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Transient Isoemissive Point Observed in the Temperature-Dependent Fluorescence Decay of J-Aggregates Adsorbed on Silica Gel

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The nonexponential fluorescence decays of J-aggregates adsorbed on silica gel, acquired at various temperatures, intersect in a well defined point. The observation of this novel phenomenon requires excitation at the high energy side of the J-aggregate absorption band, whereas excitation at the maximum yields standard fluorescence decay behaviour with a steady slowdown at lower temperatures.

The fluorescence decay of cyanine J-aggregates adsorbed on silica gel and other inert substrates is nonexponential, with typically 90% contribution of lifetime 25 ps,$^{1)}$ when excited near the maximum of the J-aggregate absorption band. The fluorescence decay is independent of excitation and emission wavelength but strongly dependent on temperature, with the lifetime of the fast component increasing to 120 ps at 25 K. Below that temperature the fluorescence decay is independent of temperature down to 4 K.$^{1)}$ The preexponential factors in a three-exponential analysis are almost independent of temperature. When excited at the high energy side of the absorption maximum, however, the fluorescence decay becomes dependent on excitation and emission wavelength and the decays acquired at various temperatures display a unique "transient isoemissive point" (Fig. 1a). The integrated fluorescence decay curve is strikingly independent of temperature

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(Table 1) in contrast to the fluorescence decay itself, which displays a pronounced temperature dependence. Figure 1 a and b contrast the temperature-dependent fluorescence behaviour, when excited at 575 and 620 nm, respectively. Table 1 lists fluorescence lifetimes and preexponential factors together with the integrated fluorescence intensity as a function of temperature. To simplify analysis, the longest lifetime had been fixed to 2 ns in the range 200 - 4 K. The integrated fluorescence intensity, $\Sigma A_i\tau_i$, is independent of temperature with a mean standard deviation of ± 2.5%.

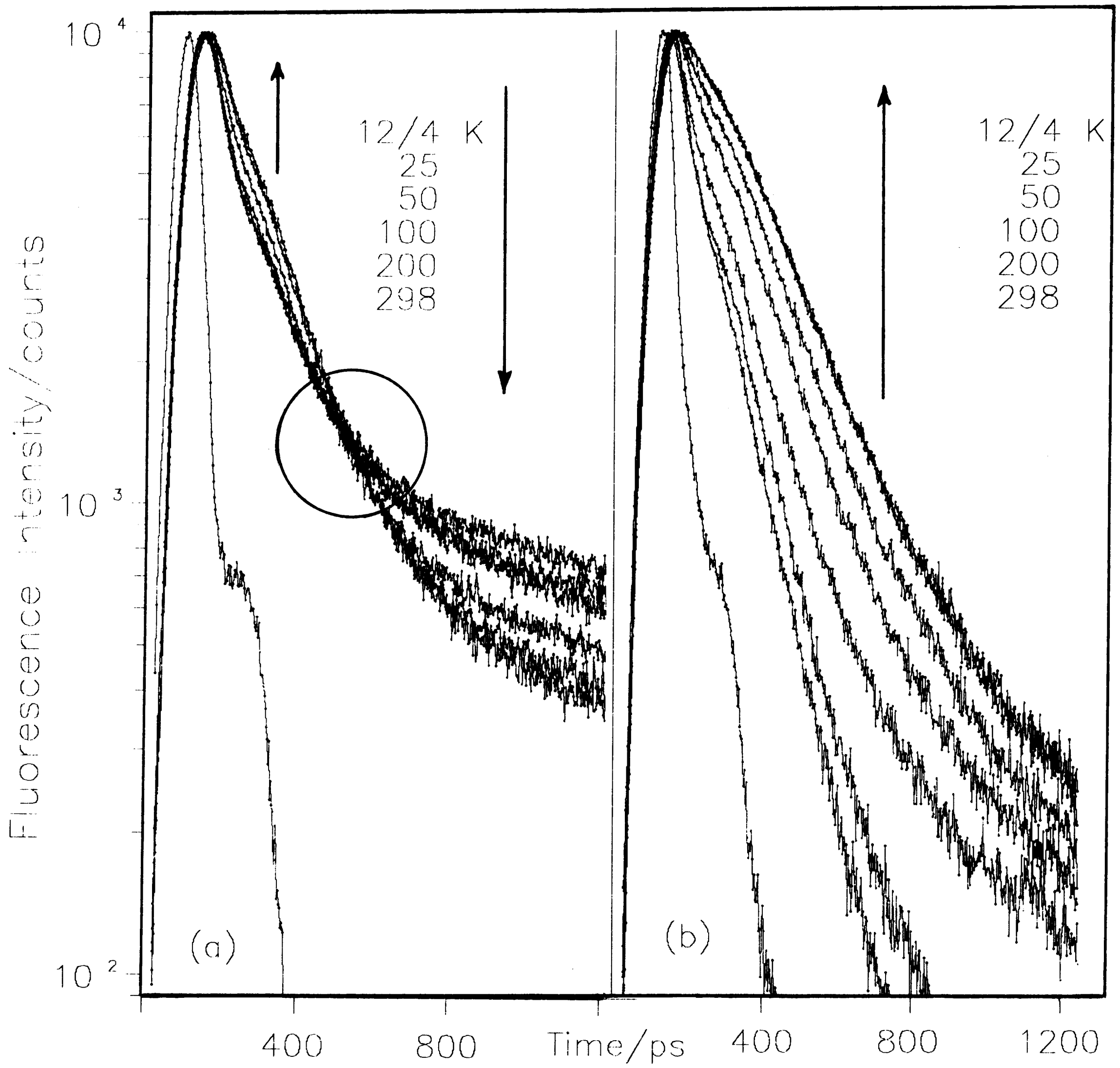

Fig. 1. Fluorescence decays in the temperature range 290 - 4 K. a) Excitation in the monomer region at 575 nm, the circle indicates the "transient isoemissive point". b) Excitation near the J-aggregate maximum at 620 nm. Emission is observed at 638 nm.

Table 1. Temperature-dependent fluorescence lifetimes (ps) and preexponential factors (%), obtained by three-exponential analysis

T	τ_1	τ_2	τ_3	A_1	A_2	A_3	$\Sigma A_i\tau_i$
298	54	182	2035	81.9	13.1	5.0	169.8
200	60	194	2000	81.8	13.5	4.7	169.3
100	65	224	2000	83.5	12.2	4.3	167.6
50	88	243	2000	87.0	9.2	3.9	176.9
25	102	235	2000	87.4	9.3	3.3	177.0
12	110	244	2000	89.0	8.0	3.1	179.4
4	113	254	2000	90.5	6.7	2.8	175.3

Figure 2 displays absorption spectra of J-aggregate and monomer of 5,5'-dichloro-3,3'-disulfopropyl-9-ethylthiacarbocyanine together with chemical structure. The arrow indicates the position of excitation, which is close to the monomer absorption maximum. The solid line represents the sample containing the J-aggregate and a small amount of the monomer species.

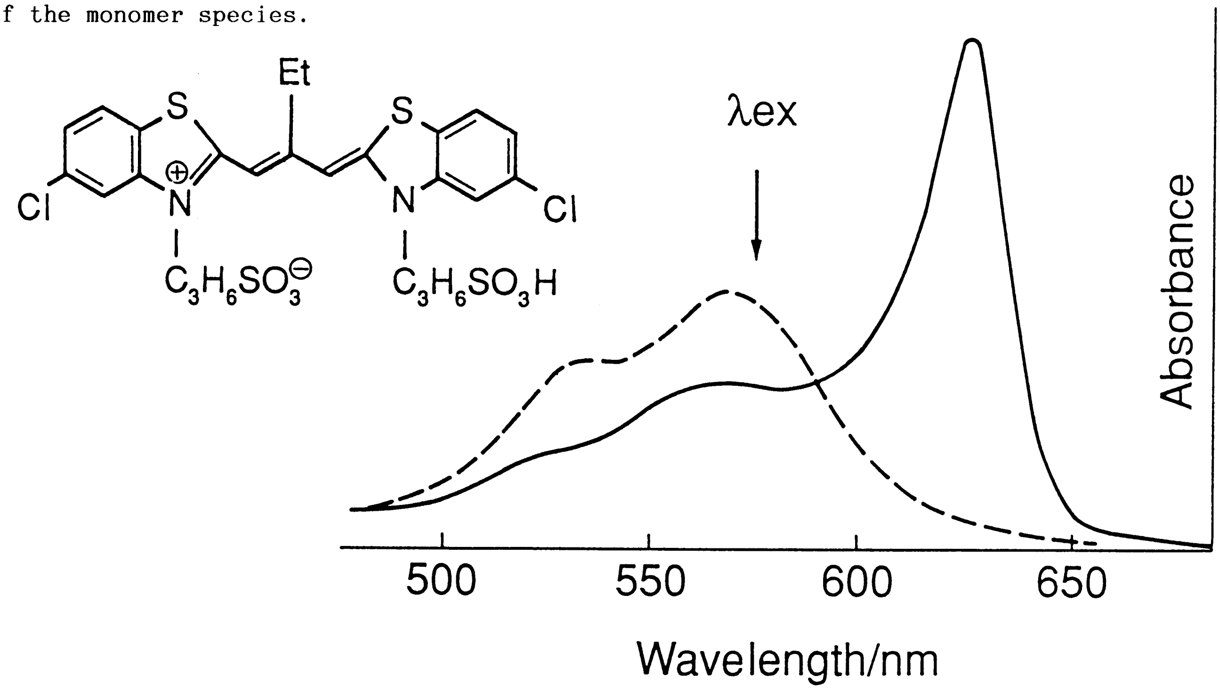

Fig. 2. Absorption spectra of J-aggregate (solid) and monomer (broken), and chemical structure. The emission band of the J-aggregate (not shown) is centered around 650 nm, that of the monomer species around 590 nm.

Figure 3 shows the fluorescence decays observed at different wavelengths, excited at 575 nm. The fluorescence decay displays a pronounced dependence on the wavelength of observation. The slow single-exponential decay observed at 590 nm is attributed to the emission of the monomer species. It has a lifetime of 2 ns and shows a clear rise of about 60 ps. The contribution of this monomer fluorescence decreases drastically when the fluorescence decay is observed at increasingly longer wavelengths, i.e., from 100% observed at 590 nm to 9% at 620 nm, and to 2.5% when observed at 640 nm. The decay time of the fast component is about 40 ps.

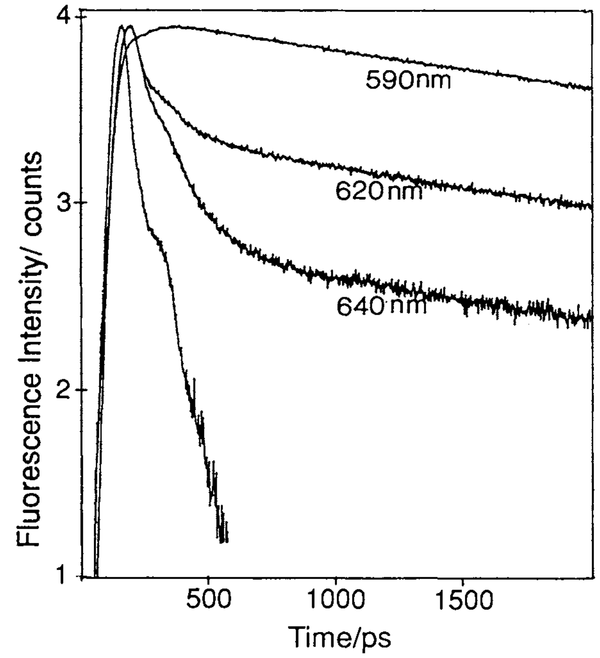

Fig.3. Dependence of fluorescence decay on observation wavelength. T = 298 K. Excitation wavelength is 575 nm. Observation wavelengths are indicated in the figure.

We interpret the rising part in the fluorescence decay observed at 590 nm as being caused by some mechanism of energy transfer from blue-edge excited J-aggregate or from excited aggregates of intermediate size that absorb at around 575 nm.

The samples studied in this work are described elsewhere, together with employed time-correlated single photon counting system and data analysis.$^{1-2)}$

Concluding we state that the above novel kinetic phenomenon is not yet understood in detail, and that the aesthetic aspect of the "transient isoemissive point" by itself would justify further investigation.

References

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