Primary photophysical processes in *J*-aggregates of spectral sensitisers

K KEMNITZ*¹, K YOSHIHARA², T SUZUMOTO³, T TANI³
M LINDRUM⁴, J MOLL⁵ and S DAEHNE⁵

¹ BioQuant Ltd., Rudower Chaussee 6, D(O)-1199 Berlin, Germany

² Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

³ Fuji Photo Film Co., Ltd., Ashigara Research Laboratories, Minami-Ashigara, Kanagawa 250-01, Japan

⁴ Free University of Berlin, Institute of Experimental Physics, Arnimallee 14, D(W)-1000 Berlin 33, Germany

⁵ Federal Institute for Materials Research and Testing, Laboratory of Time-Resolved Spectroscopy, Rudower Chaussee 5, D(O)-1199 Berlin, Germany

Abstract. We present temperature-dependent superradiant fluorescence decays and relative quantum yields in *J*-aggregates formed by two carbocyanine dyes, and compare homogeneous with heterogeneous systems. It will be shown that a generalisation of the results obtained in case of pseudoisocyanine is not appropriate, since each dye aggregate displays its own photophysical behaviour that has to be investigated individually. The exciton in the present systems seems to be coupled to an acoustic mode rather than to an optical mode, as had been found in case of pseudoisocyanine in ethylene glycol matrix. In addition, as a second novel feature, global analysis of the temperature-dependent, nonexponential fluorescence decays revealed the presence of an excited-state reaction, both in heterogeneous and homogeneous systems.

Keywords. *J*-aggregate; superradiance; spectral sensitisation.

1. Introduction

Excitonic energy transfer within *J*-aggregates of pseudoisocyanine (PIC) at very low temperatures is well established, and had been demonstrated by hole burning (De Boer *et al* 1987; Hirschmann and Friedrich 1989), photon echo (De Boer *et al* 1987; De Boer and Wiersma 1987, 1990), and time-resolved fluorescence (Fidder *et al* 1991b) techniques. Recent theories discuss, parallel to experiment, the nature of relaxation channels that are in competition with exciton migration (Spano and Mukamel 1989; Fidder *et al* 1991a). Superradiant fluorescence decays (Dorn and Müller 1987; De Boer and Wiersma 1990; Spano *et al* 1990) that become faster at low temperatures are a hallmark of coherence effects in *J*-aggregates, as is the decrease of the fluorescence lifetime with increasing aggregate size (Kemnitz *et al* 1990; Muentner *et al* 1992; Tani *et al* 1992).

Superradiant fluorescence decay is in competition with electron transfer in the photographic sensitisation process (figure 1). Since the main competitors, i.e., electron

* For correspondence

$$\Phi_s(N) = k_s(N) / [k_s(N) + k_{nr}(N) + k_r(N)] \quad (c)$$

$$k_s(N) = ?$$

$$k_{r,J}(N) = N k_{r,M} \cos^2 \alpha$$

$$k_{nr,J}(N) = k_{IC,M} N^{-(\Delta E/h\nu)} \quad \text{for IC}$$

$$k_{nr,J}(N) = ? \quad \text{for exciton trapping}$$

Figure 1. Simplified representation of spectral sensitisation with the competitive processes of: (a) electron injection into the conduction band of AgBr, $k_s(N)$, (b) superradiant decay, $k_r(N)$, and (c) nonradiative decay, $k_{nr}(N)$, where each process is a function of aggregate coherence size, N .

transfer, k_s , radiative decay, k_r , and nonradiative decay, k_{nr} , are all dependent on aggregate size, N , it is of great interest to establish the individual dependencies, with the ultimate goal of optimising the yield of sensitisation, $\Phi_R(N)$. Figure 2a shows the size dependence of k_s and that of the sum of radiative and nonradiative rate constant, k_L , obtained from fluorescence kinetics and sensitisation yields of J -aggregates adsorbed on AgBr (Tani *et al* 1992). The increase of k_L with increasing aggregate size is thought to be due to coherence effects. Figure 2b shows the size-dependent absorption spectra of the J -aggregates on AgBr, where the band maximum shifts to the red and the half width decreases with increasing aggregate size.

The decrease of k_s with increasing size in figure 2a is not well understood, at present. To improve the fundamental understanding of the electron transfer step involved in the above complex reaction scheme (figure 1), we investigated a series of dyes, shown in a classical Marcus representation in figure 3 (Tani *et al* 1992), with a prominent steep increase of the rate constant of electron transfer, as measured by the yield of sensitisation, Φ_R , with increasing half-wave reduction potential, E_R , of the dyes. Such steep increase in the normal region is caused by a very small reorientation energy, $\lambda = 0.05$ eV, typical of a solvent-free system (Kemnitz *et al* 1988). The behaviour in the inverted region (dashed), however, is unknown as yet, and new dyes will have to be used to explore this important region that will yield additional parameters, important for the complete characterisation of electron transfer in photographic systems. Once the basic parameters like intramolecular and external reorientation

Figure 2. (a) Dependence of the electron injection rate constant, k_s , and of the sum of radiative and nonradiative rate constants, k_L , on aggregate size that relates inversely to the efficiency of sensitisation, Φ_r (after Tani *et al* 1992). (b) Reflectance spectra of film samples of DCTC adsorbed on AgBr depending on aggregate size. With increasing aggregate size, N , the maxima shift to the red and the bandwidth decreases (after Tani *et al* 1992).

energy and electron-exchange matrix element are known, it might be possible, in a second step, to extract the size dependencies of these parameters that govern electron transfer in photographic sensitisation.

An alternative path of separating the individual decay processes in the sensitisation process was followed in the development of reference systems without electron transfer, i.e., J-aggregates adsorbed on SiO_2 (Kemnitz *et al* 1990) and KBr, where KBr was chosen in order to create an inert surface more similar to that of AgBr. These systems are, analogous to the homogeneous counterpart, i.e., liquid or glassy mixtures of ethylene glycol/water (EG) (Lindrum *et al* 1993), very sensitive towards changes in environment, and both heterogeneous and homogeneous systems are thus well suited

Figure 3. Simple Marcus representation of the rate constant of electron injection, as measured by the efficiency of photosensitization, Φ_r , and the reduction potential of various cyanine dyes, E_R (after Tani *et al* 1992). The reorientation energy, λ , of the solvent-free system is very small, i.e., about 0.05 eV.

Figure 4. The chemical structures of 5,5'-dichloro-9-ethyl-benzthia-carbocyanine (DTC) and 5,5',6,6'-tetrachloro-benzimido-carbocyanine (TCIC).

for the fundamental study of environmental effects on exciton-phonon coupling, and helpful in the eventual understanding of the individual size dependencies of all the processes involved.

We present fluorescence decays and relative quantum yields of *J*-aggregates formed by 5,5'-dichloro-9-ethyl-benzthia-carbocyanine (DTC, figure 4) on KBr (Kemnitz 1993) and by 5,5',6,6'-tetrachloro-benzimido-carbocyanine (TCIC, figure 4) in

ethylene glycol/H₂O (4:1) matrix (Lindrum *et al* 1993), in the temperature range 293–4 K. Both systems display enhanced fluorescence decays at low temperature, accompanied by an increase of relative fluorescence quantum yield, clearly indicating an increase of the radiative rate constants at low temperatures.

As a novel feature, the presence of an excited-state reaction was revealed by global analysis of fluorescence decays, acquired at up to 12 different temperatures (Kemnitz 1993). Various physical models to account for the complex fluorescence decay features have been tested and compared.

The individual decay characteristics depend on environment, i.e., on the substrate in case of heterogeneous systems. Figures 5a and 6 display the temperature behaviour of *J*-aggregates of DCTC, adsorbed on SiO₂ and KBr, respectively, and the opposite temperature-dependence is obvious. In case of the homogeneous systems, the fluorescence

Figure 5. Temperature-dependent fluorescence kinetics and relative fluorescence quantum yields of (a) DCTC adsorbed on KBr, and (b) TCIC in fluid and solid matrix of ethylene glycol/H₂O (4:1).

Figure 6. Environmental effect in case of DCTC/SiO₂. The fluorescence decays slow down at reduced temperature in contrast to DCTC/KBr in figure 5a.

Figure 7. (a) Three-exponential analysis of the nonexponential fluorescence decays of DCTC/KBr, and (b) two-exponential analysis of TCIC in ethylene glycol/H₂O.

dynamics depend on solvent composition, i.e., on the amount of H₂O in the EG systems (Lindrum *et al* 1993), and on the phase, i.e., on the fluid or the solid properties of the matrix (figure 7b).

2. Experimental

The time-correlated single photon counting systems (Kemnitz *et al* 1990; Rempel *et al* 1990) as well as the preparation of the heterogeneous film samples (Kemnitz *et al* 1990; Tani *et al* 1992) and that of the homogeneous EG samples (Lindrum *et al* 1993) were described previously. Excitation wavelengths were 620 and 580 nm and the emission was observed at 630 and 590 nm for DCTC and TCIC, respectively. Heterogeneous and homogeneous samples were excited at low-photon density and observed under front-face geometry. Global analysis software was from Globals Unlimited. Application and advantages of global fluorescence decay analysis are well documented in literature (Beechem *et al* 1989; Rumbles *et al* 1991; Kemnitz and Sakaguchi 1992; Boens *et al* 1992).

3. Results and discussion

3.1 Temperature-dependence of superradiant fluorescence decay

Figure 5 shows the temperature-dependent, nonexponential fluorescence decays and the relative fluorescence intensities of (a) the heterogeneous DCTC/KBr system, and of (b) TCIC in the macroscopically homogeneous EG/H₂O matrix. Both systems display enhanced fluorescence decays at reduced temperatures, accompanied by a strong increase of fluorescence intensity, thus clearly demonstrating the increase of the radiative rate constant at low temperatures. The fluorescence decays are complex and can phenomenologically be fitted by a multi-exponential function of up to three exponents. The degree of non-exponentiality varies with temperature and phase. This effect can most clearly be seen in case of TCIC in figure 7b, where the fluid phase from 293–220 K can roughly be fitted by two exponents, whereas the rigid matrix shows a smooth transition from three-exponential decay at 180 K to strictly single-exponentiality at 4 K. The heterogeneous system of DCTC/KBr in figure 7a needs three exponents within the whole temperature range, in contrast. The fluorescence lifetimes in this system are almost independent of temperature, with a slight tendency towards shorter lifetimes at lower temperatures (τ_1, τ_2). The most conspicuous feature, however, is the variation of the pre-exponential factor of the fast component, A_1 , in figure 7a (top). Global three-exponential analysis at 7 temperatures, at varying degrees of parameter-linkage, clearly shows that it is mainly the increase of A_1 at low temperatures that is responsible for the enhancement of the fluorescence decay at reduced temperatures in figure 5a. Analogously, the increase of A_1 in case of TCIC in figure 7b (top) could be shown to be an essential feature of the temperature-dependent fluorescence decays in figure 5b. Thus, any physical model has to accommodate the increase of the pre-exponential factor of the fast component, next to the decrease of the fluorescence lifetimes at low temperatures, and, of course, the pronounced increase of fluorescence intensity.

3.2 Excited-state reaction

Global analysis, employing complex excited-state schemes with numerous fit parameters, is no simple task, because there exist many local and even global minima in the multidimensional error surface, yielding mostly nonphysical fit parameters. The challenge is to locate the global minima of physical significance. Such systems turn out to be rare and highly restricted, fortunately, so that it is possible to suggest and discuss a limited number of physical models. By applying global analysis, we were able to test and compare the physical models that are displayed in figure 8. The quality of the individual models is judged by their global χ^2 , where three-exponential, unrestricted fitting is taken as ultimate quality standard. The integrity of all the present models discussed was confirmed by kinetic simulations and reanalyses of the artificial decays, convoluted with a real system response function.

The transition, mentioned above, from three- to single-exponentiality in case of TCIC upon reduction of temperature, clearly points to the existence of an excited-state reaction. The primarily excited, superradiant state relaxes, in a temperature-dependent reaction, k_{12} , towards a weakly emitting “trap”-state of longer fluorescence lifetime (figure 8c). At 4 K, the transition k_{12} is completely frozen and a single-exponential

Figure 8. Various reaction schemes that have been tested and compared by global analysis: (a) two-exponential decay caused by two S_0 species, (b) three-exponential decay caused by three S_0 species, (c) excited-state two-level scheme, (d) excited-state three-level scheme, (e) two distributed (Gaussian) S_0 species, and (f) distributed (Gaussian) excited-state two-level scheme.

decay can be observed. Scheme (c) in figure 8 can roughly fit the observed decays of the solid domain below 200 K in figure 5b, but a perfect fit is obtained only for the Gaussian-distributed analogue, scheme (f), yielding a global χ^2 -equal to that of three-exponential fitting. The distributed fit replaces a discrete fluorescence lifetime by a distribution of lifetimes whose pre-exponential factors are determined by a Gaussian envelope. Figure 9b shows the decrease of centre wavelength, C_1 , from about 130 to 90 ps at lower temperature, accompanied by a reduction of the half width, W_1 , from 90 to about 4 ps. The slow component, caused by the emission of the product-state, can be modelled by $C_2 = 725$ ps and $W_2 = 660$ ps, independent of temperature. The interconverting rate constant, k_{12} , decreases from 1/4 to 1/400 ns and is responsible, together with the decrease of W_1 , for the transition from three- to one-exponentiality at 4 K. The increase of the fluorescence intensity at low temperatures is reflected in an increase of the species-associated spectra (SAS_i). The SAS represent the intrinsic fluorescence bands of both excited-state species and are proportional to fluorescence quantum yield. Both species display increasing SAS, in case of the superradiant state due to an increase of the radiative rate constant, and in case of the trap-state, probably due to the decrease of the nonradiative decay at low temperatures. Two candidates

Figure 9. Best fits combining fluorescence decay and quantum yield data of figure 5. (a) In case of DCTC, a three-level excited-state scheme is discussed. (b) TCIC in solid matrix can best be fitted by a distributed two-level excited-state scheme.

Figure 10. Temperature-dependent maximum (a) and bandwidth (b) of absorption and fluorescence spectra of TCIC/EG.

for a weakly emissive trap state were proposed recently: (a) a structural irregularity within the aggregate, i.e., a small section forming a nonfluorescent H-dimer (Muentert *et al* 1992) and (b) thermally activated, subradiant states within the exciton band (Spano *et al* 1991).

Figure 10 shows the temperature-dependence of the maximum (a) and bandwidth (b) of absorption and fluorescence spectra of TCIC/EG (Moll *et al* 1993). The parallel blueshift of absorption and fluorescence spectra at lower temperatures in figure 10a have also been observed in case of PIC/EG and can be understood in terms of exciton coupling to low-frequency phonons (Fidder *et al* 1991b). Figure 10b displays the decrease of the fluorescence bandwidth at reduced temperatures, which is much larger than that of the absorption spectrum. In addition, the fluorescence bandwidth at room temperature is about twice the absorption bandwidth. We take this behaviour as support for our notion from above that the emission of trap states, responsible for the broadened emission band at 293 K, is reduced at lower temperatures due to reduced k_{12} .

The combination of decreasing τ_1 and of decreasing k_{12} at reduced temperatures leads to an observed lifetime, τ_{obs} , e.g., in two-exponential analysis, that is only weakly dependent on temperature. τ_1 in figures 7a and b decreases by less than 20 and 50% at 4 K, respectively, whereas the intensity increases 7 and 5 times within the same temperature range. The variation of fluorescence intensity with temperature was corrected for the shift of absorption and fluorescence bands (figure 10a). The increase of the extinction coefficient at reduced temperature was roughly cancelled by the decrease of fluorescence intensity, since excitation was at the high-energy side of the absorption band, whereas the fluorescence was observed at the low-energy side of the emission band.

In case of the heterogeneous system, the distributed two-level excited-state scheme from above is not sufficient to fit the data, and a third excited-state level has to be introduced, scheme (d) in figure 8. The parameters describing the third component, i.e., the rate constant of interconversion, k_{23} , SAS_3 , and fluorescence lifetime, τ_3 , are of secondary importance only and are very approximate. Figure 9a shows the temperature dependence of the more important parameters, i.e., the decrease of k_{12} , the increase of SAS_1 , and a decrease of τ_1 from 300 to 60 ps at 4 K. This behaviour is strictly analogous to that of the homogeneous system described in figure 9b. The

Figure 11. Temperature dependence of the coherence size, N_{eff} , of DCTC/KBr and TCIC/EG.

core of both the homogeneous and heterogeneous model is an excited-state reaction, characterised by decreasing rate constant of interconversion, k_{12} , from a superradiant to a weakly emitting state, increasing SAS_1 , and decreasing superradiant lifetime, τ_1 , at reduced temperatures. The radiative lifetime, $1/k_r(T)$, can be calculated from $SAS_1(T)$ and $\tau_1(T)$, both obtained from scheme 8(d) or (f): $1/k_r(T) = \tau_1(T)/SAS_1(T)$, under the assumption that $SAS_1(4\text{ K}) = \Phi_f(4\text{ K}) = 1$. Figure 11 displays the coherence length, N_{eff} , of TCIC/EG and DCTC/KBr, calculated according to $N_{\text{eff}} = k_r(J)/k_r(M)$, with $k_r(M) = 1/(4\text{ ns})$. Whereas N_{eff} in case of PIC in EG/H₂O is absolutely independent of temperature between 4 and 50 K, we observe a change in N_{eff} of about 100% in case of both carbocyanines in this temperature range.

Two physical models that cannot be distinguished at the current level of precision are presented in case of the liquid phase. The first model is a variant of the excited-state schemes described above. As already seen from the parameters obtained by two-exponential fitting in figure 7b (bottom), both fluorescence lifetimes, τ_1 and τ_2 , decrease at low temperatures, and we have to assume that two superradiant states are involved in this particular case. The second model, based on a Gaussian ground-state distribution of fluorescence lifetimes, does not involve an excited-state reaction, and is based on a single fluorescent state. Both models will be compared and discussed in a future paper (Kemnitz 1993) and will be contrasted by a different approach (Lindrum *et al* 1993).

Two potential alternatives for the explanation of temperature-dependent pre-exponential factors, (a) that of two emitting ground-state populations (figure 8a or 8e), where the slower decaying and more weakly emitting species would have to stop emitting at 4 K, and (b) that of a temperature-dependent ground-state equilibrium between two distributions, are inconceivable in the present systems and were discarded.

3.3 Theoretical considerations

Figure 12 displays the main results of the theory of exciton-phonon coupling, as developed by Spano *et al* (1990), and shows the dependence of coherence size, N_{eff} , on temperature, T , and on the physical aggregate size, N . Figure 12a represents the case of an optical phonon and contains the qualitative behaviour of the system of PIC in EG/H₂O by De Boers and Wiersma (1990) as bold line. They observed strictly temperature-independent behaviour below 50 K and a linear decrease of N_{eff} , by a large factor of about 50, with increasing temperature. The detailed analysis yielded the following parameters: $N = 75$, exciton-phonon coupling strength, $F_{\text{op}} = 210\text{ cm}^{-1}$, and the optical mode, $\Omega_{\text{op}} = 240\text{ cm}^{-1}$, using the nearest-neighbour dipole-dipole interaction energy, $V = 600\text{ cm}^{-1}$. The analysis was based on the experimental observation of a decrease of the fluorescence decay time by about 10 times, when the temperature was lowered from 200 to 50 K, accompanied by a change in quantum yield of less than 25%.

The experimental observations in the present carbocyanine dye systems differ in several ways from that of PIC described above: (1) complex, non-exponential fluorescence decays, as opposed to one-exponentiality, (2) relatively small changes of fluorescence lifetimes in two- or three-exponential analyses, i.e., a decrease of less than 1.5 times, when going from 293 to 4 K, with a major part of the change occurring below 50 K, (3) a strong increase of relative fluorescence quantum yield, i.e., an increase by up to

Figure 12. Theory of exciton-phonon coupling after Spano *et al* (1990), with the dependence of coherence size, N_{eff} , on temperature, T , and physical aggregate size, N . (a) Optical mode, containing the qualitative behaviour of the data on PIC by De Boer and Wiersma (1990) as bold line. (b) Acoustic mode with qualitative temperature dependence of N_{eff} of the present data as bold line.

7 times in the same temperature region, and (4) the existence of an excited-state reaction, manifest in a temperature-dependent degree of non-exponentiality, i.e., temperature-dependent pre-exponential factors obtained in multi-exponential fluorescence decay analysis.

Figure 12b shows the exciton-phonon coupling in case of an acoustic mode and displays the qualitative behaviour of the present systems of figure 11 as bold line. The increase of N_{eff} , even at very low temperatures, is typical for acoustic modes (moderate size aggregates) and is in contrast to the behaviour of optical modes in figure 12a.

It appears that the temperature dependence of N_{eff} of the present systems in figure 11 is in qualitative accord with the assumption of coupling to an acoustic mode. Coupling to low-frequency acoustic modes ($\Omega_{\text{ac}} < 30 \text{ cm}^{-1}$) had recently been suggested by Muentert *et al* (1992) to control the weakly temperature-dependent fluorescence dynamics of PIC *J*-aggregates adsorbed on AgBr.

4. Conclusions

Our investigations of the temperature-dependent superradiant fluorescence dynamics of *J*-aggregates of carbocyanine dyes in heterogeneous and homogeneous environments

led to several novel features not observed in case of PIC: (1) individual temperature behaviour, demonstrating a varying degree of exciton-phonon coupling, (2) dependence on environment, (3) coupling to an acoustic mode, and (4) the existence of an excited-state reaction.

By applying global analysis, we were able to elucidate several models of physical significance from the complex fluorescence decay behaviour. In one of the models discussed, we postulate a slight quenching of the superradiant state by weakly emitting trap states, with the trapping rate constant decreasing at reduced temperatures. The nature of the trap is unknown as yet, but its emission spectrum is currently being investigated by temperature- and emission-resolved ps spectroscopy.

The application of ground- and excited-state distributions (Gaussian or other) in fitting fluorescence dynamics of (micro)-heterogeneous systems is a very promising tool for the design of kinetic models. The conspicuous reduction at low temperatures of the Gaussian half-width in one of our kinetic models is a very attractive feature and deserves further investigation.

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