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Time-resolved excited state dynamics of a cyanine dye

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Received 5 September 1998

Abstract

The photophysics and isomerization dynamics in the excited state of a cyanine dye, 3,3'-di(3-sulfopropyl)-thiacyanine triethylammonium salt was investigated. Using the femtosecond time-resolved fluorescence up-conversion technique, wavelength-dependent fluorescence dynamics was observed and the theoretical prediction of the dual fluorescence behavior was vindicated. The results were explained using a barrierless isomerization reaction model. The origins of two decay components were assigned to the relaxation within the excited state and the $S_1 \rightarrow S_0$ transition, respectively, and the time constants were obtained. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Cyanine dyes have been of continuous interest for nearly three decades because of their extensive applications in photosensitization [1,2], biomedicine [3] and laser technology [4]. Their photophysical and photochemical properties were revealed to be unique. In solution, compared with ordinary dyes, their excited state lifetimes were very short (\sim ps) [5] and their fluorescence quantum efficiency might be very low [4]. This was due to the facile radiationless decay, which was the main relaxation path. The radiationless decay of this kind of material was considered to result from torsional motion about the C–C bond [6], which leads to *cis–trans* isomeriza-

tion. In particular, the shortest chain member of the series of material [7], in which the *cis–trans* isomerization proceeded rapidly, was even considered to be a representative of the barrierless isomerization reaction. The environment was found to influence the *cis–trans* isomerization of this kind of material markedly. Experimental results showed that the fluorescence efficiency was greatly enhanced when the dye was absorbed to a substrate [8], or incorporated into an organized assembly [3], where the torsional movement was limited.

To explain these unique photophysical and photochemical properties of cyanine dyes, several models, based on a barrierless isomerization reaction, have been developed since the initial idea was proposed by Oster and Nishijima in 1956 [9]. Later, the initially proposed flat excited state potential surface was modified into a harmonic type and a *sink* function representing the probability of radiationless de-

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cay to the ground state was included to describe the coordinate dependent non-radiative relaxation process. The most recent theory was suggested by Bagchi, Fleming and Oxtoby (BFO theory) [10]. In this theory, the reaction coordinate was the torsional angle between the two conjugated systems. Due to the steric interaction between the two systems, the excited state potential surface was a kind of downhill harmonic type. The proposed energy scheme is illustrated in Fig. 1c. When molecules were pumped to the excited state, they relaxed to the point of the minimum energy-gap, i.e. the *sink* point, along the downhill slope of the excited state potential surface. At the *sink* point, the excited molecules rapidly decayed radiationlessly to the ground state and torsional isomerization happened simultaneously. Some time-resolved work, including excited state absorption (ESA), ground state recovery (GSR) and stimulated emission (SE) experiments, has been done on 1,1'-diethyl-4,4'-cyanine (1144-C Fig. 1a) [11,12] by Åberg et al. Theoretical calculations have also been done based on a model of a barrierless excited state potential surface [13]. All of the results obtained were consistent with BFO theory. From the theoretical and experimental results, dual fluorescence was predicted [12]. Åberg et al. also made fluorescence measurements [12] using the time-correlated single-

photon counting (TCSPC) technique with an effective time resolution of about 10 ps after deconvolution. Unfortunately, limited by the time resolution and low quantum efficiency, dual fluorescence was not observed in their experiment.

In this Letter, we report the dual fluorescence behavior of a cyanine dye, 3,3'-di(3-sulfopropyl)-thiacyanine triethylaminiun salt (Fig. 1b), using the femtosecond time-resolved fluorescence up-conversion technique [14]. At the longer wavelength region of the fluorescence spectrum, the fluorescence showed a single exponential decay with a time constant of 5.8 ps; at the shorter wavelength, fluorescence showed two exponential decays with time constants of ≤ 1.1 ps and ≈ 5.4 ps, respectively. The amplitudes of the two exponential components varied with the wavelength. These results indicated wavelength-dependent dynamics and are explained using the model of Åberg et al.

2. Experiments and results

The dye was synthesized according to the method given by Hamer [15] and Ficken [16]. A solution of the dye in methanol, with a concentration of $\sim 5 \times 10^{-5}$ M, was used for steady-state spectral measurements. Excitation and fluorescence spectra were recorded with a Hitachi F-3000 spectrometer. Absorption spectra were recorded using a UVIKON 810 spectrometer. The steady-state absorption spectrum (dotted line) is illustrated in Fig. 2. The steady-state excitation spectrum (thin solid line) and fluorescence spectrum (thick solid line) are also illustrated in Fig. 2 for comparison. The absorption spectrum showed a single sharp feature at 426 nm with a moderate shoulder at 402 nm. The excitation spectrum was a kind of bimodal curve with two peaks located at 390 and 441 nm, respectively. The fluorescence spectrum showed a round peak at 484 nm with a long tail. Comparing these spectra, it was surprising that the excitation spectrum was different from the absorption spectrum and that the absorption spectrum was not a mirror image of the fluorescence spectrum. These phenomena are scarcely observed but have happened with dyes [17] similar to ours. These phenomena might be explained by the isomerization process between the dyes two isomers which absorb

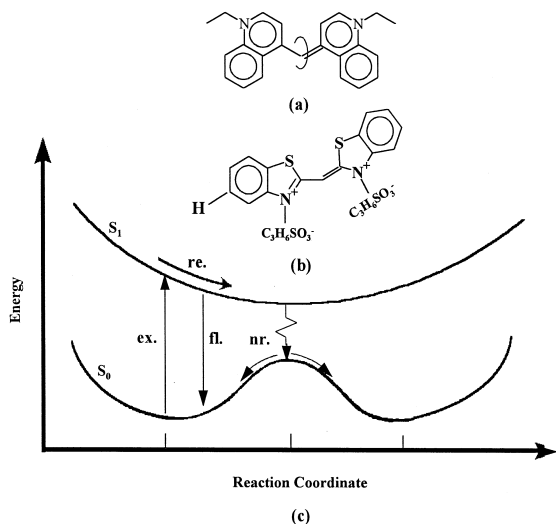


Fig. 1. (a) 1,1'-Diethyl-4,4'-cyanine. (b) 3,3'-Di(3-sulfopropyl)-thiacyanine, triethylaminiun salt. (c) The excited state potential surface of a barrierless isomerization reaction.

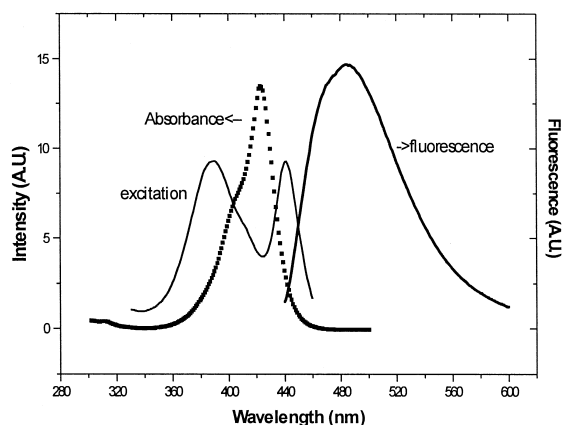


Fig. 2. The steady-state fluorescence spectrum (thick solid line, $\lambda_{\text{ex}} = 426$ nm), absorption spectrum (dotted line) and excitation spectrum (thin solid line, $\lambda_{\text{em}} = 480$ nm) of 3,3'-di(3-sulfopropyl)-thiacyanine, triethylammonium salt.

photons at different energy. A detailed analysis of steady-state spectra, together with electron spin resonance ESR and computational results, will be reported elsewhere [18].

A 2×10^{-4} M solution of the dye in methanol was used for the time-resolved experiments. The experimental arrangement is illustrated in Fig. 3. The light source was a Ti:Sapphire laser (Coherent Mira 900F) pumped by a continuous wave, multiline argon ion laser (Coherent Innova 415). The laser pulses of 820 nm had a duration of 115 fs (full width at half maximum) and a repetition of 76 MHz. The energy

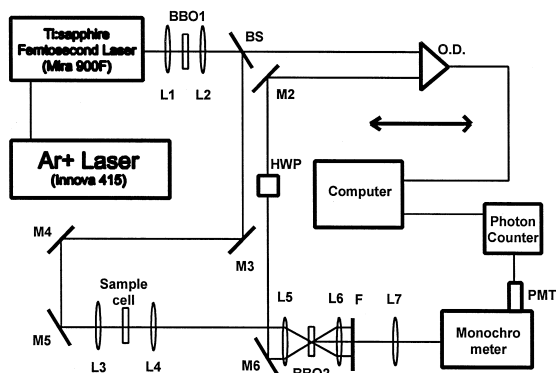


Fig. 3. The scheme of the fluorescence up-conversion setup. BBO, BBO crystal; BS, beam splitter; HWP, half-wave plate; L, lens; M, mirror; F, filter; PMT, photomultiplier tube; OD, optical delay line.

of each pulse was about 24 hJ. The fundamental pulses were focused onto a 0.5 mm thick type I BBO crystal (BBO1). The second harmonic generation (410 nm) with an energy of 0.66 nJ/pulse was reflected by a beam splitter and used to excite the dye molecules. The remaining fundamental pulses (8 nJ/pulse), used as gate pulses, passed through a half-wave plate and an optical delay line which varied the optical path that the fundamental pulses passed. The fluorescence from the dye solution was collected and collimated with the parallel-polarized gate pulses. The two beams were then focused onto another type I BBO crystal (BBO2) to generate an up-conversion signal. After a band-passing filter, the fluorescence and the gate pulses were both absorbed and the up-conversion signal beam was focused using the lens L7 onto the entrance slit of a 0.35 m monochromator. A Hamamatsu R585 photomultiplier detected the signal and sent it to a Hamamatsu C5410 photon counter. The digitalized output of the photon counter was collected by a personal computer, which also controlled the operation of the optical delay line.

Several fluorescence decays at various wavelength were obtained. Two typical curves are illustrated in Fig. 4. The results were fitted using a sum of two exponential functions or a single exponential function, depending on the probing wavelength. The fitting parameters are listed in Table 1, where α is

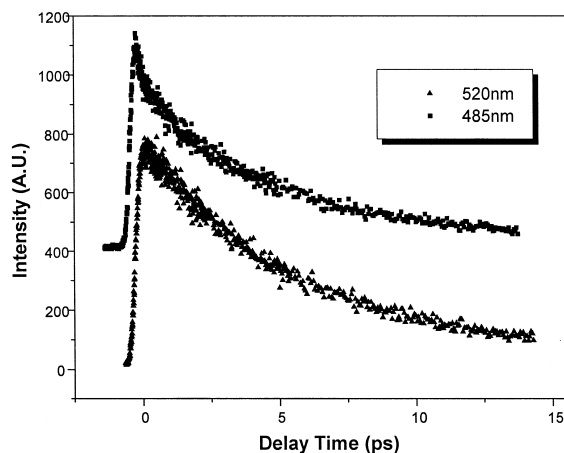


Fig. 4. Time-resolved fluorescence decay curves of 485 nm (squares) and 520 nm (triangles). The curve of 485 nm was shifted horizontally and vertically for clarity.

Table 1

Parameters obtained from exponential fits to the fluorescence decay curves

Wavelength (nm)	Mono-exponential fitting results τ (ps)	Two-exponential fitting results τ_1		Two-exponential fitting results τ_2	
		(ps)	α_1	(ps)	α_2
520	5.8	×		×	
500	×	1.1	0.10	5.5	0.90
485	×	0.72	0.22	5.35	0.78
470	×	0.3	0.25	5.3	0.75

×: not available.

Mono-exponential fitting function: $I(t) = I_0 \exp(-(t - t_0)/\tau)$.Two-exponential fitting function: $I(t) = I_0\{\alpha_1 \exp(-(t - t_0)/\tau_1) + \alpha_2 \exp(-(t - t_0)/\tau_2)\}$.

the amplitude of the corresponding exponential component and τ the time constant. From Table 1, it is obvious that the excited state relaxation dynamics varied with wavelength. This phenomenon was consistent with the prediction of Aberg et al. and could be explained using the barrierless isomerization scheme.

In the framework of BFO theory, the fluorescence decays reflected the excited state relaxation dynamics. For molecules at a particular point on the excited state potential surface, there exist two decay processes: relaxation within the excited state potential surface and transitions from the excited state to the ground state. For dyes such as 1144-C and 3,3'-di(3-sulfopropyl)-thiacyanine triethylaminium salt, at the minimum of the energy gap, i.e. the *sink* point, the radiationless decay rate was so great that there were few excited molecules at this point. The scarcity of excited molecules at this point provided a force to drive molecules at nearby points to this point. Thus, it was impossible to reach a thermal equilibrated excited state from which fluorescence was emitted. Therefore, as well as a component representing the $S_1 \rightarrow S_0$ transition, the fluorescence will include an extra component reflecting the relaxation process within the excited state potential surface. Nevertheless, for fluorescence at a different wavelength, the proportion of this component was different. Because the excited state potential surface was a downhill type, the further away from the *sink* point, the more the relaxation process within the excited state potential surface contributed to the change of the population and the faster the population decay; then the larger the corresponding component and the shorter the time constant. In Table 1, this trend has been

clearly shown. Fluorescence at a longer wavelength, i.e. closer to the *sink* point, exhibited a single exponential decay with a relative longer time constant (5.8 ps). This component came from the $S_1 \rightarrow S_0$ transition. As the detecting wavelength became shorter, the decay became non-exponential and could not be described using a single exponent function. A faster decay component (≤ 1.1 ps) coming from the relaxation within the excited state emerged and a fitting function of a sum of two exponential functions had to be adopted. The shorter the wavelength, i.e. the further away from the *sink* point, the larger the faster component and the shorter the corresponding time constant.

The fluorescence decays of the dye in pentanol and other alcohol solvents, which were more viscous than methanol, were also measured. The results showed that the time constant of the slower component was elongated to several decades of picoseconds whereas that of the faster component changed little. According to the model, the larger viscosity would hinder the torsional rotation, which resulted in a reduction of the $S_1 \rightarrow S_0$ radiationless decay rate at the *sink* point and an elongation of the excited state lifetime. Details of these experiments and discussion will be reported elsewhere [19].

3. Conclusion

Excited state dynamics of a cyanine dye, 3,3'-di(3-sulfopropyl)-thiacyanine, triethylaminium salt, was studied using the time-resolved fluorescence up-conversion technique. Fluorescence decays at various wavelengths were recorded and analyzed. By

comparing the fluorescence decays, a dependence of the fluorescence decay rates on the wavelength was observed. The result was explained using a barrierless isomerization reaction model.

Acknowledgements

This work was supported by National Natural Science Foundation of China under grants No. 19525412 and 19884001, National 86.3 High-tech Young Scholar Foundation and National Climing Plan, China.

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