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Exciton Dynamics in the J-Aggregates of a Carbocyanine Dye

J. Moll,^{1,3} S. Daehne,¹ J. R. Durrant,² and D. A. Wiersma²

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We report on the exciton dynamics in the J-aggregating dye 5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfobutyl)-benzimidazolocarbo-cyanine, which is known readily to form J-aggregates, even at room temperature and at a low concentration. We performed a series of time-correlated single-photon-counting experiments at different emission wavelengths and at different temperatures in the range between 1.5 and 125 K. Additionally, the temperature dependence of the relative fluorescence quantum yield was determined.

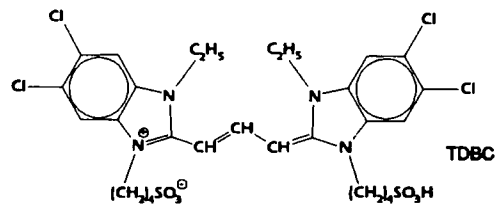
KEY WORDS: Exciton dynamics; J-aggregates; carbocyanine dye.

INTRODUCTION

J-aggregates were independently discovered by Scheibe [1] and Jelley [2] in the mid-thirties. They are assemblies of molecules with coherently coupled dipole transition moments showing an intense, narrow, and, relative to the monomers, red-shifted absorption band. J-aggregates are getting increasingly interesting not only in a fundamental sense, filling the gap between single molecules and bulk materials, but also for many applications. Today J-aggregates are used mainly for the spectral sensitization of photographic materials, but future applications in other fields such as optoelectronics and biology are possible.

The dye investigated in this paper, 5,5',6,6'-tetrachloro-1,1'-diethyl-3,3'-di(4-sulfobutyl)-benzimidazolocarbo-cyanine (TDBC), is known to easily form J-aggregates in water [3–5]. The sodium salt of TDBC was investigated some years ago by steady-state absorp-

tion [3,4] and circular dichroism [6] experiments at room temperature. Recently, TDBC has attracted some attention [5,7] because the absorption band of its J-aggregates is narrow ($\approx 230 \text{ cm}^{-1}$ at room temperature) and intense (molar absorption coefficients of up to $10^6 \text{ l mol}^{-1} \text{ cm}^{-1}$ per molecule). Additionally, TDBC does not form dimers or H-aggregates, which simplifies the interpretation of spectroscopic data.



EXPERIMENTAL

Samples were made from a highly concentrated stock solution of TDBC⁴ in doubly distilled water by dilution

⁴ TDBC was synthesized by Dr. Freyer.

¹ Federal Institute for Materials Research and Testing, Laboratory for Time-Resolved Spectroscopy, Rudower Chaussee 5, D-12489 Berlin, Germany.

² University of Groningen, Department of Chemistry, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands.

³ To whom correspondence should be addressed.

with ethylene glycol and water to the desired concentration. The experiments presented here were performed with samples in a 50/50% ethylene glycol/water mixture at concentrations of $4.4 \cdot 10^{-4}$ and $9 \cdot 10^{-5}$ M.

The steady-state and time-resolved fluorescence experiments were performed with samples having an absorbance of less than 0.2 (typically 0.1). The solution was filled in micrometer cuvettes with layer thicknesses between 5 and 30 μm , which were mounted on a copper sample holder and quickly cooled to about 100 K (≈ 15 min.). Then they were cooled to 1.5 K over a period of about 1 h. Experiments at higher temperatures were done by slowly heating the cryostat to the desired temperature.

Time-correlated single-photon-counting experiments were done using a synchronously pumped dye laser (Coherent CR599, dye: R6G). The pump laser was a mode-locked Ar⁺ laser (Coherent Innova 99). The dye laser was cavity dumped at a rate of about 94 kHz and the excitation intensities used were about 10^{11} photons cm^{-2} pulse⁻¹. The excitation wavelength was 562 nm. By variation of the laser power and comparison of the measured lifetimes, it was assured that they were not influenced by exciton–exciton annihilation [8,9]. The fluorescence from the time-resolved experiments was detected through a Zeiss M4 QIII prism monochromator and detected with a Hamamatsu microchannel plate (1534-U01V), yielding an overall system response time of about 30 ps (FWHM).

Static fluorescence and absorption spectra were measured with a conventional spectrofluorometer (Shimadzu RF-540) and spectrophotometer (Shimadzu UV 240), respectively. The fluorescence spectra were measured with a narrow (≈ 1 -nm) detection bandwidth and exciting the sample at 500 nm ($20,000 \text{ cm}^{-1}$) with a broad (≈ 10 -nm) excitation bandwidth.

RESULTS AND DISCUSSION

Figure 1 shows the absorption and fluorescence spectra of the J-aggregates of TDBC at 5 K, with maxima at about 581 nm ($\approx 17,210 \text{ cm}^{-1}$) and 582 nm ($\approx 17,180 \text{ cm}^{-1}$), respectively. Experimental determination of the temperature dependence of the relative fluorescence quantum yield (Fig. 2) was simplified by the fact that the absorption spectrum of the J-aggregates of TDBC does not change a lot below 180 K. This constancy probably is due to the fact that below the glass point of the solution (≈ 200 K), the aggregation equilibrium does not change any more and diffusion is very little. Assuming the absorption to remain constant below 125 K, which was approximately true for our sample

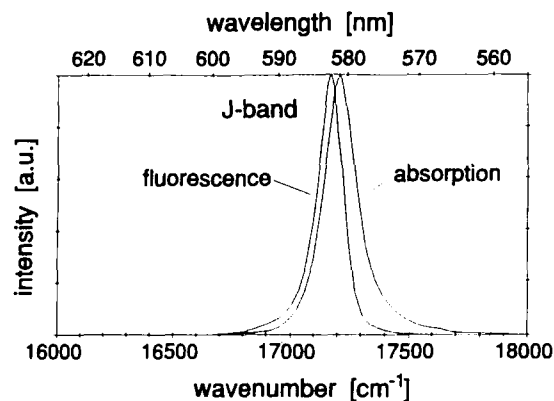


Fig. 1. Low-temperature (5 K) absorption and fluorescence spectrum of the J-aggregates of TDBC.

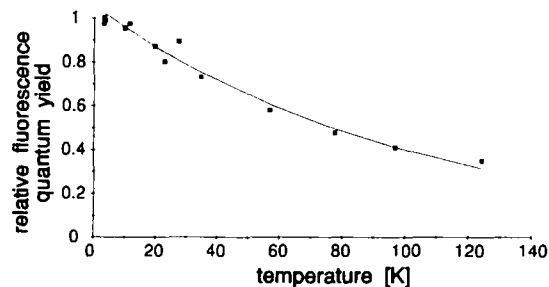


Fig. 2. Temperature dependence of the fluorescence quantum yield (relative values) of TDBC J-aggregates.

(deviations from the average values of the amplitude and width of the J-band were less than 5%), one can calculate the relative fluorescence quantum yield simply by comparison of the area of the fluorescence band. For the data in Fig. 2 we assumed the quantum yield to be 1 at 1.5 K, and to obtain absolute values, one would have to divide all values given in this paper by the absolute quantum yield of the sample at 1.5 K. The fact that the absolute fluorescence quantum yield was determined to be 0.25 at room temperature [4,10], together with the temperature dependence shown in Fig. 2, seems to indicate that the quantum yield really is close to 1 at 1.5 K. Clearly, the fluorescence quantum yield decreases with increasing temperature, at 125 K reaching a value about one-third of the fluorescence quantum yield at 1.5 K. The temperature dependence of the relative fluorescence quantum yield can be fit well by an exponential function (Fig. 2). We attribute this decrease in fluorescence quantum yield to a decreasing coupling between the molecules of the J-aggregates, leading to a decrease

in the size of the coherence domains and thus a decrease in the radiative decay rates (Fig. 3). Additionally, at higher temperatures an increasing number of temperature-activated relaxation channels may contribute to non-radiative deactivation of the exciton state, resulting in smaller fluorescence quantum yields at higher temperatures.

The temperature dependence of the radiative decay rates of TDBC at different emission wavelengths is shown in Fig. 3. The radiative lifetimes were obtained by dividing the measured fluorescence lifetimes by the relative fluorescence quantum yield (Fig. 2), assuming the quantum yield to be 1 at 1.5 K. A strong wavelength dependence at temperatures below 80 K and, depending on the emission wavelength, an increase in the radiative lifetime by a factor of 3–5 in the temperature interval between 10 and 125 K are observed for (Fig. 3). This behavior is similar to that observed PIC [11], where the fluorescence lifetime is almost constant below 50 K and increases by a factor of about 10 between 50 and 220 K. In the case of PIC, this increase in the fluorescence

lifetime is attributed to a dilution of the oscillator strength by a transfer of the population from the dipole-allowed state to other subradiant states [11]. This transfer is caused by exciton-phonon scattering, which also determines the optical dephasing of the exciton. A complete analysis of the low-temperature exciton dynamics including the investigation of the dephasing processes in the aggregates of TDBC is in preparation and will be published elsewhere [12].

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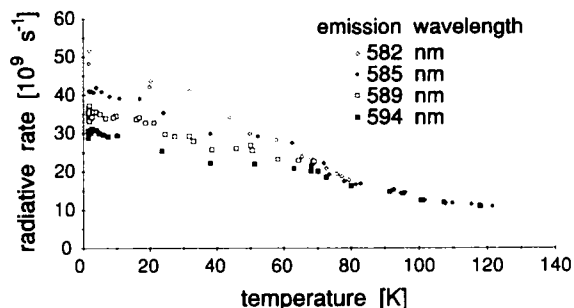


Fig. 3. Temperature dependence of the radiative decay rate of the TDBC J-aggregates for different emission wavelengths.