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Dephasing processes of coherent exciton migration in mixed aggregates with barriers of PIC-I and azaPIC-I

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Abstract

Coherence decay processes of Frenkel excitons in the mixed aggregates with barriers at low temperature were investigated using an accumulated photon echo technique. The lengthening of the dephasing times T_2 with increase of the molar fraction of azaPIC-I was observed, which is contrary to the shortening of T_2 in the mixed aggregate with traps. Exciton coherence lengths were studied theoretically and experimentally. It is demonstrated that the effective distance, passed through by excitons, is less than the exciton coherence length.

1. Introduction

Molecular aggregates, one of the attractive nanostructure materials, have sizes intermediate between isolated molecules and crystals, making them potential candidates for many technological applications. The radiative and dephasing dynamics of J-aggregates have been at the center of research in the last decade [1]. However, most investigations were made on aggregates consisting of only one kind of molecule. We doped azaPIC-I into PIC-I dye with different mixing ratios and obtained various physical sizes of J-aggregates between two barriers. Time evolution of the exciton excitation can be considered as a dynamical process consisting of two stages. The first short stage, during which the phase relation in the wave packet of excitons relaxes, lasts a dephasing time T_2. The second longer stage is a radiative and non-radiative process lasting a fluorescence time T_1. In this paper we focus our attention on the first stage. The lengthening of the dephasing time T_2 in the mixed aggregates with barriers is reported. From both theoretical and experimental aspects, the exciton coherence lengths were investigated. The effective jump distance due to coherent transfer is less than the exciton coherence length. A clear picture describing the first stage is given.

2. Experiment

The six samples were made by dissolving PIC-I (concentration 2×10^{-3}) and azaPIC-I (1×10^{-3}) in a mixture of triply distilled water and ethylene glycol (1 : 1 volume mixture). Their molecular structure are given in the inset of Fig. 1. Table 1 presents some parameters and data of these six different molar fractions. The difference in excitation energy, $\Delta = 4500\ \mathrm{cm}^{-1}$, between molecules of PIC-I and azaPIC-I leads to a barrier that strongly inhibits transfer of excitons (Fig. 2).

The setup for the accumulated photon echo (APE) experiment was similar to Ref. [1]. The excitation

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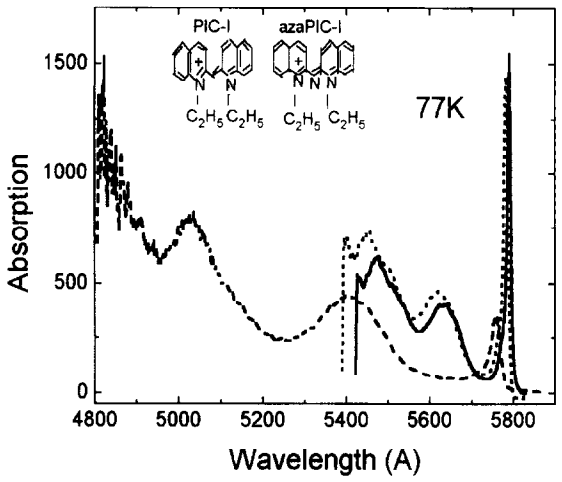

Fig. 1. Absorption spectra of the mixed aggregates of PIC-I and azaPIC-I at 77 K: – – – sample 1, ··· sample 4 and – – – – sample 5, respectively. (Wavelengths are in Å).

light source was a mode-locked Rh6G dye laser pumped synchronously by an Ar^+ laser. Both the pump (1) and probe (2) beams were modulated. In order to get a high signal-to-noise ratio, a heterodyne-detected technique was used. Autocorrelation functions were measured by a general nonlinear second harmonic generation (SHG) system. The APE signal and the autocorrelation traces could be scanned simultaneously.

3. Results and discussion

The absorption peaks of J-aggregates, located at 5790, 5780 and 5760 Å, respectively for samples 1, 4 and 5 at 77 K, are shown in Fig. 1. The blue shift and broadening of the absorption peaks of these J-bands increase with increase of the molar fractions of azaPIC-I in the mixture.

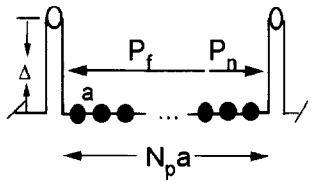

Fig. 2. Schematic of the potential energy of the mixed aggregate of PIC-I and azaPIC-I with potential barriers. P_f (P_n) is the probability of passing through the far (near) barrier for excitons: ● PIC-I molecule; ○ azaPIC-I molecule.

Since the work of Hesselink and Wiersma [2], APE experiments have proved to be a relatively simple and reliable technique for the study of dephasing processes [3]. In an APE experiment, beam 1 creates a coherence of the optical transition, which is partially converted into a frequency grating in the ground-state population by the second, delayed pulse. The next pulse of the dye laser arrives at a time τ (the interval between the pulse pairs) about 10.6 ns later. In our experiment, the population grating of the excited state decays to a triplet state, which acts as a bottleneck. From the accumulated grating remaining in the ground state, echoes are generated by beam 1 of the next cycle of the laser, as indicated in Fig. 3. Any echo generated by the first pulse of a pulse pair has only a small chance to interfere with the second pulse, so the echo amplitude instead of the echo intensity is now

Table 1
Parameters and data for the mixed aggregates of PIC-I and azaPIC-I in ethylene glycol/water glass

	PIC-I/aza-PIC ratio by volume	Physical size of J-agg. between two barriers N_p	Coherence length calculated by		APE decay constant	
			Eq. (2) N_c	Eq. (3) N_c	Fast component τ_1 (weight) (ps)	Slow component τ_2 (weight) (ps)
1	1.00/0.00	∞	∞	33	8 (0.15)	30 (0.85)
2	0.99/0.01	198	399	77	20 (0.15)	70 (0.85)
3	0.98/0.02	98	199	112	27 (0.03)	102 (0.97)
4	0.90/0.10	18	37	114	28 (0.05)	104 (0.95)
5	0.80/0.20	8	17	116	25 (0.28)	106 (0.72)
6	0.75/0.25	6	13	123	29 (0.26)	112 (0.74)

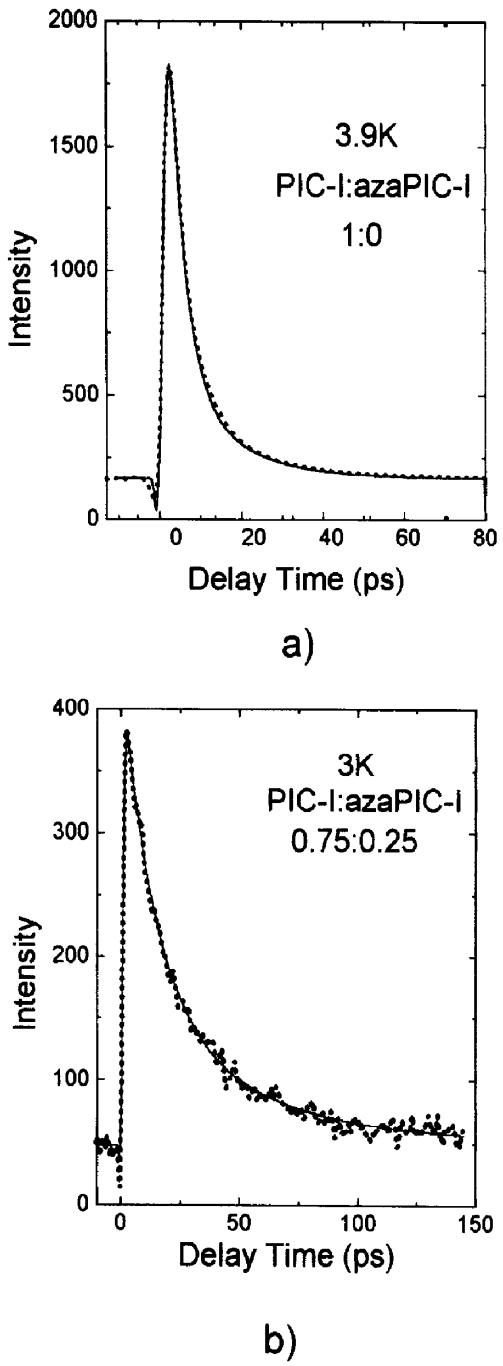

Fig. 3. Accumulated photon echo decay data (.....) and fits (———): (a) for sample 1 and (b) for sample 6.

detected. In this case, the decay constant of APE measured is $\frac{1}{2}T_2$. Since there is a distribution of aggregate lengths, the APE decay is nonexponential. The decay consists of two parts: the fast (τ_1) and the slow (τ_2) components with weights W_1 and W_2, respectively. The APE signal can be written as

$$S(\tau,\tau') = -2\,\mathrm{Im}\int \mathrm{d}t\, E_2^*(t-\tau)P^{(3)}(k_2,t)$$

$$\propto A(\tau')\sum_l W_l \exp\left(\frac{-\tau}{\tau_l}\right) \quad (l=1,2), \qquad (1)$$

where τ is the delay time between the two pulses. The fits for the whole echo decay curves for samples 1 and 6 are given in Fig. 3(a) and (b), respectively. The slow component of sample 1 (pure PIC-I) with $\tau = 30$ ps and $W_2 = 0.8$ were extracted from the fit of its echo decay curve. As the APE decays with $\frac{1}{2}T_2$, $T_2 = 60$ ps. The fit of $T_2 = 60$ ps agrees well with the result of hole burning experiments [3]. For sample 6, with PIC-I : azaPIC-I = 0.75 : 0.25, the slow component of the echo decay is 112 ps with weight $W_2 = 0.74$, corresponding to $T_2 = 224$ ps. The results for the other samples are listed in Table 1. It is apparent there is a lengthening of the dephasing times with increasing molar fractions of azaPIC-I. This is contrary to the results for Thiacyanine (TD) : PIC with traps reported by De Boer et al. [4]. When the mixture ratio of TD : PIC was increased from 1 : 1000 to 1 : 250, a substantial shortening of the echo decays was observed. De Boer pointed that this shortening could be unambiguously assigned to trapping. In our case, if the motion of excitons is completely coherent, the exciton is reflected back and forth with constant absolute momentum between the two barriers, leading to a lengthening of the exciton lifetime, further lengthening T_2.

The exciton coherence length N_c, over which excitons move coherently, dominates the size effect of aggregates. This is already noticeable in linear spectroscopy, as an exchange narrowing of absorption spectral lines and as a shortening of the radiative lifetime of fluorescence decays. The exciton coherence length for a infinite mixed aggregate chain can be written [5] as

$$N_c = \frac{\sum_N N^2 m_f^2 (1-m_f)^{N-1}}{\sum_N N m_f^2 (1-m_f)^{N-1}}, \qquad (2)$$

where m_f is the molar fraction of azaPIC-I. The values of the coherence length N_c, calculated using Eq. (2), are listed in Table 1. Comparing the coherence length N_c with the physical length N_p of an aggregate between two barriers we have $N_c \approx 2N_p$. Since $N_c > N_p$, a Boltzmann equilibrium can be achieved. The exciton coherence length can be estimated [6] using

$$N_c = \langle V_g(T) \rangle T_2(T), \tag{3}$$

where $\langle V_g(T) \rangle$ is the average group velocity of an exciton wave packet at temperature T, given by

$$\langle V_g(T) \rangle = \left(\frac{2Ja}{\hbar}\right)\left(\frac{2kT}{\pi J}\right)^{1/2}\left[\frac{I_{1/2}(y)}{I_0(y)}\right] \tag{4}$$

where $I_{1/2}(y)$ and $I_0(y)$ are modified Bessel function with $y = 2J/kT$:

$$I_{1/2}(y) = \left(\frac{y}{2\pi}\right)^{1/2}\int_0^{\pi} \exp[\pm\cos(ka)]\sin(ka)\,\mathrm{d}(ka),$$

$$I_0(y) = \left(\frac{1}{\pi}\right)\int_0^{\pi} \exp[y\cos(ka)]\,\mathrm{d}(ka). \tag{5}$$

Using Eq. (3), the nearest-neighbor interaction $J = 600\ \mathrm{cm}^{-1}$ and $a = 0.3$ nm, an average group velocity $\langle V_g(T) \rangle = 1.67 \times 10^4$ cm/s was calculated. Then exciton coherence lengths of 33, 77, 112, 114, 116 and 123 were obtained from Eq. (3) using the experimental values of T_2. These results have discrepancies with the theoretical results calculated from Eq. (2) (see Table 1). The main reason may be due to not considering the effect of different molecular interactions J for the different samples.

The maximum exciton effective jump distance is

$$S_{\mathrm{eff}} = [1 + (p_f + p_n) + (p_f + p_n)^2 + \cdots]\,N_p\,a = \frac{2 - T}{2 - 2T}\,N_p\,a, \tag{6}$$

where T is the transmission coefficient and p_f (p_n) is the probability of passing through the far (near) barrier (Fig. 2). Then $S_{\mathrm{eff}} = 1.03\,N_p\,a$, for $k = \pm\pi/2a$, from Eq. (6). Obviously, this value of S_{eff}/a is less than the exciton coherence length $N_c \approx 2N_p$. This means that the excitons in the one-dimensional chain behave like a giant molecule in phase within the coherence length, but a single exciton can pass through a maximum effective distance of $S_{\mathrm{eff}} (< N_c)$ only.

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