LETTERS

Strong Nonmonotonous Temperature Dependence of Exciton Migration Rate in J Aggregates at Temperatures from 5 to 300 K

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This contribution presents the first measurement of the rate of exciton−exciton annihilation in J aggregates for which a strong nonmonotonous temperature dependence was found. Annihilation is suppressed at low temperature ($T < 20$ K), very pronounced in the temperature region of 20−70 K, and it decreases again while temperature increases from 70 to 300 K. We suggest that an exciton hopping process occurs at low temperature ($T < 20$ K), a coherent wave-packet-like exciton transport occurs in the intermediate temperature region (20−70 K), and a strong exciton scattering occurs on optical phonons at high temperatures (70−300 K). The exciton migration properties in J aggregates were compared with those in molecular crystals.

Molecular aggregates of organic dyes (so-called J aggregates[1,2]) reveal a long-distance migration of the delocalized excited states (Frenkel excitons). This energy migration can be observed by the occurrence of bi-exciton quenching or exciton−exciton annihilation (EEA) at high excitation intensities.[3−7] Despite continuous efforts, the particular mechanism of migration and interaction of highly delocalized excitons (ca. 30−100 molecules at low temperature) is still unclear. The phenomenon of very fast energy migration in dye monolayers and LB films[8] as well as in J aggregates in solution[5,6] makes molecular aggregates an interesting object for potential application in developing artificial light-harvesting antennae and effective organic photodetectors. Up to now, there has been no definitive conclusion on the physical nature of ultrafast exciton migration, which can be wave-packet-like coherent motion or incoherent hopping.

The triethylammonium salt of 3,3′-disulfopropyl-5,5′-dichloro-9-ethylthiacarbocyanine (THIATS) (see Figure 1) in a 3/2 volume mixture (C=1.5×10^{-4} M) of water/ethylene glycol was found to build a type of aggregates with 2 molecules per unit cell, which has been proved by various spectroscopic investigations.[9] Due to the effect of Davydov splitting, the lower exciton transition (J transition) carries only 1/30 of the total oscillator strength.[9] Therefore, a distinguishing feature of this system in comparison with other J aggregates is a very long fluorescence decay time[10] of ca. 5 ns at $T < 100$ K. Nevertheless, the exciton cooperative effects are very strong in the system, as indicated by the extremely narrow absorption (fwhm$_{abs}$ = 82 cm^{-1}) and fluorescence (fwhm$_{flu}$ = 56 cm^{-1}) bands at 5 K.

In the current letter, we present results of the determination of the EEA rate γ at temperatures from 5 to 300 K. To our knowledge, it is the first time that the temperature dependence of γ for J aggregates has been presented.

The EEA rate can be estimated from measurements of the fluorescence quantum yield Φ at different excitation intensities

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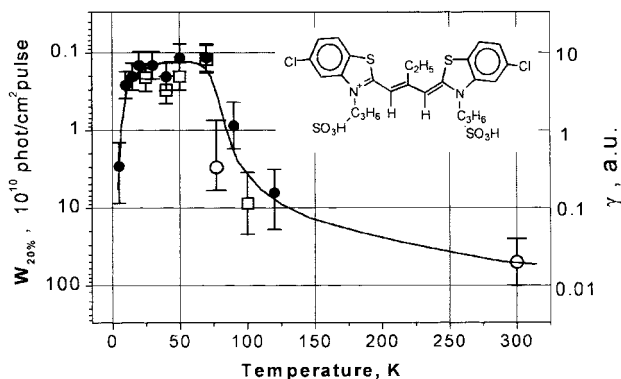‡ Katholieke Universiteit Leuven.

Figure 1. Temperature dependence of γ or $W_{20\%}$ over the entire temperature region. The solid line is to guide the eyes. Insert: chemical structure of THIATS.

W relative to the value extrapolated to zero intensity. To obtain the intensity dependence of the relative fluorescence quantum yield $\Phi(W,T)$, we used data of fluorescence decay measurements. This method results in lower error than ordinary stationary measurements. The fluorescence decays were measured by time-correlated single-photon counting using a picosecond dye laser for excitation, as described elsewhere.[10] The instrumental response function possessed a fwhm of 0.7 ns. The sample was excited at 565 nm, and the fluorescence light was collected from the whole emission band, which had a maximum at 614 nm. The excitation photon flux (*W*) was varied from 2.7 $\times 10^{10}$ to 10^8 photons/cm^{2}pulse.

At each temperature *T*, we measured a set of decay curves $f(t,W)$ at different *W*, which were normalized on their intensity in the maximum. Then we have[11]

$$\Phi(W) = k_f \int_0^\infty f_{norm}(t,W)\, dt = k_f F(W)$$

where k_f is the radiative decay rate. As k_f is independent of the excitation intensity, we have $\Phi(W) \sim F(W)$. To estimate the EEA efficiency from the plot of $\Phi(W)$ versus *W*, we determined the excitation photon flux when 20% of exciton quenching has been reached ($W_{20\%}$). According to Paillotin[11]

$$\Phi(W) = \Phi(0)\frac{2K}{\gamma Z}\ln\left(1 + \frac{\gamma Z}{2K}\right)$$

where $K = k_f/\Phi(0)$ is the single-exciton decay rate, γ the EEA rate, and Z the number of excitons created in an aggregate domain by the excitation pulse; thus, Z $\sim$ W. For $\Phi(W_{20\%}) = 0.2$, the product $\gamma W_{20\%}$ is constant, which means that $\gamma \sim 1/W_{20\%}$.

The values of $W_{20\%}(T)$ are shown on the Figure 1. We also added data for *T* = 77 and 300 K (open circles), which were taken from the previous studies of THIATS J aggregates.[6] As the experimental procedure contains a lot of experimental difficulties resulting in a rather large experimental error, we paid special attention to the reliability of the data. The data shown by the solid circles and open squares correspond to two different experiments with two different samples. These two data sets when plotted on the graph are in good agreement. Although the values taken from ref 6 were obtained with the use of a completely different experimental setup leading to important deviations, they follow the trend, and there is no reason to reject the point at 300 K.

The most pronounced feature of γ is a strong nonmonotonic temperature dependence. The entire temperature region investigated can be divided in four temperature intervals: 0–20 K,
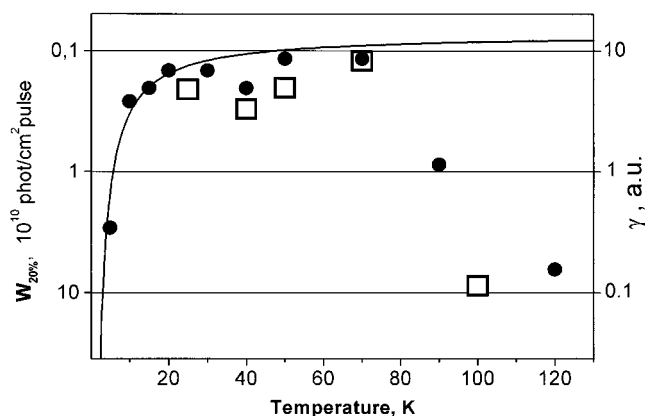

Figure 2. Temperature dependence of γ or $W_{20\%}$ in the low-temperature region. The solid line is an approximation by an exponential function $\exp(-E_a/T)$ with activation energy $E_a = 10.5$ cm^{-1}.

20–70 K, 70–110 K, and 110–300 K. In each temperature region, the EEA rate γ and, in turn, the ability of the exciton to migrate exhibit completely different behaviors.

We observed strong blocking of the EEA process when *T* is below 10 K or above 80 K and an almost constant EEA rate between 20 and 70 K. For both data sets (squares and circles), a minimum in γ(T) can be seen for $T \approx 40$ K (Figure 2). However, this variation is rather close to the experimental error. We have to emphasize here that our results are completely different from those obtained for PIC monolayers with traps,[8] where the energy transfer rate was found to be proportional to *T* in the temperature region of 20–300 K and associated with incoherent exciton hopping.

It is well-known from the theory of molecular excitons[12,13] that the temperature dependence of the exciton diffusion constant *D* ($\gamma \sim D$ at first approximation) is completely different for coherent excitonic transport and incoherent hopping. *D* increases with increasing temperature for incoherent hopping and scales to $\exp(-E_a/T)$, where E_a is the activation energy.[12,13] In the case of coherent motion, *D* decreases with increasing *T* and scales to T^{-m} where $m = 0$–1.5, depending on the particular parameters of the exciton–phonon system.[12,13]

In comparison with that of molecular crystals, the resonance coupling strength is approximately 10 times larger in J aggregates. The exciton bandwidths are 3100 and 300 cm^{-1} for THIATS and anthracene, respectively. On the other hand, dye molecules in aggregates are not packed with the same perfection as anthracene molecules in bulk single crystals. This leads to a static energetic disorder Δ, which plays an important role in the exciton dynamics, especially at low temperatures.[15,16] Moreover, the system under investigation reveals a very interesting combination of excitonic parameters. On one hand, it possesses very strong intermolecular coupling, and on the other hand, the exciton lifetime is very large (5 ns) due to the small value of the transition dipole moment of the lowest excited state (J state).

The most effective EEA process with almost constant γ was observed in the temperature region of 20–70 K. It was found that the exciton emission had been quenched already by 20% under an excitation photon flux of ca. 10^9 photons/cm^{2}pulse. This intensity corresponds to approximately 1 absorbed photon per 10^7 dye molecules. This observation clearly demonstrates very large exciton mobility in this temperature region (questions concerning dimensionality of the exciton motion in THIATS aggregates were discussed in refs 6 and 10). The very effective and temperature-independent EEA process suggests a coherent (wave packet-like) exciton motion for this temperature region.

The effect of "freezing" the fast coherent exciton motion can be observed at $T < 10$ K. This phenomenon is attributed to the blocking of the exciton by energetic barriers in a disordered chain. In the case where kT is smaller than value of the disorder Δ, the exciton, delocalized over the coherent length of 20−100 molecules, becomes blocked between energetic barriers. Thus, we assume that temperature-activated hopping between two coherent segments is probably the main mechanism, which can provide exciton migration at such low temperatures. In Figure 2, the experimental data for $T < 20$ were fitted to an Arrhenius equation with a hopping activation energy $E_a = 15$K$= 10.5$ cm^{-1}, which gives us an estimation of the energetic disorder Δ. However, even at 5 K the EEA is still pronounced, corresponding to exciton migration over ca. 3×10^4 dye molecules. This observation is not in agreement with the common opinion that the excitons in J aggregates are almost immobile quasiparticles at such a low temperature.[17]

In the temperature region between 70 and 110 K, γ starts to be strongly temperature-dependent again. The diffusion coefficient decreases by almost 2 orders of magnitude when the temperature is increased only by 50%. This strong temperature dependence cannot be explained in the framework of exciton scattering on acoustic phonons or optical phonons with small frequencies ($\omega \ll kT$). This mechanism can only lead to a rather slow decrease of D (see above). Such strong decrease of the exciton migration rate means that in this temperature region, another mechanism starts to become important. We attribute this effect to the scattering of coherent excitons on optical phonons with frequencies $\Omega_{opt} = 40$−60 cm^{-1}. Optical phonon modes with such frequencies are often considered for explaining exciton dynamics in J aggregates.[18] The strong temperature dependence comes from the fact that contrary to acoustic phonons, the optical phonons are dispersionless. Therefore, the exciton does not interact with the optical phonon mode at all until $T < \Omega_{opt}$. When $T \sim \Omega_{opt}$, interaction begins, and exciton scattering starts to be strongly temperature dependent (D decreases by several orders of magnitude).[12,14] When $kT > \Omega_{opt}$, we return back to the "normal exciton phonon coupling" but with another exciton−phonon coupling constant, due to the involvement of optical phonons into the scattering process. There are no doubts that in the high-temperature region (110 K $< T < 300$ K) the exciton dynamics is very strongly influenced by exciton−phonons scattering.[18] We observed a decrease of γ of about 1 order of magnitude when the temperature increases from 110 to 300 K. However, even at room temperature the exciton is still delocalized over a coherence length of about 4−10 dye molecules.[10,15] This means that the exciton migration cannot be considered as a simple incoherent hopping from one molecule to another. This feature also distinguishes J aggregates from anthracene-like molecular crystals where excitons are completely localized on a single molecule at room temperature and migrate through the lattice by incoherent hops.[12,13] Moreover, for incoherent hopping, an increase of γ with increasing T should be expected,[12] but we observed the opposite.

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