

Time-Resolved Fluorescence of Crown Ether Styryl Dyes

M. V. Alfimov,¹ V. F. Kamalov,^{1,2} I. A. Struganova,^{2,3} and K. Yoshihara⁴

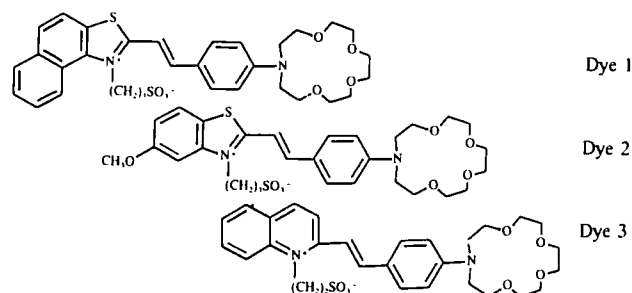
Received October 18, 1993

Photophysical processes are studied in a new class of dyes containing a chromophoric part and a crown ether part. Fluorescence decays were observed to be strongly dependent on temperature in the range from 294 to 4 K. Photoinduced isomerization and electron transfer are considered as possible mechanisms to explain the results.

KEY WORDS: Crown ether styryl dyes; time-resolved fluorescence.

INTRODUCTION

Crown ethers covalently linked to styryl dyes are a new class of dye molecules, which was synthesized recently [1,2]. These dyes contain crown ether on one side and a chromophoric part on the other side. The family of crown ethers is a subject of great interest [3], but the absence of visible and near-UV absorption prevents studying these molecules by optical spectroscopy in this region. The combination of crown ether and a chromophoric part in one molecule gives versatile possibilities of molecular functions. In this paper we present the results of a study of the photophysical processes of three compounds of crown ether styryl dyes.



¹ Institute of Chemical Physics Russian Academy of Sciences, Kosygin Street 4, 117977, Russia.

² Kwansai Gakuin University, Uegahara, Nishinomiya 662, Japan.

³ Lasers for Photochemistry Ltd., Novatorov Street 7/a, Moscow, Russia.

⁴ Institute for Molecular Sciences, Myodaiji, Okazaki 444, Japan.

The structure of the dyes studied allows us to suppose that the trans-cis isomerization around the C=C double bond could be the main mechanism of excited-state relaxation (similar to the well-known trans-cis isomerization of stilbene [4-7]). To show the existence of photoinduced trans-cis isomerization in dyes, their fluorescence decays at different temperatures were measured.

Data obtained for Dye 3 are essentially different from those for Dyes 1 and 2. Photoinduced electron transfer is proposed as a possible excited-state relaxation channel of Dye 3.

EXPERIMENTAL

The time-correlated single-photon counting technique was used to measure the fluorescence decays [8]. The specific apparatus used in this study has been described previously [9]. The instrumental response, measured by scattering of the excited laser pulse in colloid, gave a pulsewidth of 70 ps (FWHM). The repetition rate of the dye laser (rhodamine 6G used as active medium; pulsewidth about 10 ps) was 1 MHz and the count rate was always kept below 10 kHz.

Crown ether styryl dyes, Dyes 1-3, were synthesized by S. P. Gromov and coauthors. The method of synthesis is described elsewhere [1,2,10]. The solutions of dyes in ethanol and water/ethylene glycol mixtures

were studied at a concentration of 10^{-5} M. The absorption spectra of the dyes studied were similar and characterized by a broad structureless absorption band with a maximum at 538 nm for Dye 1, 536 nm for Dye 2, and 532 nm for Dye 3 (FWHM, about 30 nm).

The wavelength of excitation was 595 nm close to the 0–0 transition. The wavelength of observation was chosen close to the maximum of the fluorescence band. The excitation beam was linearly polarized, and the polarizer used before the monochromator was mounted at a magic angle (54.7°). An optical helium cryostat (Oxford Instruments) was used to vary the temperature from 295 to 4 K.

RESULTS AND DISCUSSION

Fluorescence decay profiles of Dye 1 measured at different temperatures are shown in Fig. 1. The fluorescence decay profiles were fit with a single exponential. Fittings are shown in Fig. 1 as smooth solid lines. These are with a χ^2 (least-squares normalized deviation of residuals) value of 1.25 and a decay time of 500 ps at 285 K, a χ^2 of 1.25 and decay time of 890 ps at 255 K, and a χ^2 of 0.97 and decay time of 2.42 ns at 118 K. The temperature dependence of the fluorescence decay profiles of Dye 2 is similar to that of Dye 1. Fluorescence

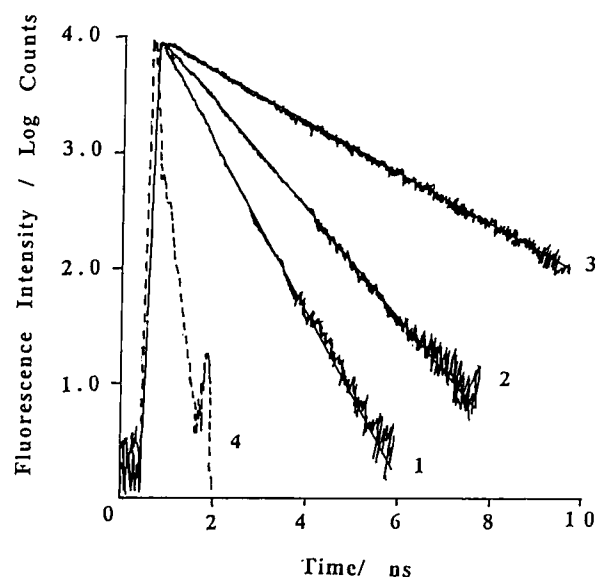


Fig. 1. Fluorescence decay curves for crown ether styryl Dye 1 in ethanol at different temperatures: 285 K (curve 1), 205 K (curve 2), and 118 K (curve 3). Solid lines are the best fit by single-exponential decay, convoluted with the instrument response function (curve 4).

lifetimes of Dyes 1 and 2 in ethanol obtained at different temperatures are plotted in Fig. 2 (curves 1 and 2, respectively). For both Dye 1 and Dye 2, fluorescence lifetimes increase monotonically with a decrease in temperature from 294 to about 180 K and are constant at lower temperatures.

It can be seen that the fluorescence lifetimes of Dyes 1 and 2 in ethanol at room temperature are shorter than the (nanosecond) radiative lifetimes. Both the temperature dependence of the fluorescence lifetime and the structure of dyes suggest that isomerization around the C=C double bond is the nonradiative relaxation channel which decreases the fluorescence lifetime of Dyes 1 and 2. The hypothesis of isomerization is supported also by the study of the fluorescence lifetime viscosity dependence of Dye 2 [10]. The observation of no changes at temperatures below the freezing point of ethanol (156 K) indicates that the isomerization is the main channel of the relaxation of the excited electronic state.

We used Kramers' model for the first estimation of the photoinduced isomerization activation barrier [11]. The activation barrier ΔE was calculated to be $\Delta E = 2.30$ kcal/mol for Dye 1 and 1.52 kcal/mol for Dye 2. A more detailed description is given in Ref. 12.

In Fig. 3 the fluorescence decay profiles of Dye 3 in ethanol at temperatures of 285 K (curve 1), 220 K (curve 2), and 170 K (curve 3) are presented. The best

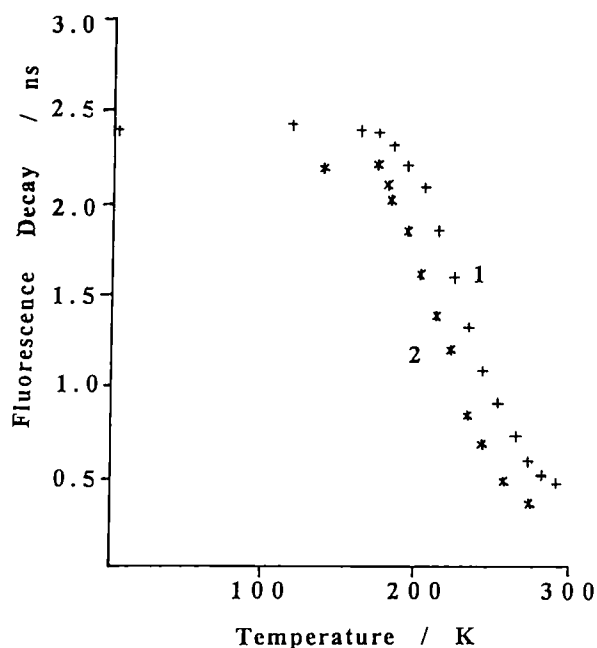


Fig. 2. Fluorescence decay time temperature dependence for crown ether styryl dyes in ethanol: curve 1, Dye 1; curve 2, Dye 2.

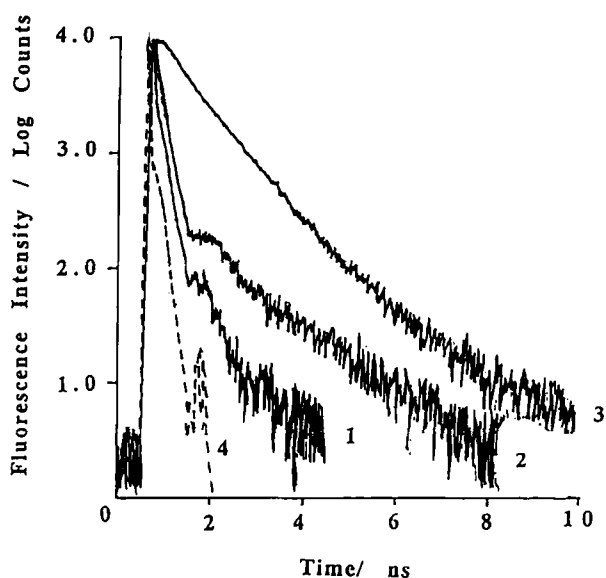


Fig. 3. Fluorescence decay curves for Dye 3 in ethanol at different temperatures: 285 K (curve 1), 220 K (curve 2), and 170 K (curve 3). Curve 4, response function.

fit was obtained with two exponents with the following parameters: lifetimes $\tau_1 = 26$ ps (fast component) and $\tau_2 = 200$ ps (slow component), ratio of preexponential factors $A_1/A_2 = 15.0$ at 285 K; $\tau_1 = 130$ ps, $\tau_2 = 1.55$ ns, and $A_1/A_2 = 10.0$ at 220 K; and $\tau_1 = 800$ ps, $\tau_2 = 2.6$ ns, and $A_1/A_2 = 10.0$ at 170 K. The fluorescence decay looks nonexponential from room temperature to 150 K; from 150 to 4 K the fluorescence decay can be fitted by a single exponent. In Fig. 4 fluorescence lifetimes (fast and slow components) of Dye 3 in ethanol are presented. The slow component of fluorescence decay increases monotonically from 35 ps to 2.6 ns in the temperature range from 294 to 180 K and stays constant at lower temperatures. The fast component increases from 20 ps at 295 K to 2.6 ns at 100 K and then stays also constant. Similar fluorescence decay profile temperature dependences were observed for Dye 3 in a water/ethylene glycol mixture.

Comparing the fluorescence decay temperature dependences of Dyes 1 and 2 and Dye 3, it is clearly seen that they are very different. The fluorescence decay of Dye 3 at room temperature is not exponential and more than 10 times faster than those of Dye 1 and Dye 2. The temperature range in which fluorescence decays undergo significant changes in the case of Dye 1 and Dye 2 (Fig. 2) also is different from that of the fast component of Dye 3 (Fig. 3). These data allow us to suppose that the nature of the main relaxation channel of the excited elec-

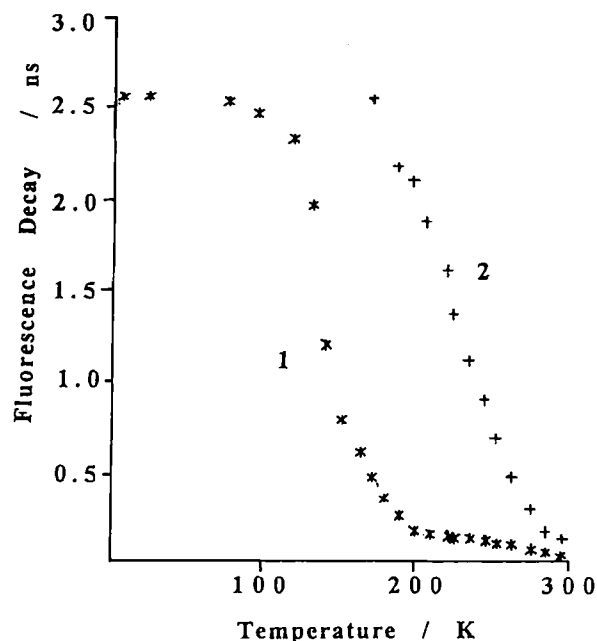


Fig. 4. Fluorescence decay time temperature dependence of Dye 3 in ethanol. Curve 1, fast component of decay; curve 2, slow component.

tronic state of Dye 3 in an ethanol and water/ethylene glycol mixture is different from those of Dyes 1 and 2.

The possible relaxation channel is photoinduced intramolecular electron transfer, because Dye 3 has a strong electron donor (dimethylaniline fragment) and a strong electron acceptor (quinoline heterocycle). Dyes 1 and 2 have the same electron donating part, but both of them do not have a strong acceptor part. This is the reason that in the case of Dyes 1 and 2, electron transfer is nonefficient and photoisomerization is the main relaxation channel of the excited electronic state. More detail study to support this assumption is in progress now.

CONCLUSION

Relaxation of the excited electronic state of three new crown ether styryl dyes in ethanol and water/ethylene glycol mixtures was studied. The photoinduced isomerization is proposed to be the main channel of non-radiative relaxation of the S_1 state of Dyes 1 and 2. The possibility that photoinduced electron transfer is the main channel of nonradiative relaxation of the S_1 state of Dye 3 is discussed.

ACKNOWLEDGMENT

We would like to thank Dr. O.A. Fedorova and Dr. S. P. Grumov for providing us crown ether styryl dyes.

REFERENCES

1. S. P. Gromov, M. V. Fomina, E. N. Ushakov, I. K. Lednev, and M. V. Alfimov (1990) *Dokl. Acad. Nauk SSSR* **314**, 1135.
2. S. P. Gromov, O. A. Fedorova, E. N. Ushakov, O. B. Stanislavsky, I. K. Lednev, and M. V. Alfimov (1991) *Dokl. Acad. Nauk SSSR* **317**, 1134.
3. F. Vogtle and E. Weber (Eds.) (1985) *Host-Guest Complex Chemistry Macrocycles*, Springer, Berlin.
4. J. Saltiel and J. T. D'Agostino (1972) *J. Am. Chem. Soc.* **94**, 6445.
5. J. A. Syage, P. M. Felker, and A. H. Zewail (1984) *J. Chem. Phys.* **81**, 4706.
6. J. H. Frederick, Y. Fujiwara, J. H. Penn, K. Yoshihara, and H. Petek (1991) *J. Phys. Chem.* **95**, 2845.
7. M. Sumitani, N. Nakashima, K. Yoshihara, and S. Nagakura (1977) *Chem. Phys. Lett.* **51**, 183.
8. D. V. O'Connor and D. Phillips (1984) *Time-Correlated Single Photon Counting*, Academic Press, London.
9. K. Kemnitz, N. Tamai, I. Yamazaki, N. Nakashima, and K. Yoshihara (1986) *J. Phys. Chem.* **90**, 5094.
10. M. V. Alifimov, O. E. Buevich, O. A. Fedorova, S. P. Gromov, V. F. Kamalov, and A. P. Lifanov (1991) *Dokl. Akad. Nauk SSSR* **319**, 1152.
11. H. A. Kramers (1940) *Physica* **7**, 284.
12. M. V. Alfimov, V. F. Kamalov, I. A. Struganova, and K. Yoshihara (1992) *Chem. Phys. Lett.* **195**, 262.