Incoherent Energy Migration In Optically Active J-Aggregates

S. Daehne[a], U. De Rossi[a], S. Kirstein[b], A. Pawlik[b], and C. Spitz[a]
[a] Federal Institute for Materials Research and Testing, Berlin, Germany
[b] Max Planck Institute for Colloids and Surfaces, Berlin, Germany

Abstract

Depending on the nitrogen substituents of the 5,5',6,6'-tetrachlorobenzimidacarbocyanine chromophore **1** two basically different types of J-aggregates are formed. One type having a single J-absorption band, like TDBC, shows the phenomenon of coherent energy migration well characterized by time-resolved spectroscopy in the past. The other type exhibits a Davydov-splitted J-absorption band whose spectroscopical features, like the non-exponential fluorescence decay, the decrease of its fluorescence lifetime with inreasing temperature, the strong dependence of its fluorescence lifetime on the emission wavelength, the dependence of the position and shape of its fluorescence spectrum on the time delay of measurement, the pressure dependence of its absorption spectrum, and its optical activity cannot be understood on the basis of coherent energy migration. A consistent description of all properties observed provides the theory of incoherent energy migration. Presumedly it is the degree of disorder which determines the kind of energy migration.

Introduction

Coherent energy migration in J-aggregates of pseudo-isocyanine (PIC) and 5,5',6,6'-tetrachloro-1,1'-diehyl-3,3'-bis(4-sulfo-*n*-butyl)-benzimidacarbocyanine (TDBC) is now well established.[1-3] Due to strong coupling of molecules in the aggregates at very low temperature the radiative lifetime of the monomeric molecules is strongly shortened caused by delocalization of the excitation energy over more than 100 molecules. Consequently, dephasing within the coherence domain is with several ten picoseconds rather long. However, at room temperature the delocalization length is reduced by one order of magnitude to about 15 molecules, and dephasing happens within few femtoseconds.[4] For these reasons, coherent energy migration cannot explain the high efficiency of J-aggregates in spectral sensitization of silver halides which is powerful also within some picoseconds at room temperature.[5,6] In the present paper it will be shown that spectroscopy and photophysics of J-aggregates of one and the same chromophore can be drastically changed when the architecture of its aggregates is altered through variation of the nitrogen substituents which do not influence the

chromophoric system itself. In this way even optically active J-aggregates can be spontaneously generated from achiral monomeric precursors.[7] In respect to spectral sensitization it turned out that incoherent energy migration processes are dominant in many J-aggregates.

Experimental Results

The experiments were performed with the 5,5',6,6'-tetrachlorobenzimidacarbocyanine chromophore **1** present also in the dye TDBC whose 1,1'-substituents were *n*-alkyl groups of varied chain length, and whose
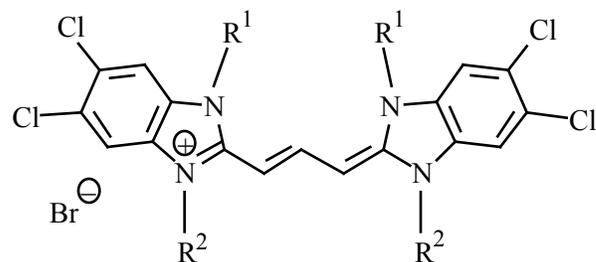
1

3,3'-substituents were either ω-sulfo-*n*-alkyl or ω-carboxy-*n*-alkyl groups of varied chain length likewise. As shown in Figure 1 in aqueous solutions two basically different types of J-aggregates are formed. One type (Figure 1a) exhibits only a single, very small J-absorption band in resonance with the fluorescence band. In dependence on the substituents both bands may be shifted in wavelength and varied in their halfwidth indicating different coupling strength and different disorder of the molecules in the aggregate. This type is preferred with 1,1'-di-*n*-alkyl substituents shorter than heptyl and with 3,3'-bis(ω-acido-*n*-alkyl) substituents shorter than ethyl or longer than propyl.

The other type (Figure 1b) displays in the absorption spectrum a so-called Davydov-splitted J-band having two or even three components whereas the fluorescence spectrum has one emission band likewise in resonance with the longest wavelength component of the absorption spectrum. This type comes out with 1,1'-di-*n*-alkyl substituents longer than hexyl and with the 3,3'-bis(2-acidoethyl) and 3,3'-bis(3-acido-*n*-propyl) substituents. In some instances

the two types can reversibly be converted one in another on changing the temperature, or the concentration, or the storage time of the solution.
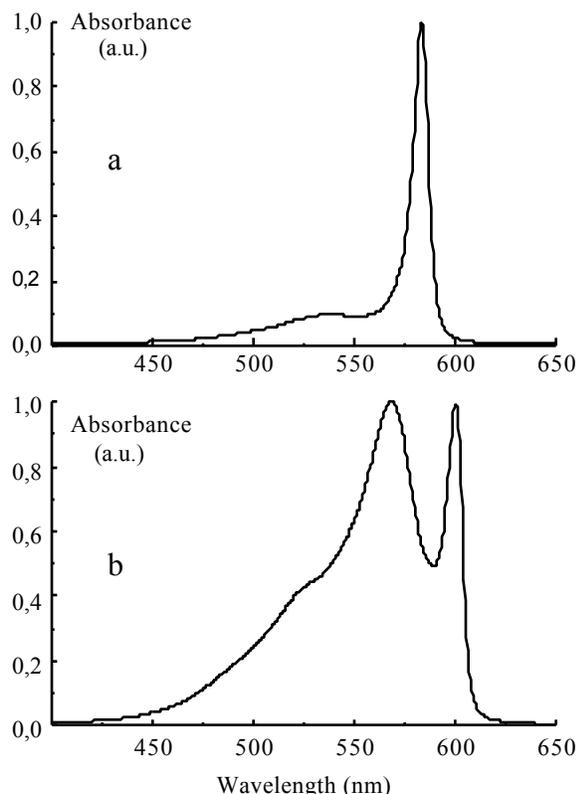

Figure 1. J-aggregate absorption spectra in 0.01 N sodium hydroxide solution containing 10% methnol
Dyes: *a = 1, $R^1 = C_8H_{17}$ $R^3 = C_4H_8COOH$*
          b = 1, $R^1 = C_7H^{15}$ $R^3 = C_3H_6COOH$

Similar to the spectral behaviour also the photophysical relaxation processes are quite different of the two types of J-aggregates. Figure 2 gives an example of the fluorescence decay curves. The decay is single-exponential for dye TDBC with one J-band, and clearly non-exponential for the fluorescence band of the Davydov-splitted J-aggregates. Assuming an overlap of three exponentials the fluorescence lifetimes of the three components are in the order of $\tau_1 = 20$-80 ps, $\tau_2 = 200$-300 ps, and $\tau_3 = 1500$-2000 ps depending on the temperature and detection wavelength.

Also the temperature dependence of the shortest fluorescence lifetime of both J-aggregate types is quite different as shown in Figure 3. Whereas the fluorescence lifetime of J-aggregates of TDBC having only one J-band increases with rising temperature due to the shortening of the exciton's delocalization length (Figure 3, curve a), the fluorescence lifetime of the Davydov-splitted J-aggregates strongly decreases with rising temperature because competing thermal deactivation processes are coming into play (Figure 3, curve b). Finally the fluorescence lifetime

depends on the emission wavelength in such a way that it increases at the lower energy side of the emission. But this increase is much more pronounced with the Davydov-splitted J-aggregates (Figure 4b) than with the J-aggregates of TDBC having only one single J-band (Figure 4a).
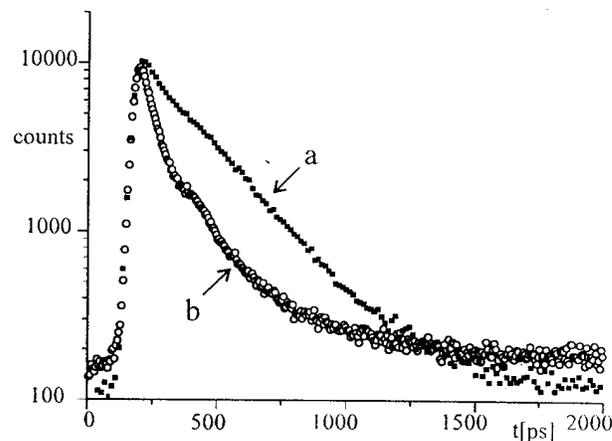

Figure 2. Fluorescence decay curves of J-aggregates in aqueous solution.
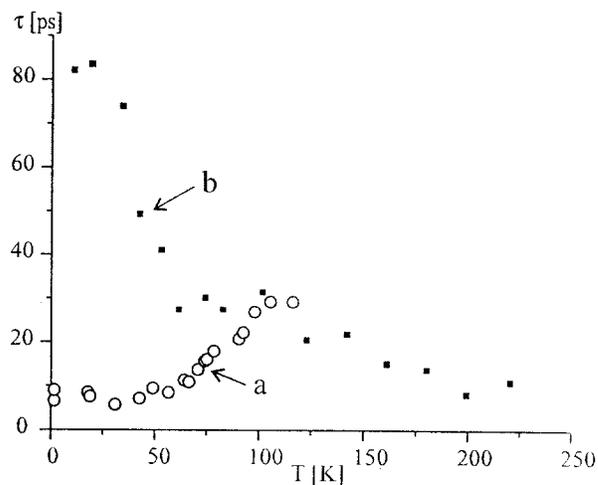*Dyes: a – TDBC; b – 1, $R^1 – C^3H^{17}$, $R^1 –C_3H_6COOH$.*

Figure 3. Fluorescence lifetime of -aggregates in dependence on temperature.
Dyes: a = TDBC; b 1, R_1 C_8H_{17} R_2 - C_3H_6COOH

Time-resolved fluorescence spectra bring about further information on the photophysics of the Davydov-splitted J-aggregates.[8] Measurements at 200 K show that on excitation at 532 nm the position and the shape of the fluorescence band depend on the time delay between the excitation pulse and the measurement. The longer this time delay the greater is both the dynamic Stokes-shift of the fluorescence band to the red (being 30 cm^{-1} when measured 100 ps after excitation) and the broadening of the fluorescence band indicating that there must be an overlap of two emission

bands. But no effect can be observed with excitation at 580 nm. The same is true for measurements at 50 K but the dynamic Stokes-shift as well as the broadening of the fluorescence band is less than at 200 K.
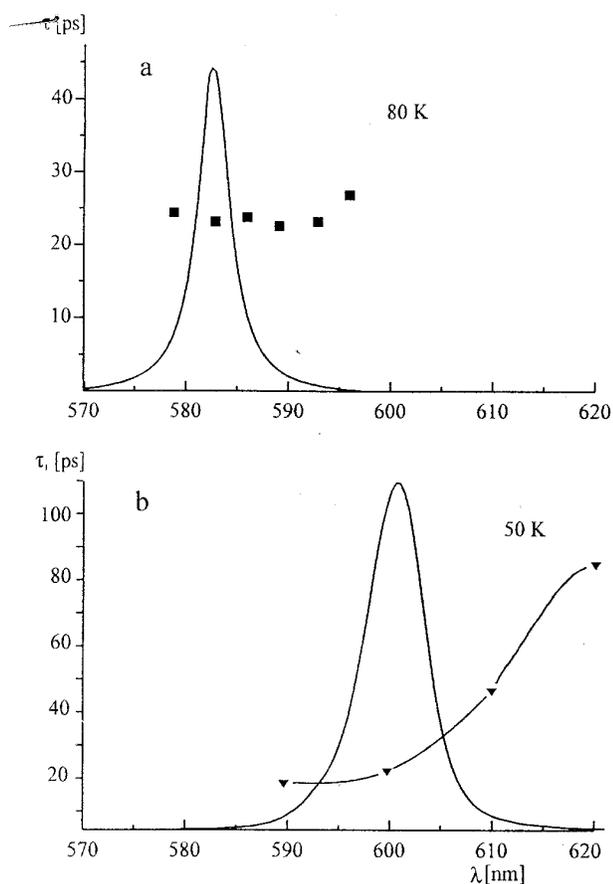

Figure 4. Fluorescence lifetime of J-aggregates in dependence on emission wavelength. The full line is the absorption spectrum for comparison. Dyes: a = TDBC; b = 1, R^1= C_8H_{17}; R^2 = C_3H_6COOH
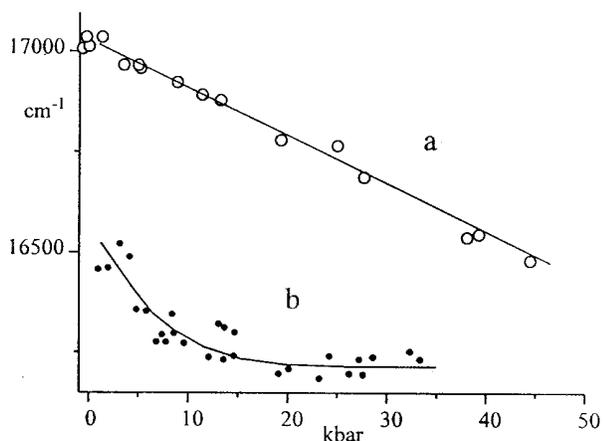

Figure 5. Pressure dependent' shift of the J-aggregates' absorption energy
Dyes: a = TDBC; b = 1, R^1 =C_8H_{17}; R^2 = C_3H_6COOH

Finally both types of J-aggregates manifest quite different dependences of their absorption spectrum on pressure. Whereas the J-aggregates of TDBC with increasing pressure show a linear red-shift of the position of their absorption band over the whole range of measurement (Figure 5, curve a) the red-shift of the absorption band of the Davydov-splitted J-aggregates is much stronger at pressures up to 15 kbar but keeps constant using higher pressures (Figure 5, curve b).

Discussion

Recapitulating the above mentioned results with the Davydov-splitted J-aggregates it would be impossible to explain them on the basis of coherent energy migration. But several other models are conceivable to give an interpretation. For instance, Kamalov et al.[9] applied the model of exciton self-trapping to explain energy relaxation in BIC (1, R^1 = C_2H_5; R^3 = $C_3H_6SO_4Na$) whose energy relaxation in some respects is similar to that of the Davydov-splitted J-aggregates. However, the self-trapping mechanism cannot explain the observed dependence of the dynamic Stokes-shift on excitation wavelength.

Therefore, the model of incoherent energy migration, designated also energy hopping model and first used to describe energy relaxation in organic polymers such as PPPV (para-polyphenylene-vinylene),[10,11] seems to correspond much better with the results observed. The model can be applied to ensembles of chromophores whose electronic transitions are inhomogeneously broadened due to disorder causing localization of the excitation energy. Then the primary excitation energy may randomly walk within the inhomogeneously broadened density of states (DOS) aided by strongly Coulomb correlated electron-hole pairs. The consequence would be that the hopping time of the excitons would depend on the excitation energy. As shown in Figure 6 a demarcation energy E_{loc} can be defined, above which the energy hopping process to sites having lower energy takes place causing a delay of the measured fluorescence lifetime at longer wavelengths whereas below E_{loc} the radiative recombination of the electron-hole pairs is more likely and thus there is no longer any wavelengths-dependent delay of the fluorescence lifetime. Incoherent energy hopping should be the stronger the greater the localization of the excitation energy meaning the greater the disorder in the J-aggregates. If the disorder should be of phonon-induced dynamic nature the effect should be slowed down on lowering the temperature as it was really observed. An important consequence of incoherent energy migration would be that the mean hopping time of the excitation should be much longer as compared to the exciton delocalization time of coherently coupled molecules.

It is obvious that the experimentally observed differences between J-aggregates having a single J-band like PIC and TDBC and those with Davydov-splitted absorption

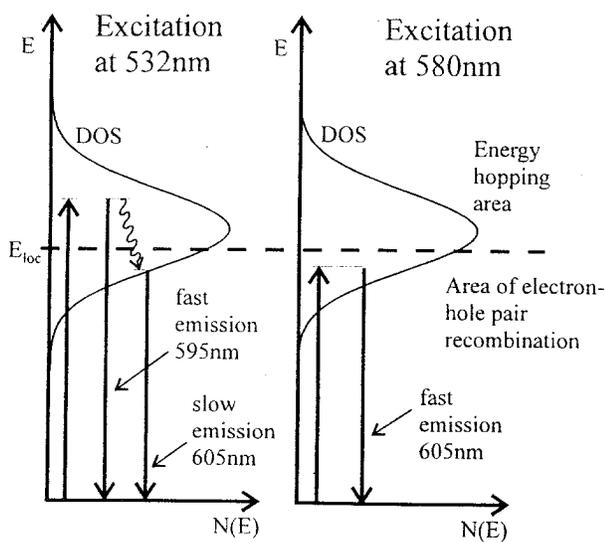bands can be well understood by the two models of coherent and incoherent energy migration.

Figure 6. Model of incoherent energy migration and energy hopping relaxation, respectively. DOS = density of states; E = energy; N (E) = quantity of states; E_{loc} = demarcation energy.

Coherent energy migration can tentatively be characterized by:[2,3]

- long dephasing time in the picosecond domain as shown by accumulated photon echos,
- single-exponential fluorescence decay,
- increase of the radiative lifetime with rising temperature due to shortening of the coherence length from more than 100 molecules at low temperature down to some 10 molecules at room temperature,
- small dependence of the fluorescence lifetime on the emission wavelength,
- insignificant dynamic Stokes-shift of the fluorescence spectrum.

On the other hand incoherent energy migration can tentatively be characterized by:[12]

- very short dephasing time in the femtosecond domain,
- non-exponential fluorescence decay,
- decrease of the radiative lifetime with rising temperature caused through competing radiation-ess relaxation processes,
- on short wavelength excitation strong dependence of the fluorescence lifetime on the emission wavelength, pronounced dynamic Stokes-shift of the fluorescence spectrum as well as broadening of the fluorescence spectrum brought about by

competition between fluorescence governed by the energy hopping and spontaneous fluorescence due to the fast recombination of Coulomb-correlated electron-hole pairs,

- on long wavelength excitation no dependence of the fluorescence lifetime on the emission wave-length, no dynamic Stokes-shift, and no broad-ening of the fluorescence spectrum due to preference of the spontaneous emission through recombination of the Coulomb correlated electron-hole pairs.

Structural Consequences

Eventually the reason for the quite different behaviour of the two types of J-aggregates originating from the same chromophore should be considered. As Davydov splitting of the J-aggregates' absorption spectrum exclusively occurs with dyes having 1,1'-di-*n*-alkyl substituents longer than hexyl in combination with 3,3'-bis(2-acidoethyl) or 3,3'-bis(3-acido-*n*-propyl) substituents it is obvious that the dyes must have amphiphilic lipid character. Such molecules are known to form micelles whose shape can be estimated from the so-called surfactant parameter N_s which is determined by the structure of the molecules considered. Ideal spheric micelles are produced by molecules with $N_s = 0.33$, ideal cylindric micelles are formed by molecules with $N_s = 0.5$, and planar lipid double layers are obtained by molecules having $N_s = 1.0$.[12] With dyes **1** the surfactant parameter N_s amounts near to 0.5 pointing to easy formation of cylindric micelles.[14]

The formation of micelles gives a plausible explanation of the different pressure dependences of the two types of J-aggregates shown in Figure 5. J-Aggregates with linear or planar structure like those of TDBC are obviously compress-ible over a wide range causing a linear red-shift of the transition energy proportional to decreasing distance between the molecules in the aggregates. As opposed to this beha-viour one has to assume that the cylindric micelles under pressure are first collapsing into flat-pressed tubes causing a strong red-shift of the transition energy whereas at higher pressures the distance between the molecules cannot be further diminished, and thus there is no longer any red-shift.

The assumption of micelle formation is in agreement with the results recently obtained by Harrison et al.[15] who proved experimentally that in the liquid-crystalline layers of an oxacarbocyanine dye indeed exist cylindrically shaped micellar structures. However, in contrast to the latter one, the much more diluted aqueous solutions of the Davydov-splitted J-aggregates of chromophore **1** are optically active[7,14] indicating that the molecules in these aggregates must be not only radially but even helically arranged. Only in this way the formation of left- and right-handed cylindrical micelles can be understood. Figure 7 shows a possible structure of such chiral micelles.
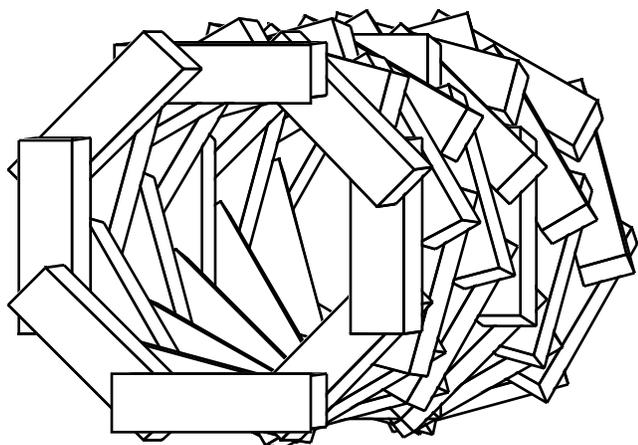
Figure 7. Model of a helical micelle of Davydov-splitted J-aggregates. The hydrophobic 1,1'-di-n-alkyl chains are confined within the inner core of the micelle

Conclusions

The new finding of spontaneous generation of optically active J-aggregates in aqueous solution from achiral precursors certainly will be important in the understanding of the laws of micelle formation as well as of the enantioselective processes which in primeval times must have taken place in nature. But with regard to the basic question for explaining the J-aggregates' high efficiency in spectral sensitization we have some indications that micellar structures are not the only possibility to enhance incoherent energy migration. Presumedly it is the degree of disorder in J-aggregates which governs the type of energy migration. By chance, high disorder is also present in micelles. Future research work will have to answer this question.

Reference

1. H.P. Dorn, A. Mueller, *Appl. Phys.*, **B43**, 167 (1987).
2. S. De Boer, K. J. Vink, D. A. Wiersma, *Chem. Phys. Lett.*, **137**, 99 (1987); S. De Boer, D. A. Wiersma, *Chem. Phys. Lett.*, **165**, 45 (1990).
3. J. Moll, S. Daehne, J. R. Durrant, D. A. Wiersma, *J. Chem. Phys.*, **102**, 20 (1995).
4. Ian Burgel, D.A.Wiersma, K.Duppen, *J. Chem.Phys.*, **102**, 20 (1995).
5. T. Tani, T. Suzumoto, K. Kemnitz, K. Yoshihara, *J. Phys. Chem.*, **96**, 2778 (1992).
6. A. A. Muenter, D. V. Brumbaugh, J. Apolito, L. A. Horn, F. C. Spano, S. Mukamel, *J. Phys. Chem.*, **96**, 2783 (1992).
7. U. De Rossi, S. Daehne, S. C. J. Meskers, H. P. J. M. Dekkers, *Angew. Chem.*, **108**, 827 (1996); *Angew. Chem. Int. Edit. Engl.*, **35**, 760 (1996).
8. We thank Drs. H. Port and U. Gomez, 3rd Institute of Physics, University of Stuttgart, Germany, for their cooperation to perform the time-resolved fluorescence measurements.
9. V. F. Kamalov, I. A. Struganova, K. Yoshihara, *J. Phys. Chem.*, **100**, 8640 (1996).
10. H. Baessler, V. Brandl, M. Deussen, E. O. Goebel, R. Kersting, H. Kurz, U. Lemmer, R. F. Mahrt, A. Ochse, *Pure Appl. Chem.*, **67**, 377 (1995).
11. U. Lemmer, R. F. Mahrt, Y. Wada, A. Greiner, H. Baessler, E. O. Goebel, *Chem. Phys. Lett.*, **209**, 243 (1993).
12. U. De Rossi, S. Daehne, U. Gomez, H. Port, to be published.
13. D. F. Evans, H. Wennerstroem, *The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology Meet*; VCH Publishers, New York, Weinheim, Cambridge, 1994.
14. A. Pawlik, S. Kirstein, U. De Rossi, S. Daehne, to be published.
15. W. J. Harrison, D. L. Mateer, G. J. T. Tiddy, *J. Phys. Chem.*, **100**, 2310 (1996).