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[2+2] Photocycloaddition of Styryl Dyes in the Cucurbit[8]uril Cavity and Its Ultrafast Dynamics

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Abstract— [2+2] Photocycloaddition of a series of styryl dyes (\mathbf{a} , \mathbf{b} , and \mathbf{c} , see text) in the cavity of cucurbit[8]uril (CB8) in aqueous solutions has been studied by optical spectroscopy. The complex formation constants were calculated for the 1 : 1 and 2 : 1 complexes of the styryl dyes with CB8. The optimal CB8 to dye molar ratios that correspond to the highest concentrations of the 2 : 1 complexes in the solution have been determined as 0.5, 0.3, and 1 for dyes \mathbf{a} , \mathbf{b} , and \mathbf{c} , respectively. The quantum yields of photocycloaddition have been calculated from the results of dye photolysis in the presence of CB8: 0.06, 0.02, and 0.04 for \mathbf{a} , \mathbf{b} , and \mathbf{c} , respectively. The fluorescence decay kinetics has been studied on the picosecond timescale. The lifetimes found are 1–2 ps, which correspond to the characteristic time of the solvation shell effect on the redistribution of the dye charge in the excited state. The long component of the fluorescence decay on the order of tens of picosecond is also observed. This component decreases in the presence of CB8, indicating the formation of dimeric state.

Keywords: styryl dyes, cucurbit[8]uril, [2+2] photocycloaddition **DOI:** 10.1134/S0018143919030147

INTRODUCTION

Cucurbit[*n*]urils (**CB**[*n*]) are hollow macrocyclic cavitands consisting of *n* glycoluril units (n = 5-8, 10) linked by pairs of methylene bridges [1]. The trivial name of these molecules is due to their shape and originates from the Latin word cucurbitus, which means pumpkin. Cucurbiturils were synthesized for the first time in 1905. [2]; however, their structure was unknown until 1981 [3]. The carbonyl oxygen atoms with partial negative charge are at the ends of molecules of the cucurbituril series, framing cavity portals. This feature promotes bonding between cucurbiturils and relatively small organic cations to form host-guest complexes. The rigid structure. as well as the possibility of the formation of host-guest complexes, makes cucurbiturils attractive compounds for design of new supramolecular systems [1, 4].

The concept of controlling photochemical processes in homogeneous liquid solutions with the use of preorganization into supramolecular ensembles, including cucurbiturils host–guest complexes, has become popular in recent years [5-7]. The cavitand CB8 with a large enough (479 Å³ [1]) and relatively rigid cavity is of a special interest. These features allow CB8 to selectively form host–guest complexes of the 2 (guest) : 1 (host) composition with various organic molecules. The guest preorganization of this kind in the CB8 cavity can be successfully used for controlling photochemical processes and even allows using CB8 as a supramolecular catalyst [8].

The 1 : 1 and 2 : 1 host-guest complexes between dye **a** (Fig. 1) and CB8 were detected in aqueous solutions by NMR spectroscopy and spectrophotometry by Gromov et al. [9], and it was shown that the photolysis of these solutions gives cyclobutane stereoisomer **d** (Fig. 1). It is worth noting that even an amount of CB8 as low as 5 mol % is enough for the almost complete dye conversion into the cyclobutane derivative. This confirms the ability of the CB8 cavitand to be a supramolecular catalyst. Moreover, the reaction proceeds stereospecifically; i.e., only one of eleven theoretically possible cyclobutane isomers is formed, for which strictly defined relative spatial orientation of interacting molecules is required.

The above-described reaction between two dye **a** molecules is an example of one of the most important photochemical reactions, [2+2] photocycloaddition. These reactions are quite extensively investigated due to their considerable practical applicability [10]. The studies of photochemical reactions in the cavity of var-



Fig. 1. Structures of styryl dyes **a**, **b**, and **c**; cucurbit[8]uril; and cyclobutane product of photochemical reaction **d**.

ious macrocyclic cavitands, such as cyclodextrins, calixarenes, carbon nanotubes, and, of coarse, cucurbiturils, occupy significant part in the field [11]. In particular, many examples of [2+2] photocycloaddition that efficiently proceeds in the cucurbit[8]uril cavity can be found in the literature [12-17]. However, the ultrafast kinetics of [2+2] photocycloaddition has not vet been studied in sufficient detail. Hover et al. [18] studied the dimerization of α -cyano-4-hydroxycinnamic acid and sinapic acid in crystals by subpicosecond time-resolved fluorescent methods [18]. The dimerization of α -cvano-4-hydroxycinnamic acid and sinapic acid was observed on 10 ps and subpicosecond timescales, respectively. Using picosecond X-ray diffraction, Hallmann et al. [19] showed that α -styrylpyridinium trifluoromethanesulfonate undergoes ultrafast photoinduced transformation in crystalline phase to give a dimeric product.

The aim of this work is to study the ultrafast kinetics of [2+2] photocycloaddition for a series of styryl dyes in the cucurbit[8]uril cavity in aqueous solutions.

EXPERIMENTAL

Millipor Simplicity water was used for preparation of solutions. Cucurbit[8]uril purchased from Sigma-Aldrich was used without further purufication. In weighing cucurbituril samples to prepare the solu-

HIGH ENERGY CHEMISTRY Vol. 53 No. 3 2019

tions, the results of NMR study on the amount of water in the cavity of dry CB8 were taken into account. Styryl dyes **a**, **b**, and **c**, which structures are given in Fig. 1, were synthesized according to the procedure described elsewhere [9]. The dye concentration in all samples was 10^{-5} mol/L. The CB8 concentration varied from 0 to 9×10^{-5} mol/L. In order to avoid spontaneous photochemical reactions, all sample preparation operations and all measurements were carried out in the dark at room temperature.

Absorption spectra were recorded in standard quartz cells with an optical pathlength of 1 cm on a Shimadzu UVmini 1240 spectrophotometer. Fluorescence spectra were recorded on a Fluorolog 3 Tau fluorimeter. The fluorescence spectra were measured at the excitation wavelengths of 415 nm for **a** and **c** and 410 nm for **b**, because absorbance of all samples at these wavelengths in corresponding titration series differs insignificantly, although these points are not isosbestic. Furthermore, these wavelengths are close to the absorption maximums for all the samples. It should be taken into account that photochemical reactions actively proceed in the samples under the action of light at 400 nm and the fluorescence measurement itself affects the result (the fluorescence intensity at maximum changes by 5% between two successive measurements). In order to avoid the accumulation of the measurement errors, a separate sample was prepared for each point of the fluorescent titration. The complexation constants were determined from the results of fluorescent and spectrophotometric titrations with the use of the program HypSpec of the Hyperquad package [20].

Photolysis of the samples was carried out as described elsewhere [21]. The procedure of up-conversion experiment on the measurement of ultrafast fluorescence decay time is described in [22]. The experimental data obtained on the up-conversion setup were the time dependence of fluorescence intensity at a given wavelength with femtosecond resolution. For more accurate description of the data, this dependence can be described by a set of descending and ascending exponential functions.

To obtain quantitative parameters of the exponentials, the reconvolution of exponential functions and the Gauss function that describes the excitation laser pulse was used. The FluoFit (Picoquant) software was used to reduce routine calculations.

RESULTS AND DISCUSSION

Steady-State Study

Figure 2 shows absorption spectra for an aqueous solution of styryl dye **b** in the presence of CB8. The main absorption maximum of the dye is at 388 nm. In the presence of CB8, a bathochromic shift of the absorption maximum is observed, with the highest value of the shift being 15 nm and the intensity in the



Fig 2. Absorption spectra of aqueous solutions of dye b (10^{-5} mol/L) depending on the CB8 concentration in the range of [0; 9 × 10^{-5}] mol/L.

maximum decreasing approximately by 10%. The short-wavelength absorption maximum (257 nm) does not shift, but its intensity decreases also by 10%.

The results of fluorescent titration in the form of dependence of the fluorescence intensity at maximum on the ratio of CB8 and dve molar concentrations are given in Fig 3. The shape of the fluorescence spectrum of dye b in the presence of CB8 almost does not change over the entire range of CB8 concentration. Only a small (5 nm) shift of the fluorescence maximum to shorter wavelengths is observed. The fluorescence intensity at maximum first decreases with increasing cucurbituril concentration and then increases, reaching a saturation value (Fig. 3b). The decrease in the fluorescence intensity is observed at a CB8 to dye **b** concentration ratio of n < 0.3 and corresponds to the concentration quenching of the dye in the cavity for 2: 1 complexes [21]. The further increase in the CB8 concentration shifts the equilibrium toward the 1 : 1 complexes, for with the fluorescence rise is more significant as compared with the free dye. At a CB8 to **b** concentration ratio of n > 10, all of the dye molecules are bound into the 1 : 1 complexes, and the increase in the CB8 concentration does not change the fluorescence.

The changes in the absorption and fluorescence spectra for dyes **a** and **c** in titration by CB8 are similar to those for dye **b**. However, one can see in Fig. 3 that the highest concentration of the 2:1 complexes for **a** and **c** corresponds to the CB8 : dye molar ratios in the solution of 0.5 and 1, respectively (Table 1). The fluorescence intensity increases almost linearly with an increase in the CB8 concentration in this range of molar ratios and does not attain the limiting value for dye **c**.

The complex formation constants calculated with the use of HypSpec from the spectrophotometric and fluorescent titration data in the approximation of the absence of fluorescence for the 2 : 1 complex are listed in Table 1.

To rum the photolysis, the initial ratio of dye and CB8 concentrations was chosen so that the concentrations of the 2:1 complexes would be maximum (Table 1). Figure 4 shows the absorption spectra of a

Table 1. CB8 to dye molar ratio *n* corresponding to the highest amount of the 2 : 1 complexes; formation constants of 1 : 1 $(\log K_1)$ and 2 : 1 complexes $(\log \beta)$ for dyes **a**, **b**, and **c** with CB8; and the quantum yield of photochemical reaction (φ)

Dye	a	b	c	
n	0.5	0.3	0.1	
$\log K_1$	6.2	6.3	5.4	
logβ	11.9 (log $K_2 = 5.7$)	12.6 ($\log K_2 = 6.3$)	11.2 ($\log K_2 = 5.8$)	
φ	0.06	0.02	0.04	



Fig. 3. Fluorescence intensity at maximum for aqueous solutions of styryl dyes and CB8 as a function of CB8 to dye molar ratio n. The black, red, and blue symbols refer to dyes \mathbf{a} , \mathbf{b} , and \mathbf{c} , respectively.

dye **b** sample irradiated in the photolysis setup for 283 min. The intensity of the main absorption maximum (390 nm for **b**) is decreased by irradiation, but the absorbance increases in the short-wavelength spectral range (near 230 nm), which corresponds to the absorption of the cyclobutane derivative formed in the photochemical reaction. The absorption spectra of dyes **a** and **c** behave similarly in photolysis. To calculate the quantum yield of the photochemical reaction, plots of the absorbance at maximum depending on the photolysis time were built (Fig. 5). The distinguishing feature of dye **b** is that the absorbance of the main band does not disappear completely after irradiation for five hours. This means that the photochemical reaction does not occur after a certain point of time. However, the absorbance of **a** and **c** disappears completely during the photolysis, indicating high performance of CB8 as a supramolecular catalyst in the course of this photochemical reaction. The quantum yields of photochemical reactions were calculated from the photolysis data according the procedure described in [21] (Table 1).

It can be assumed from the fluorescent titration data that the formation of the 2 : 1 complexes of dye **b** with cucurbit[8]uril is hindered as compared with dyes **a** and **c**. This behavior of dye **b** is due to electrostatic repulsion, since the molecule of **b** has the highest charge (+2) among all the dyes under consideration. At the same time, the binding of **b** with CB8 in the 1 : 1 complex, in contrast, is better than that for **a** and **c** because of interaction with the carbonyl portals of cucurbituril. Furthermore, dye **b** can form complexes of other stoichiometry, for example 1 : 2; i.e., two CB8 molecules per **b** molecule at CB8 concentrations that significantly exceed the dye concentration. However, application of this model significantly complicates the calculation of the complexation constant; therefore, the model taking into account only 1:1 and 2:1 complexes was used, probably having lowered the accuracy of calculation. The above assumptions explain the findings that the photolysis of dye **b** with CB8 is much less effective than that of the other dyes and the calculated quantum yield of this reaction is significantly lower. The sample with dye **a** has the highest quantum yield of the reaction (Table 1). The quantum yield of the reaction for dye **c** is lower, which is due the lower binding constant for the 2:1 complex.

Time-Resolved Study

Ultrafast kinetics of fluorescence decay was studied for dves **a**, **b**, and **c** and for their 2 : 1 complexes with CB8. Figure 6 exemplifies fluorescence decay curves on the timescale of 10 ps for free dye **a** and for its 2:1 complex with CB8 at the highest concentration of the 2 : 1 complexes, i.e., 0.5 equiv. of CB8. The stvryl dyes under study have several characteristic decay times in water (Table 2). A short time on the order of 1-2 ps is observed in the short-wavelength spectral range. This is a characteristic time of the response of the solvation shell on the charge redistribution in the excited-state dye. Since water is the solvent for all the samples, this exponential is similar for all the dyes. On passing to the long-wavelength portion of the spectrum, the amplitude of this exponential decreases and an ascending exponential with a time of 250-700 fs appears in the right wing of the spectrum. The third exponential existing in all studied dyes is characterized by a decay time of 20-75 ps depending on the sample.



Fig. 4. Photolysis of dye b (10^{-5} mol/L) with CB8 at n = 0.3, i.e. at the minimum of the titration curve. Irradiation time is 283 min.



Fig. 5. Absorption intensity at maximum as a function of irradiation time. The black, red, and blue symbols respectively refer to dyes **a**, **b**, and **c**.

Ultrafast exponents of 1-90 fs observed in the shortwavelength spectral range should also be noted, but the experimental conditions and parameters of the setup do not allow their exact characterization. The addition of CB8 affects the third time; it decreases twofold for dye **a** or by a factor of 1.5 for **c** and remains almost unchanged for dye **b**. The addition of CB8 does not affect the second time. The measurement results correlate well with the photolysis data. The quantum yield of photochemical reaction is the highest for dye **a** among the dyes under consideration, and the highest change of the second positive exponential in the fluorescence decay is observed for this dye. The corresponding change is observed for the other dyes as well. This implies that the charge and the structure of the dye molecule have a significant effect on the photochemical reaction of the dyes in the cucurbit[8]uril cavity.

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Fig. 6. Fluorescence decay for dye a (red) and dye a in the 2 : 1 complex with CB8 (blue), λ_{ex} 417 nm and λ_{f1} 530 nm.

Table 2. Characteristic fluorescence decay times at 530 nm for dyes **a**, **b**, and **c** and their complexes with CB8. *A*1, *A*2, and *A*3 are the amplitudes of corresponding components

Sample	<i>T</i> 1, ps	<i>A</i> 1	<i>T</i> 2, ps	A2	<i>T</i> 3, ps	A3
a	-0.18	-2650	1.43	4880	50	11000
$\mathbf{a} + \mathbf{CB8}$			1	2200	19	2100
b	-0.32	-3500	2.1	3000	38	17000
$\mathbf{b} + \mathbf{CB8}$	-0.3	-13600	1	8800	30	36000
c	-0.28	-1700	1.2	2600	75	7300
$\mathbf{c} + \mathbf{CB8}$	-0.89	-184	1	240	51	430

tific Research Center in part of steady-state measurements.

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HIGH ENERGY CHEMISTRY Vol. 53 No. 3 2019

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