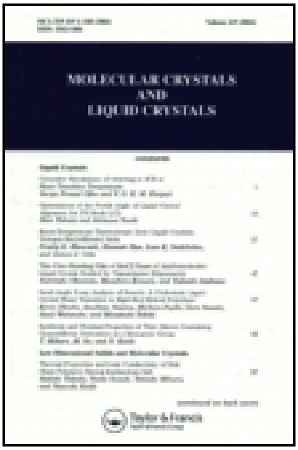

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LARGE OPTICAL NONLINEARITY IN PSEUDOISOCYANINE J-AGGREGATES

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Abstract The resonant optical nonlinearity in pseudoisocyanine J-aggregate is investigated. Large degenerate four wave mixing signals and negative absorption changes at the wavelengths corresponding to J-aggregate absorption band are observed. It is concluded that the origin of the large optical nonlinearity is mainly due to the absorption saturation of J-band. The mechanism of the absorption saturation is discussed on the bases of exciton delocalization effect.

INTRODUCTION

Low dimensional materials possessing an exciton absorption such as CdS quantum dots and GaAs quantum wells have attracted interest, both for the physical insight which gave and for their potential applications in nonlinear optics. One of the cyanine dye, 1,1'-Diethyl-1,1'-cyanine [pseudoisocyanine (PIC)] halide forms a molecular aggregate[1] (J-aggregate) which is believed to be one-dimensional in nature.[2] The J-aggregate shows intense and narrow absorption bands and also strong emission bands with little Stokes shift. These characters are explained by the strong intermolecular coupling which delocalizes the molecular excitation and the exchange narrowing effect which averages out the local inhomogeneities.[3] Because of these properties PIC J-aggregates are expected to have a large optical nonlinearities in the resonant region. In this paper we report the detailed studies of the third-order nonlinear optical properties of the PIC J-aggregates, using degenerate-four-wave-mixing (DFWM) and pump-probe absorption spectroscopy.

RESULTS and DISCUSSION

Two types of aggregates are known as PIC J-aggregates which show different absorption peaks. Two different materials were used in this studies to get each J-aggregates. One is PIC bromide (PICBr) for J_S-aggregate which shows a shorter wavelength absorption peak and the other is PIC iodide (PICI) for J_L-aggregate. Samples were made by dissolving PIC to a concentration of (2-4)mM in a mixture of deionized water and ethylene glycol (50/50 vol%). Solutions were kept between flat sapphire plates using a (12-24) μm Mylar film as a spacer. These samples were cooled down to 230K just above the glass transition temperature of the solvent mixture and hold for an hour yielding J-aggregates, then rapidly cooled down to 77K in a few minutes. All measurements were done at 77K. In these experiments a YAG-pumped dye laser (6ns pulse) was used. A boxCARS type configuration was used for DFWM and pump-probe absorption spectroscopy.

A large DFWM signal was observed when the laser frequency was in the resonance with the sharp J-band. Figure 1 shows the dependence of the DFWM diffraction signal intensity of PICBr J_S-band on the pump beam power. At the lower pump power the slope is 2 (on a log-log plot) which is expected for a $\chi^{(3)}$ process and deviates

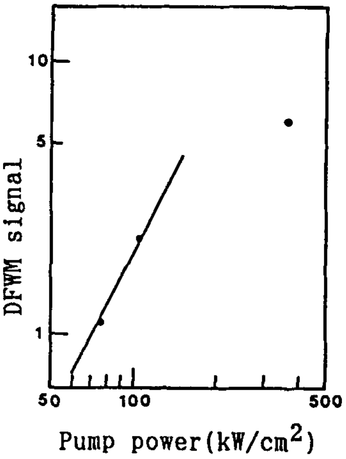


Fig.1. Pump power dependence of the DFWM signal at 571.2nm.

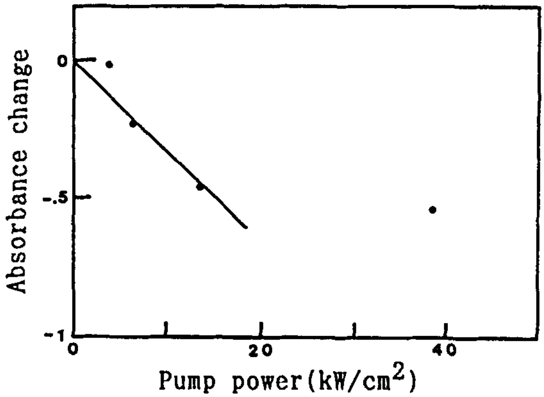
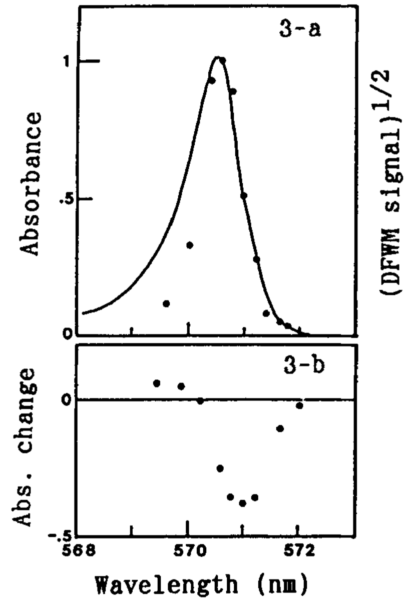


Fig.2. Pump power dependence of the bleached absorbance at 571.2nm.

from it with increase in power. Figure 3-a shows the absorption spectrum of PICBr J_S-band and the spectral dependence of the DFWM signal which overlaps approximately with the J-band at the longer wavelength side of the peak but decreases at the shorter wavelength side.

Pump-probe absorption spectroscopy shows that the J-band can be bleached by very low intensity of pump beam. The bleached absorbance of PICBr J_S-band is plotted in Fig.2 as a function of pump beam power. Figure 2 shows that the magnitude of the bleached absorbance increases initially with the pump power and then levels off. The maximum breaching at saturation is 59%. Figure 3-b shows the spectral dependence of the breached absorbance (taken as a pump power of 10kW/cm^2). The bleaching spectrum agrees well with the J-band absorption spectrum, except that the peak of the former is red-shifted compared with the latter. At the short wavelength side of the J-band, one can observe positive induced absorption. This is responsible for the red shift in the bleached absorption peak and the decrease in the DFWM signal intensity at the shorter wavelength



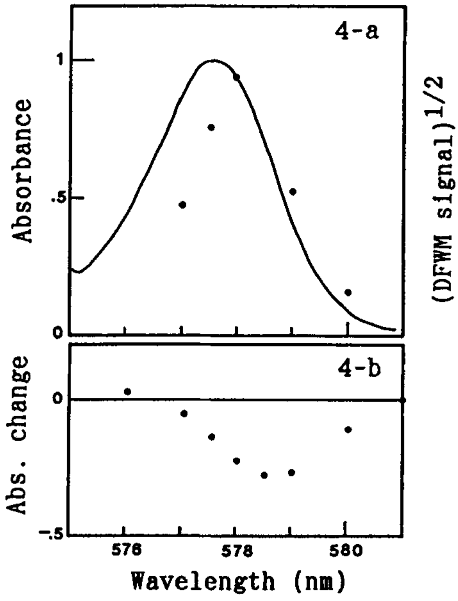


Fig.3. Absorption spectrum (a:solid line), DFWM signal (a:full circle) and bleached absorbance (b) of PICBr J_S-band at 77K.

Fig.4. Absorption spectrum (a:solid line), DFWM signal (a:full circle) and bleached absorbance (b) of PICI J_L-band at 77K.

side of the peak.

Figure 4 shows the spectral dependence of linear and nonlinear absorption and DFWM of PICI J_L-band. The spectral width at half maximum ($\Delta\nu_h$) of the absorption spectrum of J_L-band is $70cm^{-1}$ which is twice as broader than that of PICBr J_S-band ($\Delta\nu_h$ is $30cm^{-1}$). The feature of the DFWM and the bleached absorbance are similar to these of PICBr J_S-band. The positive induced absorption is also observed at the short wavelength side of the J_L-band.

The similarity of the spectral dependence of the DFWM and that of bleached absorbance suggests that the origin of the resonant optical nonlinearity is the saturation of absorption which can be described by the two-level system. The lifetime of the excited state of PIC J-aggregate is less than 400ps and is shorter than the excitation laser pulse, then the steady state condition can be applied in our case to solve the rate equation of the dynamics of the two-level system caused by light absorption. The power, Ip, dependence of the absorption coefficient is $\alpha=\alpha_0/(1+I_p/I_S)$, where α_0 is the linear absorption coefficient, $I_S=(\alpha_0/\alpha_2)$ is saturation intensity and α_2 represents the first order nonlinear absorption coefficient. In the resonant case α_2/α_0 is a relevant parameter to compare the optical nonlinearity of materials.

Table 1 lists the α_2/α_0 and the $\Delta\nu_h$ of PIC monomer and J-aggregates in various conditions. The nonlinearity of PIC is suddenly changed with aggregate formation. When the temperature is lowered to 77K the nonlinearity is increased by two order of magni-

Table 1

	temp (K)	α_2/α_0 (cm^2/W)	$\Delta\nu_h$ (cm^{-1})
PICBr monomer	298	$3x10^{-9}$	1,000
PICCl J-aggregate[4]	r.t.	$2.6x10^{-7}$	180
PICI J-aggregate	77	$4.6x10^{-6}$	70
PICBr J-aggregate	77	$3.4x10^{-5}$	30

tude and the $\Delta\nu_h$ is decreased. At 77K PICBr J_S-band has larger optical nonlinearity than PICI J_L-band which shows wider absorption spectrum.

The absorption saturation of the exciton band can be described by the phase-space-filling model,[5] which is a blocking mechanism based on the exclusion principle; i.e. transition into occupied final sates are forbidden. It was reported that the minimum number of molecules required to yield the J-band is 7 monomer units.[2] If the 7 monomer units is the exciton size in PIC J-aggregates, we could not explain the large enhancement of the nonlinearity with decreasing temperature by the phase-space-filling model. PIC J-aggregate is believed to be one dimensional. The intermolecular coupling of the molecular excitation delocalize the excitons which average over the various local inhomogeneities and the exchange narrowing effect reduces the inhomogeneous linewidth. This exciton delocalization effect can be attributed to the extremely large absorption saturation of PIC J-aggregates. The close correlation between the bleached absorbance and the $\Delta\nu_h$ supports this model.

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