



Ultrafast relaxation of electronically-excited states of a styryl dye in the cavity of cucurbit[*n*]urils ($n = 6, 7$)



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ABSTRACT

The ultrafast relaxation of an electronically-excited styryl dye and its complexes with cucurbit[*n*]urils was studied by the fluorescence up-conversion technique at various fluorescence wavelengths. The relaxation is faster at a blue side of the fluorescence band than at a red one where a fluorescence rise was observed. Addition of either cucurbiturils significantly increases the longest decay time from about 50 ps to that in the range of 100–200 ps. Such features are attributed to displacements of the electronically-excited styryl dye deep into the cavity, increasing the potential barrier between the intramolecular charge transfer state and the conical intersection region.

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1. Introduction

Over the last years a significant interest has been aroused in photophysical properties of inclusion complexes of organic fluorescent dyes with cucurbit[*n*]urils (CB[*n*]), which are a relatively new family of barrel-shaped macrocyclic cavitands that consist of *n* glycoluril units (basically $n = 5-8$) bound by pairs of methylene groups [1]. There are many experimental observations on considerable changes in photophysical properties of organic dyes upon their encapsulation in the cucurbituril cavity, in particular, a significant enhancement of fluorescence as compared with free dyes [2]. This feature of such supramolecular systems looks promising for potential biological and environmental applications but the mechanism of the cavity effect still remains unclear.

A representative family of organic fluorescent dyes is styryl dyes (see review [3]) that have relatively high photostability and can be used in various applications, for example, in biology as a staining agent for mitochondria in living cells [4]. In addition they can produce inclusion complexes with CB[*n*] (for $n > 5$). For example, a styryl-pyridinium dye (**1**) (Figure 1) can produce 1:1 inclusion complexes with CB[7] (the binding constant of about 10^6 M^{-1}) and its quantum yield of fluorescence is enhanced by a factor of 5 upon complexation [5]. The calculated energy-minimized structure of

the inclusion complex in the ground state has shown that only the pyridinium moiety of the dye is embedded into CB[7] cavity as its larger part, the styryl moiety, is exposed to water molecules from the bulk.

Recently Li and coworkers [6] have found that the addition of CB[6] in aqueous solution of a styryl dye, trans-4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide (DSMI), results in a 270-fold enhancement of fluorescence, quantum-chemical calculations indicating the ground state structure of the inclusion complex similar to that of CB[7].

DSMI and **1** are close analogs; the main difference is that in the latter there are two methoxy groups in the styryl moiety instead of a dimethyl amino group in the *para* position in DSMI. The enhancement of dye fluorescence in the inclusion complexes with CB[6] by two order of magnitudes obviously means that the fluorescence of the dye is strongly quenched in the bulk water. The addition of CB[6] to aqueous solution of **1** leads to the production of 1:1 inclusion complexes with the binding constant of 10^5 M^{-1} and to the enhancement of the quantum yield of fluorescence by a factor of 12.6 [7]. The latter is much below than that of DSMI but **1** seems more suitable for studying the effect of cavity on photophysical properties of guest fluorophores because it is less sensitive to solvent properties (e.g., acidity).

Here we report on ultrafast measurements of an initial stage of relaxation of electronically excited **1** in the presence of either CB[6] or CB[7] at various fluorescence wavelengths that could shed light upon the relaxation mechanism of an electronically-excited guest molecule in the cucurbituril cavity.

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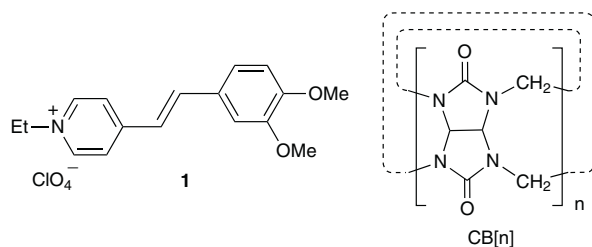


Figure 1. The structural formula of dye **1** and cucurbit[*n*]uril (CB[*n*]).

2. Experimental details

The styryl dye, 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (**1**) – the chemical structure is shown in Figure 1 was obtained according to the procedure described in Ref. [8]. Cucurbiturils CB[6] and CB[7] were purchased from Aldrich and used without further purification. To prepare samples, cucurbiturils dissolved in aqueous solutions of **1** (Millipore water) so that the concentration of **1** was about 5×10^{-6} M for steady-state measurements and about 2×10^{-4} M for time-resolved measurements; concentrations of CB[7] and CB[6] were approximately equal to that of **1**. In view of a large binding constant between the cavitands and **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, by a Fluorolog-3 τ spectrofluorometer (Jobin Yvon).

A time-resolved fluorescence up-conversion technique was used to study a fast relaxation of the dye excited state. Briefly, a Cr:Forsterite laser produces 90 fs pulses centered around 1280 nm at 96 MHz repetition rate with the pulse energy about 7 nJ. A common scheme with a two-step consecutive mixing in nonlinear crystals was used to produce pulses centered around 427 nm (the third harmonic) which then excited dye solutions placed in the 2 mm cell. After the second mixing, the residual part of fundamental pulses with the energy about 2.5 nJ was used as the gating beam after passing through an optical delay line with the range of 1 ns. The fluorescence from the dye solution and the gating beam were collected and focused on a 0.5 mm type I BBO crystal to generate sum-frequency signal. The up-converted beam was selected by a band-pass filter and focused on the entrance slit of a Solar M 266 monochromator. A spectrally resolved signal was measured by a Hamamatsu photon counter. A personal computer collected the digital output of the photon counter and controlled an optical delay line. The temporal resolution of the scheme was estimated to be 210 fs and the spectral resolution, about 20 nm. The Fluofit package was used to fit experimental results. The fitting quality was judged by the reduced χ^2 .

3. Results and discussion

Figure 2 shows steady-state absorption spectra of aqueous solutions of **1** and those in the presence of either CB[6] or CB[7]. Unbound **1** has a peak at about 380 nm that shifts to a red region by less than 25 nm varying in the amplitude on the addition of an equimolar amount either of cucurbiturils. On doing so, the peak of fluorescence of **1** shifts to a blue spectral region by about 20 nm for CB[7] and 40 nm for CB[6] (see Figure 3).

Representative fluorescence decay-curves of **1** at different wavelengths in the presence of CB[7] are shown in Figure 4. The excited complexes of **1** with CB[7] relaxes faster at a blue side of the fluorescence band than at a red one. Moreover, in the red side of spectrum there exists a fluorescence rise. Such features have been

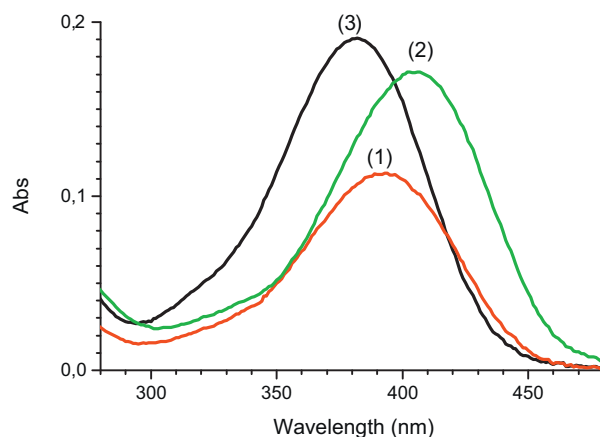


Figure 2. Absorption spectra of aqueous solution of dye **1**: (1) in the presence of CB[6]; (2), CB[7] and (3) without cucurbiturils.

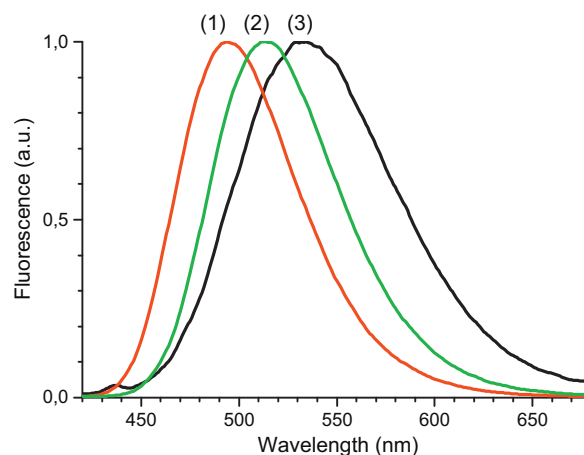


Figure 3. Fluorescence spectra, normalized to unit, of aqueous solution of dye **1**: (1) in the presence of CB[6]; (2) CB[7] and (3) without cucurbiturils.

found to be qualitatively common for unbound **1** and its complexes with CB[6], consistent with photophysical behavior observed for DSMI in methanol [9].

The observed decay curves at different wavelengths can be fitted by convolution between the instrument response function and a multi-exponential decay

$$I(t) = R \otimes \sum_i A_i \exp\left(-\frac{t}{\tau_i}\right), \quad (1)$$

where R is the instrument response function, τ_i is the lifetime of the i th component, A_i is the preexponential factor of corresponding components. In all cases, a satisfactory fitting of the fluorescence decay for free and bound **1** has been gained by two- or three-exponential functions, the results of which are listed in Table 1.

The obtained results can be considered on the basis of the following qualitative model which is similar to that commonly used for describing the photophysical behavior of styryl dyes (see [9] and references therein). Figure 5 shows a simplified one-dimensional profile of the potential energy surface of the ground state, S_0 , and first excited state S_1 of the dye. In solution, the population of the Franck–Condon (FC) state is initially produced by photoexcitation of the trans form of styryl dyes. Relaxation can be considered as downhill movements along the reaction coordinate. The initial step is associated with a very fast – on the subpicosecond time scale – vibrational cooling and intramolecular charge transfer (ICT) that is accompanied by a significant change in the dipole moment of

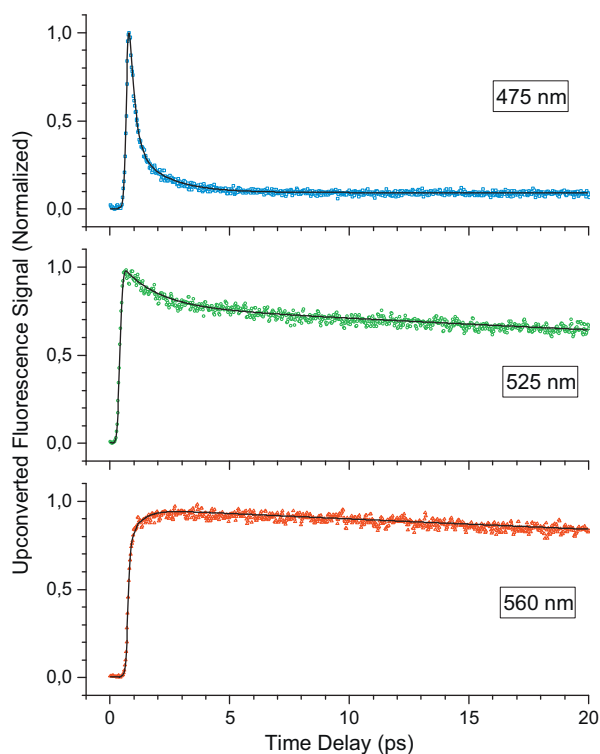


Figure 4. Representative fluorescence decays of **1** in water in the presence of CB[7] at 475, 525, and 560 nm detection wavelengths.

Table 1

The results of fits of the fluorescence decay of free and bound **1** to a sum of two or three exponentials at various wavelengths.

λ (nm)	A_1 (%)	τ_1 (ps)	A_2 (%)	τ_2 (ps)	A_3 (%)	τ_3 (ps)	χ^2
1							
475	78	0.22	18	1.08	4	42	0.66
530	–	–	52	1.36	48	58	0.63
540	–57	0.05	20	1.58	23	59	0.63
560	–41	0.13	16	1.92	43	71	0.67
580	–40	0.16	–	–	60	45	1.55
1 + CB[6]							
460	78	0.14	16	0.81	6	118	1.39
475	60	0.15	28	0.94	13	173	1.13
525	–	–	25	1.3	75	80	1.4
540	–	–	28	1.76	72	92	0.50
560	–36	0.20	–	–	64	200	1.09
1 + CB[7]							
475	78	0.22	17	1.36	5	100	0.97
525	–	–	23	1.56	77	104	1.29
560	–18	0.51	–	–	82	148	0.91

the dye molecule. This change results in a fast – on the picoseconds time scale – reorganization response of the solvation shell that significantly diminishes the potential energy of the system. The dye molecule, which is supposed to be approximately planar at this stage of relaxation [9], emits light at wavelengths that become longer upon diminishing the potential energy of the S_1 state and concomitantly increasing that of the S_0 state. A slower step of relaxation is associated with intramolecular rotations of the styryl dye. These include rotations around the double bond, i.e. isomerization, and around either single bonds in the C–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 non-radiative ‘sink’ region, the conical intersection (CI); a typical time

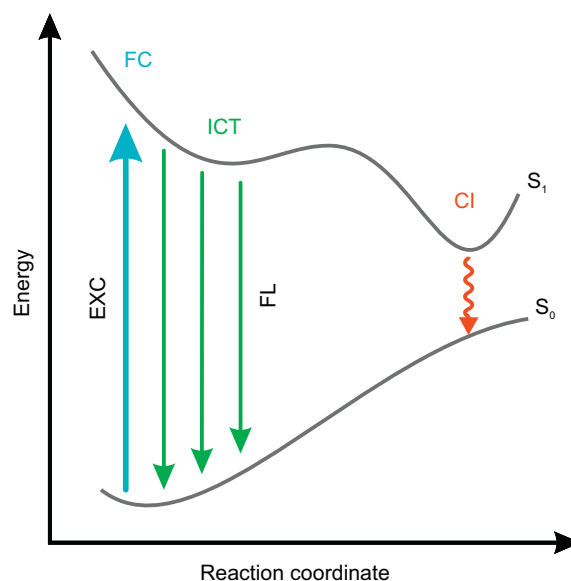


Figure 5. Schematic energy diagrams describing the relaxation of the styryl-dye excited state (for explanation, see text).

of internal conversion through the CI is of the order of 100 fs [10]. The vibronically-relaxed ICT state emitting light can get the ‘sink’ region over a low energy barrier.

In the framework of the above model, a short decay time τ_1 in the range of 100–200 fs, observed in the blue side of fluorescence band of free and bound **1**, should be attributed to vibrational cooling. These components disappear for the decay at wavelengths around the fluorescence peak and, in the red side of the fluorescence band, there exist rising components with time constants of the same order of magnitude.

The production of inclusion complexes with either cucurbiturils obviously increases the decay time τ_3 from about 50 ps for free **1** to that in the range of 100–200 ps for bound **1** (see also Ref. [11]). So in terms of the suggested model, the complexation increases the barrier between the ICT and TICT states. In other words, cucurbiturils place constraints on an intramolecular rotation of the dye.

In this connection, it is worth noting that Glasbeek and coworker have shown that rotations around single bonds are the main non-radiative relaxation route of styryl dyes [12]. Covalently fixing of both C–C bonds by the bridge of two carbon atoms strongly increases the lifetime of the fluorescent state and does not affect ICT significantly. However the presence of only one unbridged single bond allows a non-radiative decay with efficiency, which is almost the same as that of a completely unbridged molecule. In view of this fact, the mentioned previously structure of inclusion complexes for the ground state S_0 of styryl dyes with CB[6] an CB[7], cannot impose a significant restriction on all intramolecular rotations of the bound dye in the excited state S_1 .

On the other hand, calculations, reported in Ref. [5], have predicted an extra local minimum in energy that corresponds to the structure of electronically-excited complexes, in which **1** is more deeply embedded in the cavity of CB[7]. This state is 18 kcal/mol higher in energy with respect to the ground state but can be populated upon photoexcitation, imposing a more efficient restriction on all rotating bonds of the dye. In terms of the suggested above model (see Figure 5) it increases the potential barrier between the ICT state and the ‘sink’ CI region. The driving force of such a movement inside the cavity is a coulombic interaction between negatively charged portals of macrocycles and a positive charge of the dye molecules that shifts to the styryl group upon ICT.

A general possibility of such a restructuring of the inclusion complex with CB[6] is confirmed by the NMR data obtained by Li and coworker [6]. They have found that when DSMI is protonated in the ground state, i.e. the aminogroup becomes positively charged, the aniline ring shifts to the CB[6] cavity. In this sense, protonation can play a role similar to that of the photo-induced ICT.

In view of the hypothesis for the displacement of the dye deep into the cavity, one may expect a more extended decay-time of fluorescence in a red side of the fluorescence peak in the presence of cucurbiturils, consistent with what is actually observed. The diameter of the CB[6] portal is less than that of CB[7] by about 1.5 Å [1] so that the former imposes a more rigorous restrictions on rotations around single and double bonds as compared with the CB[7] cavity. This manifests itself in a significantly larger fluorescence quantum-yield of complexes with CB[6].

The move of electronically-excited **1** inside the cavity is a part of the reorganization of the solvation shells caused by ICT. This seems to have the same physical nature as the response of the water dipoles in the hydration shell to a displacement of the positive charge along the dye particle. Such a reorientation of water molecules has found to take about 2 ps [13]. This is close to the observed values of decay time τ_2 , which should be related to such a solvation restructuring. The difference in these values does not look significant and one may suggest that displacement of the dye in the cavity occurs on the same time scale as the reorganization of the solvation shells in agreement with experimental findings.

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