



A fast relaxation of electronically-excited inclusion complexes of a styryl dye with cucurbit[7]uril



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ABSTRACT

The relaxation of electronically-excited states of styryl dye (**1**) and its complexes with cucurbit[7]uril (CB[7]) in aqueous solution was studied by fluorescence steady-state and upconversion techniques. The decay of fluorescence, a 5-fold enhancement of which was observed upon addition of CB[7], was fitted to three exponential functions with time constants of 274, 43 and 1.8 ps in the presence of CB[7], and 100, 30, and 1.9 ps without it. In the framework of a simple model, based on the two-dimensional potential energy surface, the obtained results indicate that upon complexation the fluorescence rate constant of dye **1** increases by 3.8 times.

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1. Introduction

Cucurbit[*n*]urils (CB[*n*], *n*=5–10), a relatively new family of pumpkin-shaped cavitands [1], have recently attracted considerable interest as macrocyclic hosts for producing inclusion complexes with fluorescent dyes [2]. The photophysical properties of fluorescent guests, for example, the quantum yield of fluorescence, are often changed upon encapsulation in macrocyclic hosts as compared with the guests in aqueous solution. This feature looks promising from the viewpoint of potential biological and environmental applications. Whereas the supramolecular systems based on other cavitands, for example cyclodextrins, have been extensively studied [3], the effect of complexation of CB[*n*] on organic dyes has remained relatively unexplored in particular in the field of an ultrafast relaxation of electronically excited states. In this letter, we report on ultrafast fluorescence measurements that could shed light upon the relaxation of an electronically-excited guest molecule in the cucurbituril cavity.

As a representative example we refer to a styryl dye (**1**), which can produce 1:1 complexes with CB[7] (the binding constant of about 10^6 M^{-1}) and its fluorescence is significantly enhanced upon complexation [4]. It is worth noting that CB[7] has the most favorable combination of cavity size and high water solubility among other cucurbiturils and its binding constants with cationic organic

guests are typically several order of magnitude larger than those of other cavitands with a similar cavity size. The structures of CB[7] and dye **1** are shown in Figure 1.

2. Experimental details

The styryl dye, 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (dye **1**), the chemical structure of which is shown in the inset of Figure 1, was obtained according to a known procedure [5]. CB[7] was purchased from Aldrich and used without further purification. To prepare samples, aqueous stock solution of dye **1** was added to aqueous solution of CB[7] (distilled water high performance liquid chromatography grade, Aldrich) so that the concentration of dye was about 10^{-5} M^{-1} for steady-state measurements and about $2 \times 10^{-4} \text{ M}^{-1}$ for time-resolved measurements; concentration of CB[7] was about equal to that of dye **1**. In view of a large binding constant between CB[7] and dye **1**, this molar ratio of the dye to cavitand provides almost a complete complexation of the dye in both the cases.

Absorption spectra were recorded by a UV-3101PC spectrophotometer (Shimadzu) with an increment of 1 nm in 1-cm quartz cells at room temperature. Steady-state fluorescence spectra of solutions were recorded by a Fluorolog-3 τ spectrofluorometer (Jobin Yvon).

The conventional time-resolved fluorescence up-conversion technique was used to study a fast relaxation of the dye excited state. Briefly, a Ti:Sapphire laser produces 80 fs pulses centered around 830 nm at 76 MHz repetition rate and pulse energy about

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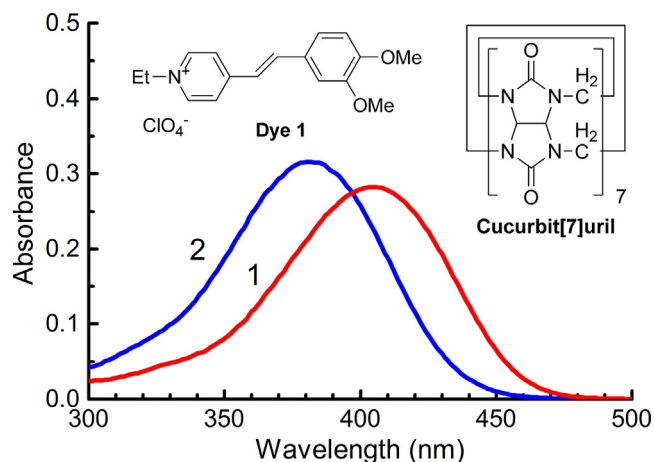


Figure 1. Absorption spectra of aqueous solution of dye **1**: (1) in the presence of an equimolar amount of CB[7] and (2) without it. Inset: The structural formula of dye **1** and cucurbit[7]uril (CB[7]).

10 nJ. The fundamental pulses were doubled by a 0.3 mm type I BBO crystal and were split into two beams, one of which (415 nm, about 1 nJ/pulse) was used for the excitation of dye solution placed in the 1 mm rotating sample cell. Another beam at 830 nm was used as the gating beam after passing through an optical delay line. The fluorescence from the dye solution and the gating beam were collected and focused on another type I BBO crystal to generate the sum-frequency signal. The up-converted signal beam, which was selected by means of a band-pass filter placed after the crystal, was focused on the entrance slit of a monochromator. A Hamamatsu R585 photomultiplier, which detected the signal, was connected to a photon counter. The polarization of the excitation beam was parallel to that of the gating beam so that the up-converted signal carried information on the fluorescence depolarization of the styryl dye. This allows a direct comparison with results on fluorescence anisotropy obtained in Ref. [4].

A personal computer collected the digital output of the photon counter and controlled an optical delay line. The Fluofit package was used to fit experimental results; the quality of the fits was judged by the reduced χ^2 and by the distribution of residuals.

3. Results and discussion

A steady-state absorption spectrum of aqueous solution of dye **1** has a peak at 380 nm that shifts to red region by about 24 nm slightly

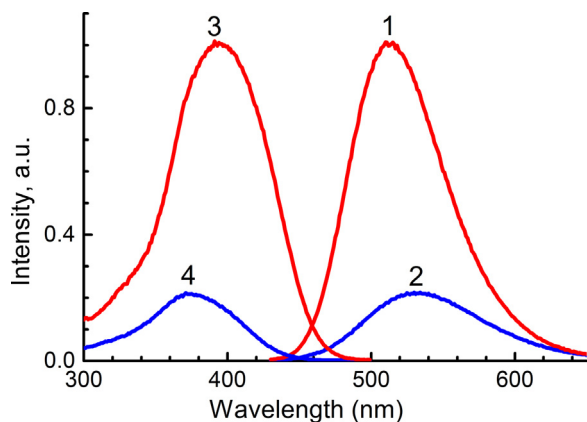


Figure 2. Fluorescence and corresponding excitation spectra of aqueous solution of dye **1**: (1 and 3) in the presence of an equimolar amount of CB[7] and (2 and 4) without it.

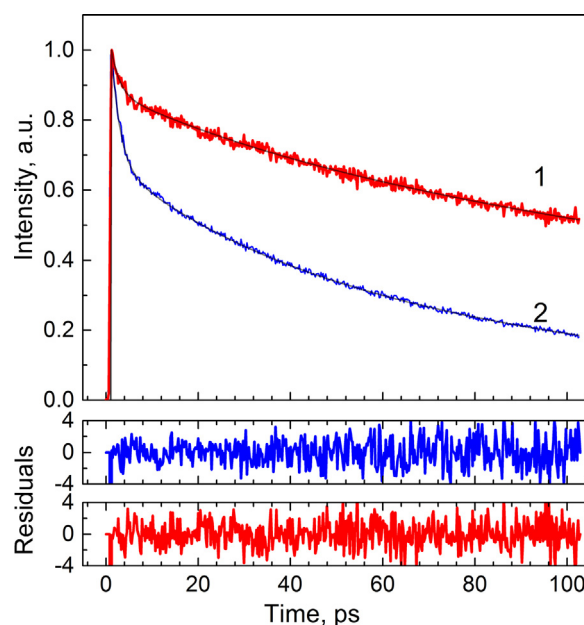


Figure 3. Normalized fluorescence decay curves of aqueous solutions of dye **1**: (1) in the presence of CB[7] and (2) without it; corresponding residuals are shown for a three-exponential fit.

varying in amplitude on the addition of about an equimolar amount of CB[7] (see Figure 1). Figure 2 shows steady-state fluorescence spectra of dye **1** excited at 396 nm as well as its excitation spectra detected at about 525 nm in the presence of about 1 equiv. of CB[7] and without it. Upon addition of CB[7], the peak of fluorescence shifts to a blue spectral region by about 20 nm and its intensity increases by a factor of about 5.

Figure 3 shows the typical decay curves of dye fluorescence (detected at 530 nm, and excited at 390 nm) in the presence of CB[7] and without it. Three exponential functions have been used to fit the data; fitting results are listed in Table 1. The shortest time constant (τ_1) of about 2 ps are almost the same for free and complexed to CB[7] molecules of dye **1**; the pre-exponential factor significantly decreases upon the addition of CB[7]. The production of complexes with CB[7] moderately affects the second term of the fitting function. On the other hand, the addition of CB[7] increases the longest time constant (τ_3) by a factor of about 3 and the corresponding pre-exponential factor by about 50%.

First, under used experimental conditions corresponding to a case of parallel polarizers, time constants τ_3 can be attributed to a rotational depolarization of fluorescence. These values are in an excellent agreement with rotational relaxation times of dye **1** reported in Ref. [4] (119 ± 14 ps without CB[7] and 277 ± 35 ps in the presence of CB[7]) that have been obtained by the steady-state anisotropy fluorescence method. This is in agreement with the suggestion [4] that dye **1** embedded in the cavity rotates as a whole with CB[7].

Second, in order to characterize relaxation processes related to τ_1 and τ_2 , let us consider a commonly accepted picture of styryl-dye photophysics that has been intensively studied in various solvents (see, for example, Ref. [6] and references therein as well as review by Glasbeek and Zhang [7]). In solution, the population of the S_1 state at the Franck-Condon (FC) point is produced by photoexcitation of the *trans* form of styryl dyes. It is followed by an intramolecular charge transfer resulting in a significant change in the dipole moment of dye molecules. This is accompanied by a fast (on a few picoseconds scale) reorientation of water molecules in the dye's hydration shell that significantly diminishes the potential energy of the system.

Table 1

The best-fit values of the time constants τ_i , their pre-exponential factors α_i ($i = 1, 2, 3$) and the reduced χ^2 for aqueous solutions of dye **1** in the presence of CB[7] and without it.

	$\tau_1(\alpha_1)$ (ps)	$\tau_2(\alpha_2)$ (ps)	$\tau_3(\alpha_3)$ (ps)	χ^2
Dye 1	1.86 ± 0.05 (32.4%)	30.11 ± 4.34 (18.6%)	100.23 ± 5.88 (49.0%)	1.26
Dye 1 + CB[7]	1.83 ± 0.24 (12.3%)	43.24 ± 19.94 (15.3%)	273.83 ± 63.23 (72.4%)	1.12

Intramolecular rotations determine a slower step of a nonradiative relaxation of excited state of styryl dyes. These include rotations around the double bond, i.e. isomerization, and around either single bonds in the C=C–C fragment. It is widely believed that the latter leads to a twisted intramolecular charge-transfer (TICT) excited state. The TICT state is located in the region of the S_1 energy minimum that is also associated with a nonradiative “sink” region, the conical intersection (CI). Note that a typical time of internal conversion through the CI seems to be of the order of 100 fs (see a relevant review by Levine and Martinez [8]).

There exists the state emitting light, the vibronically-relaxed local excited (LE) state. The nonradiative relaxation of the LE state is also possible over a low energy barrier to the “sink” region. Figure 4 shows the simplest picture of one-dimensional reaction coordinate that allows the description of decay from S_1 . Such a scheme is commonly used for describing the behavior of fluorescent dyes (see for example Ref. [9]). However, the two-dimensional potential energy surface is a more adequate model [8] that implies the existence of a non-radiative bypass (not shown) of the fluorescent LE state from the FC excited region directly to the ground state via the CI region.

The fluorescence up-conversion method allows the detection of the transient behavior of the population in the S_1 state. In the framework of the above model it is reasonable to attribute time constants τ_1 to reorientation of water molecules in the first hydration shell of dye **1** as a response to the intramolecular electron transfer. The diminution of α_1 upon complexation may indicate the replacement of some water molecules in the hydration shell by the CB[7] macrocycle.

The second term of several tens of picoseconds which is not strongly influenced by complexation may be associated with intramolecular rotations. This corresponds to results of quantum-chemical calculations that have been reported in Ref. [4]. The calculated energy-minimized structure of the inclusion complex

shows that only the pyridinium moiety of the dye is embedded into CB[7] cavity when its larger part, the styrene fragment, is exposed to water molecules from the bulk. Thus one may expect that complexation does not impose a strong restriction on intramolecular rotations of the complexed dye molecule as compared with a free one. Glasbeek and coworkers [10] have shown experimentally that the rotation around single bonds is of great significance for a non-radiative relaxation. Bridging of both C–C bonds of the ethylene fragment (i.e. covalently fixing these bonds by chain of two carbon atoms) strongly increases the lifetime of the fluorescent state and does not affect intramolecular charge transfer significantly. It is worth noting that the presence of only one unbridged single bond allows a non-radiative decay whose efficiency is almost the same as that of a completely unbridged molecule. Obviously, inclusion complexes of dye **1** with CB[7] resemble single-bridged styryl dyes in terms of their photophysics. Thus the values of τ_2 may be associated with the lifetime with respect to the emitting transition from the LE state to the ground state. The complexation slightly affects a non-radiative relaxation of electronically-excited state of styryl dye **1** and a 5-fold enhancement in fluorescence still requires explanation.

In the framework of the above scheme, the quantum yield of fluorescence – the probability of emitting light after excitation in the FC state – is equal to the product of probability of escaping non-radiative relaxation via “hot” sublevels of S_1 , and the probability of emitting light from vibronically-relaxed S_1 , i.e. $k_f\tau_2$.

$$\phi = (1 - q)k_f\tau_2, \quad (1)$$

where k_f is the radiative (i.e. fluorescence) rate constant, τ_2 is the lifetime of the emitting state, and q , by definition, is the nonradiative quantum efficiency, i.e. the probability of relaxation through a completely non-radiative route after excitation to the FC state. The expression, easily derived from Eq. (1), for a relative change in the radiative rate constant upon complexation is as follows

$$k'_f = k_f \left(\frac{\phi'}{\phi} \right) \left(\frac{1 - q}{1 - q'} \right) \left(\frac{\tau_2}{\tau'_2} \right), \quad (2)$$

where the primed symbols refer to dye **1** complexes with CB[7].

On the basis of comparison of the dye's excitation and absorption spectra by the procedure outlined in Ref. [11], we have estimated the quantum efficiency of the non-radiative route to be $q = 0.29$ for aqueous solution of dye **1**, and $q' = 0.35$ in the presence of CB[7]. This increase in the probability of non-radiative relaxation to the ground state may be attributed to the fact that upon encapsulation dye molecules obtain additional degrees of freedom for vibration.

Substituting $(\phi'/\phi) \approx 5$ and measured values of q' , q , τ'_2 and τ_2 to Eq. (2), we have obtained that $k'_f \approx 3.8k_f$. In other words, upon complexation the fluorescence rate constant increases significantly. Replacing some water molecules in the close environment of dye **1** by the CB[7] macrocycle, complexation might make the hydration shell more “rigid” that could affect the radiation ability of the solute. A similar effect, the influence of the dynamical properties of the preferential solvation shell on the radiative decay of electronically excited states of TDCI cyanine dye in toluene/DMSO liquid mixtures, was observed in Ref. [12]. However, how modification of the hydration shell significantly influences on the radiative rate

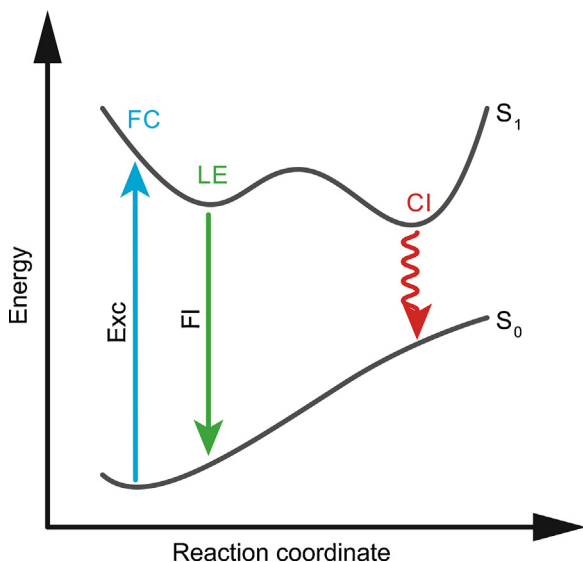


Figure 4. Schematic energy diagrams describing the relaxation of the styryl-dye excited state (for explanation, see text).

constant is still not understood in a quantitative sense and requires further experimental and theoretical investigations, which are now in progress in our research group.

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References

- [1] J.W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.* 36 (2003) 621.
- [2] R.N. Dsouza, U. Pischel, W.M. Nau, *Chem. Rev.* 111 (2011) 7941.
- [3] A. Douhal, *Chem. Rev.* 104 (4) (2004) 1955.
- [4] D.A. Ivanov, N.Kh. Petrov, E.A. Nikitina, M.V. Basilevsky, A.I. Vedernikov, S.P. Gromov, M.V. Alfimov, *J. Phys. Chem. A* 115 (2011) 4505.
- [5] A.I. Vedernikov, et al., *Russ. Chem. Bull. Int. Ed.* 56 (9) (2007) 1860.
- [6] Y. Huang, T. Cheng, F. Li, C.-H. Huang, S. Wang, W. Huang, Q. Gong, *J. Phys. Chem. B* 106 (39) (2002) 10041.
- [7] M. Glasbeek, H. Zhang, *Chem. Rev.* 104 (2004) 1929.
- [8] B.G. Levine, T.J. Martinez, *Annu. Rev. Phys. Chem.* 58 (2007) 613.
- [9] Y. Huang, et al., *J. Phys. Chem. B* 106 (39) (2002) 10031.
- [10] M.J. van der Meer, H. Zhang, W. Rettig, M. Glasbeek, *Chem. Phys. Lett.* 320 (2000) 673.
- [11] N.Kh. Petrov, M.N. Gulakov, M.V. Alfimov, G. Busse, B. Frederichs, S. Techert, *J. Phys. Chem. A* 107 (33) (2003) 6341.
- [12] N.Kh. Petrov, M.N. Gulakov, M.V. Alfimov, G. Busse, S. Techert, *Z. Phys. Chem.* 221 (4) (2007) 537.