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ARTICLE

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The 1:1 Host−Guest Complexation between Cucurbit[7]uril and Styryl Dye

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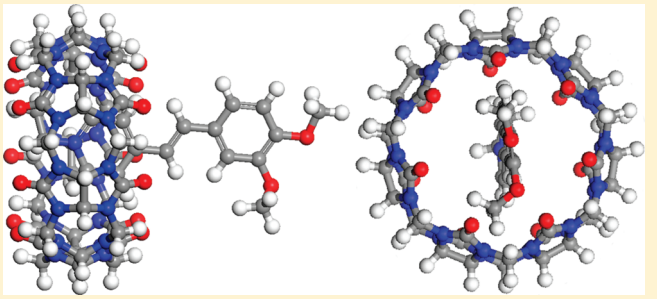
ABSTRACT: The photophysical properties of aqueous solution of styryl dye, 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (dye **1**), in the presence of cucurbit[7]uril (CB[7]) was studied by means of fluorescence spectroscopy methods. The production of 1:1 host−guest complexes in the range of CB[7] concentrations up to 16 μM with $K = 1.0 \times 10^6$ M^{-1} has been observed, which corresponds to appearance of the isosbestic point at 396 nm in the absorption spectra and a 5-fold increase in fluorescence intensity. The decay of fluorescence was found to fit to double-exponential functions in all cases; the calculated average fluorescence lifetime increases from 145 to 352 ps upon the addition of CB[7]. Rotational relaxation times of dye **1** solutions 119 ± 14 ps without CB[7] and 277 ± 35 ps in the presence of CB[7] have been determined by anisotropy fluorescence method. The comparison of the results of quantum-chemical calculations and experimental data confirms that in the host cavity dye **1** rotates as a whole with CB[7].



1. INTRODUCTION

The encapsulation of fluorescent dyes in cucurbiturils has been recently found to result in significant changes in photophysical properties of the dyes. Commonly, the observed changes happen to be an actual improvement of photophysical properties of fluorescent molecules. For example, Koner and Nau[1] have observed a significant increase in fluorescence intensity and the fluorescence lifetimes of some organic dyes (macrolex yellow 10 GN, dapoxyl and 4-(dimethylamino)benzonitrile) intercalated in the cucurbit[7]uril (CB[7]) cavity; these findings were attributed to a specific property of the host cavity, i.e., its low polarizability. Megyesi and co-workers have reported[2] that addition of CB[7] to aqueous solution of berberine, a biologically important dye, results in a 500-fold increase in the dye fluorescence intensity. Recently we have found[3] that the addition of CB[7] to aqueous solutions of 3,3′-diethyl-thiacarbocyanine iodide (DTCI) significantly changes the DTCI absorption spectrum and results in a 5-fold increase in the fluorescence quantum yield of DTCI. In assumption that DTCI and CB[7] produce a 1:1 inclusion complex, the association constant has been found $K \approx 3 \times 10^4$ M^{-1}.

CB[7] is a representative of a relatively new family of the cavitands (see Figure 1) that has a hydrophobic cavity, the size of which is suitable to encapsulate a large variety of molecular organic cations.[4] However, unlike β-cyclodextrin, another famous cavitand with cavity of a similar size, there exist little data on complexation with cucurbiturils and their influence on photophysical properties of fluorescent guest molecules.

Ionic styryl dyes, whose transition to electronically excited states is accompanied by significant charge redistribution, have interesting photophysical properties that allow the use of styryl dyes as spectral sensitizers, laser dyes, fluorescent probes in chemistry and biology,[5] and as recently was found, styryl dyes can produce inclusion complexes with CB[7].[6,7]

The purpose of this work was to study the production and structure of 1:1 inclusion complexes of a styryl dye with CB[7] in more detail by means of the fluorescence spectroscopy and quantum-chemical calculations.

2. EXPERIMENTAL SECTION

The styryl dye, 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate, whose chemical structure is shown in Figure 1 (dye **1**), was obtained according to a known procedure.[8] 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 for steady-state measurements and about 7×10^{-5} M for time-resolved measurements. The concentration of CB[7] was varied from 0 to 16 μM corresponding to the production of 1:1 inclusion complexes. All solutions prepared were kept in darkness to avoid photoreactions.

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 emission spectra of solutions were recorded by a Fluorolog-3τ spectrofluorometer (Jobin Yvon) in the range of 420−700 nm

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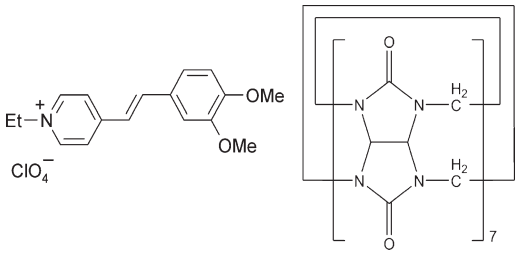

Figure 1. The structural formula of styryl dye, 4-[(*E*)-2-(3,4-dimethoxyphenyl)ethenyl]-1-ethylpyridinium perchlorate (**1**), and cucurbit[7]uril (CB[7]).

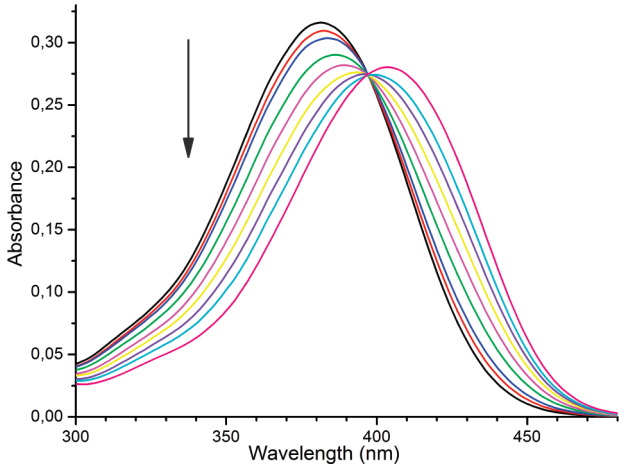

Figure 2. The absorption spectra of aqueous solutions of dye **1** in the range of CB[7] concentration from 0 to 16 μM.

with increment of 1 nm in 1-cm quartz cell. The samples were excited at the isosbestic point observed in the absorption spectra at λ = 396 nm.

The fluorescence quantum yield of aqueous solution of styryl dye without CB[7] was estimated by a common procedure[9] that is based on the comparison of areas under the corrected emission spectrum curve of dye and that of perylene in cyclohexane as the fluorescence standard (the quantum yield 0.94). On doing so the corrections for difference in optical densities of samples at an excitation wavelength of 410 nm and for refractive indices difference of the used solvents were also taken into consideration.

Steady-state fluorescence depolarization experiments were carried out by a Fluorolog-3τ spectrofluorometer using automatically operated polarizers (the DataMax software) with excitation at the peaks of the absorption spectra, i.e., 380 nm for dye **1** and 405 nm for dye **1** in the presence of CB[7], and emission at the peaks of the fluorescence spectra 525 and 512 nm, respectively. By definition, the measured anisotropy of fluorescence is $r = (I_V - GI_H)/(I_V + 2GI_H)$ where I_V and I_H are the fluorescence components parallel and perpendicular to the plane of polarization of the excitation beam, respectively, and G is the correction factor that was taken into account in the course of experiment (the DataMax software).

The conventional time-correlated single-photon counting technique was used for lifetime measurements by a Fluotime 200 fluorometer comprising a PDL800-B unit with a LDH-P-C 400 laser-diode head (PicoQuant, Germany) as a source of exciting light. Fitting of data obtained was made with a FluoFit software (PicoQuant).

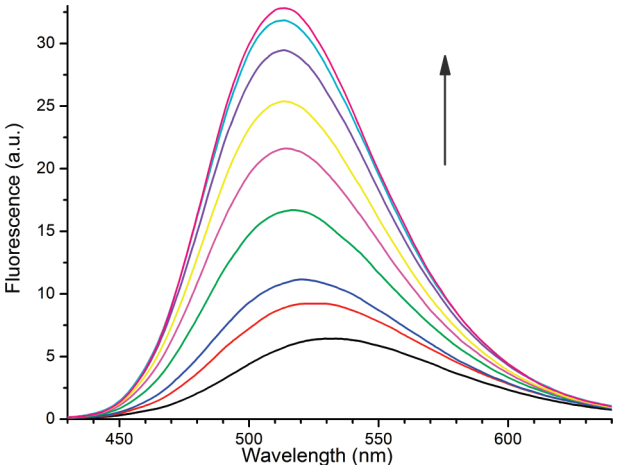

Figure 3. The fluorescence spectra of aqueous solutions of dye **1** (excitation at 396 nm) in the range of CB[7] concentration from 0 to 16 μM.

The quantum chemical calculations were carried out by the PM3 method combined with the continuum-level COSMO algorithm for treating the solvation contribution. The Gaussian 03 package was used.[10] The corresponding molecular structures were found with full geometry optimization. For the computation of volumes the molecular particles were considered as collections of overlapping atomic spheres with van der Waals radii.[11]

3. RESULTS AND DISCUSSION

Figure 2 shows absorption spectra of aqueous solutions of dye **1** in the presence of various concentration of CB[7]. Without cucurbituril absorption spectrum of dye **1** has a peak at 380 nm. Upon adding CB[7], the peak shifts to a red spectral region by 30 nm and varies in amplitude. There is a clear isosbestic point at 396 nm that destroys for CB[7] concentrations higher than 20 μM (not shown). That can be attributed to producing complexes with different stoichiometry that were observed previously.[6,7] The existence of the isosbestic point is in agreement with the suggestion that dye **1** produces a 1:1 inclusion complex with CB[7] in this range of cucurbituril concentration.

Figure 3 shows steady-state fluorescence spectra of the dye in the presence of various concentration of CB[7] on excitation at the isosbestic point, i.e., 396 nm. The peak of fluorescence shifts to a blue spectral region by 20 nm when concentration of CB[7] increases. On doing so the peak of fluorescence intensity increases by a factor of about 5. The fluorescence quantum yield of aqueous solution of dye **1** without CB[7] has been measured to be 0.026. Such a significant increase in emission intensity is suitable to carry out titration in order to estimate the association constant of complex (assuming 1:1 binding between the dye **1** and CB[7])

$$1 + \mathrm{CB[7]} \leftrightarrow 1@\mathrm{CB[7]} \qquad (1)$$

In equilibrium the association constant is as follows

$$K = \frac{x}{([\mathrm{CB[7]}] - x)([\mathrm{D}] - x),} \qquad (2)$$

where [CB[7]] and [D] are initial concentrations of the cucurbituril and dye **1**, respectively, x is the concentration of

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complexes **1**@CB[7] at equilibrium. Upon excitation at the isosbestic point λ = 396 nm, the intensity of fluorescence of aqueous solution of dye **1** in the presence of CB[7] is as follows

$$F = \varphi_1 \varepsilon([D] - x) l I_0 + \varphi_2 \varepsilon x l I_0 \quad (3)$$

where φ_1 and φ_2 are the quantum yields of fluorescence of the dye **1** and the complex of dye **1** with CB[7], respectively; ε is the extinction coefficients of solutions at isosbestic point; l is the optical length. Taking into account that the fluorescence quantum yield is by definition $\varphi \equiv F/\varepsilon[D]lI_0$, we rewrite eq 3

$$\varphi = \varphi_1 + (\varphi_2 - \varphi_1)\frac{x}{[D]} \quad (4)$$

The exact solution of eq 2 with respect to a physically meaningful x can be easily obtained

$$x = \frac{1}{2}\left([CB[7]] + [D] + \frac{1}{K}\right) - \left\{\frac{1}{4}\left([CB[7]] + [D] + \frac{1}{K}\right)^2 - [CB[7]][D]\right\}^{1/2} \quad (5)$$

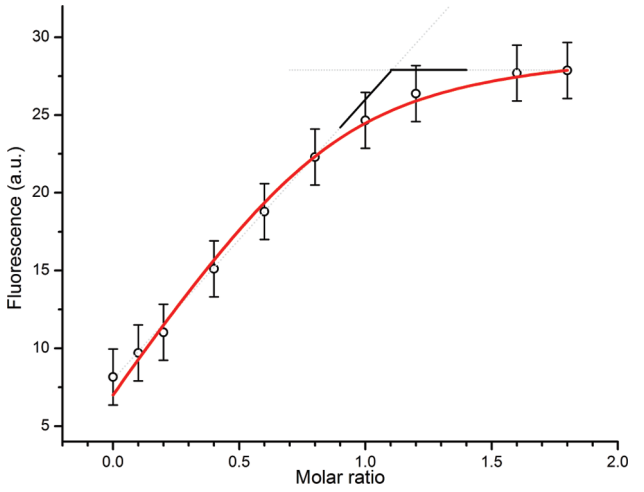

Figure 4. The peak fluorescence of aqueous solutions of dye **1** (open circles) as the function of molar ratio of CB[7] to dye **1**. The solid line has been obtained by fitting with eq 6 and the association constant $K = 1.0 \times 10^6$ M^{-1} as a parameter.

Substituting this expression to eq 4 gives

$$\varphi = \varphi_1 + \frac{(\varphi_2 - \varphi_1)}{2}\left(1 + \frac{[CB[7]]}{[D]} + \frac{1}{K[D]}\right) - \left\{\frac{1}{4}\left(1 + \frac{[CB[7]]}{[D]} + \frac{1}{K[D]}\right)^2 - 4\frac{[CB[7]]}{[D]}\right\}^{1/2} \quad (6)$$

It is worth noting that eq 6 is exactly the same as eq 1 as that reported by Megyesi, Biczok and Jablonkai.[2]

The data fit the eq 6 reasonably well (see Figure 4) that confirms 1:1 complex stoichiometry with a good degree of confidence and gives $K = 1.0 \times 10^6$ M^{-1}.

In addition, the composition of the complex can be also estimated by a location of the inflection point in the plot of fluorescence intensity versus the molar ratio of CB[7] to dye **1**, i.e., by the molar ratio method.[12] As seen from Figure 4, the inflection point corresponds to [CB[7]]/[dye **1**] = 1.1 that is in a good agreement with the 1:1 guest−host composition.

The magnitude of the association constant is fairly large so that the dye should be rigidly held with respect to the CB[7] cavity. The energy-minimized structure of inclusion complex dye **1**@CB[7] obtained by HF, PM3 quantum-chemical calculations and by a COSMO method is shown in Figure 5. The peridinium moiety is located inside the CB[7] cavity as another part of dye **1** is outside of it. The obtained structure of dye **1**@CB[7] complex is rather common.[27] However, the inclusion complexes, in which guest dyes of comparable sizes are embedded deeper in the CD[7] cavity, have been reported (for example, tricyclic basic dyes[13]). It is worth noting that for the dye **1**@CB[7] complex we also have found a local minimum in energy that corresponds to a similar structure, in which dye **1** is located almost completely inside the cavity. However, this structure is18.5 kcal/mol higher in energy than that presented in Figure 5 and hardly can be considered as the equilibrium state.

We have found that in all cases the observed decays of fluorescence fit well to double-exponential functions (see Table 1)

$$I(t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (7)$$

The calculated average lifetime, $\tau_{Av} = \alpha_1\tau_1 + \alpha_2\tau_2$, clearly shows that the addition of CB[7] in aqueous solution makes the relaxation of excited state of dye **1** significantly slower. This can be rationalized on the basis of findings made by van der Meer,

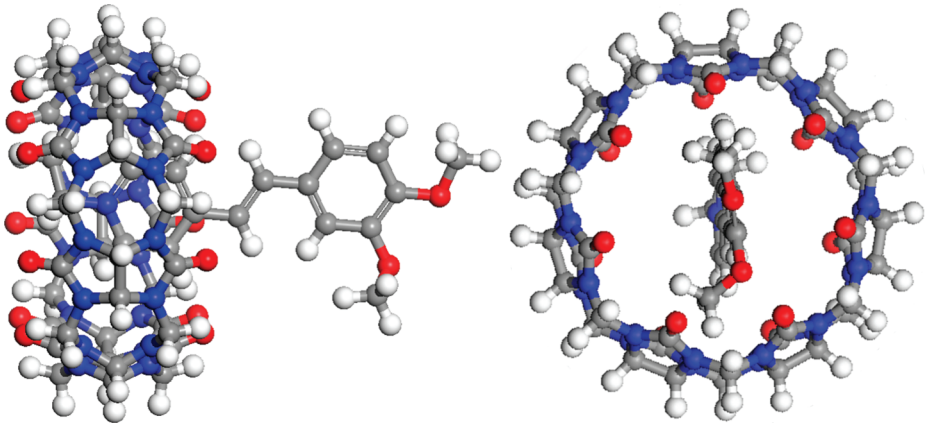

Figure 5. The energy-minimized structure of the inclusion complex dye **1**@CB[7] (the front and side views are shown).

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Table 1. Fluorescence Lifetimes τ_i, Their Relative Pre-Exponential Fractions α^i (in Parentheses) and Averaged Lifetimes τ_{Av} for Aqueous Solution of Dye 1 in the Presence of CB[7] and without It

	τ_1, ps	τ_2, ps	τ_{Av}, ps
dye **1**	125 (0.92)	377 (0.08)	145.2
1@CB[7]	236 (0.90)	1150 (0.10)	351.7

Table 2. The Effective Volumes σV, van der Waals volumes V, and σ Factors for Dye 1, CB[7], and Their Inclusion Complex Dye 1@CB[7]

	σV, Å^3	V, Å^3	σ, Å^3
dye **1**	488 ± 57	344	1.42 ± 0.16
1@CD[7]	1136 ± 144	1396	0.81 ± 0.11
CB[7]	817[a]	1189	0.68

[a] The value was taken from ref 19.

Zhang, Rettig, and Glasbeek.[14] They have studied selectively bridged ionic styryl dyes and found that twisting over single bonds is an effective route of the relaxation of the electronically excited singlet states of these dyes. This is in agreement with the fact that an increase in viscosity of microenvironment of the styryl dye (for example, as a result of decreasing temperature[15]) leads to an enhancement of fluorescence.[16] Embedding the pyridine ring of dye **1** in the cavity of CB[7] leads to a significant restriction on the intramolecular motion of dye **1** and, therefore, to decreasing nonradiative process in favor of fluorescence that is confirmed by experiment. A double-exponential fashion of fluorescence decay seems to be associated with existence of conformer equilibrium that also depends upon complexation.

The measurements of fluorescence depolarization are commonly used in specifying the structure of inclusion complexes. It is well-known[17] that experimentally determined steady-state fluorescence-anisotropy of fluorophores is defined by

$$r = \frac{\int_0^\infty I(t)r(t)\mathrm{d}t}{\int_0^\infty I(t)\mathrm{d}t} \qquad (8)$$

where $I(t)$ is the intensity of fluorescence as a function of time and $r(t)$ describes the anisotropy decay in time. This is associated with a rotation diffusion of the solute in solvent. In principle, the number of independent decay components varies from five to one, depending upon symmetry of fluorophore molecule.[18] However, the anisotropy decay is commonly assumed to be single exponential for solutes of an ellipsoid shape, which is a reasonable approximation to styryl dyes,[19] i.e., $r(t) = r_0 \exp(-t/\phi)$ This approximation is fairly good, provided that r_0, the initial fluorescence anisotropy, is close to the limiting value $^2/_5$. This is the case for dye **1** $r_0 = 0.360$ measured in glycerol. The time of rotational relaxation φ is determined by eq 9

$$\phi = \frac{V\eta}{k_B T}(Cf) \qquad (9)$$

Here k_B is the Boltzmann constant, T absolute temperature, η the viscosity of water, and V the van der Waals volume of the solute; the parameters C and f take into account the solute shape and diffusion boundary conditions, respectively. Mohanty et al.[20] observed a single exponential fluorescence-anisotropy decay in aqueous solution of Neutral Red in the presence of CB[7] that is a relevant example of this empirical rule.

Substituting a double-exponential function $I(t)$ in eq 8 easily gives the following formula that describes depolarization in the framework of the one relaxation-time approximation for a double-exponential fluorescence decay

$$r = \frac{r_0}{\tau_{Av}}\left[\frac{\alpha_1\tau_1}{1+\left(\frac{\tau_1}{\phi}\right)} + \frac{\alpha_2\tau_2}{1+\left(\frac{\tau_2}{\phi}\right)}\right] \qquad (10)$$

We have measured $r = 0.16$ for aqueous solution of dye **1** without CB[7] and $r = 0.15$ in the presence of CB[7]. Calculations by eq 10 have given rotational relaxation times of 119 ± 14 and 277 ± 35 ps for solutions without and with CB[7], respectively. It is worth noting that the latter is in the range of relaxation of times of inclusion complexes with β-cyclodextrin, i.e., 200 −300 ps.[21]

The above values of relaxation times correspond to the effective volumes σV (where $\sigma \equiv Cf$) of 488 ± 57 Å^3 and 1136 ± 144 Å^3 for dye **1** and dye **1**@CB[7], respectively. The measured effective volumes and the calculated van der Waals volumes are compared in Table 2. The effective volume of complex **1**@CB[7] is smaller than its van der Waals volume, i.e., $\sigma = 0.81 \pm 0.11$. Price and coworkers[22] measured a diffusion coefficient of CB[7] in D_2O by pulsed gradient spin−echo nuclear magnetic resonance spectroscopy. In the spherical approximation of CB[7] they calculated a hydrodynamic radius of 5.80 Å using the Stokes−Einstein equation that corresponds to the volume of 817 Å^3. This value can be used as the estimate for the effective volume of CB[7] in the context of diffusion relaxation. Its comparison with the calculated van der Waals volume gives $\sigma = 0.68$ that is in a good agreement within experimental errors with data obtained from fluorescence anisotropy measurements.

The rotational relaxation of dye **1** distinguishes from that of dye **1**@CB[7] owing to the difference in molecular shape and boundary conditions that reflects in $\sigma = 1.42 \pm 0.16$. Unlike the inclusion complex, the σ factor of dye **1** is lager than unity that is in agreement with the results by Di Paolo and Tocho[23] who studied the polarization anisotropy of the fluorescence of some cyanine dyes in ethanol that are similar in molecular structure and shape to styryl dyes. They found that the polarization anisotropy of the fluorescence of cyanines is well described by effective volumes that are larger than the cyanine van der Waals volumes (σ factors are about 1.29) with the slip boundary condition, i.e., the tangential forces between the solute and solvent being negligible. The authors suggested that the appearance of larger volumes can be attributed to attractive interactions between the cyanine cation and the polar solvent. In other words, the effective volume of dye can be considered as that of its associate with some molecules of water; the dye molecule and its hydration shell can rotate as a single particle.

To specify this point quantum chemical calculations have been made in the present work. In aqueous solutions, the dye cation forms hydrogen bonds that are much stronger than those of neutral species. This can produce stable associates with water molecules. The Gibbs energy of such associates can be calculated as follows. Several molecules of water within the nearest vicinity of the cation are taken into account at quantum-chemical level so that the structure and energy of associates **1** nH$_2$O are determined.

Table 3. Calculated Changes in the Gibbs Energy, $\delta\Delta G(n)$, of the Production of Associates between Dye 1 and n Molecules of Water and Effective Volumes of Associates, $V(n)$

n	$V(n)$, Å^3	$\delta\Delta G(n)$, kcal/mol
0	344	0
1	379	−1.2
2	414	−2.4
3	451	−2.5
4	490	3.8
5	509	9.9

Then their solvation is estimated in the framework of the continuum solvent model. Thus three processes are taken into consideration: (i) association of the dye cation with n molecules of water $\mathbf{1} + n\mathrm{H_2O}$ with a corresponding change in the Gibbs energy $\Delta G_1(\mathrm{n})$; (ii) hydration of 1 with ΔG_2; and (iii) hydration of $n\mathrm{H_2O}$ with ΔG_3. The Gibbs energies $\Delta G_1(n)$, ΔG_2, and ΔG_3 are calculated as described in section 2. Calculated changes in the Gibbs energy $\delta\Delta G(n) = \Delta G_1(n) - (\Delta G_2 + \Delta G_3(n))$, that corresponds to the equilibrium

$$1 + n\mathrm{H_2O} \leftrightarrow 1n\mathrm{H_2O} \tag{11}$$

are presented in Table 3. The value of $\delta\Delta G(n)$ determines the stability of the associate with n molecules of water; the value of $\delta\Delta G(n)$ becomes negative for $n = 1$, 2 and 3, $\delta\Delta G(0)=0$ and it is positive for $n \geq 4$. The probability of existence of the associate with n water molecules is

$$P_n = \frac{P(n)}{\sum_{n=o} P(n)} \tag{12}$$

where $P(n) = \exp(\delta\Delta G(n)/k_BT)$. Thus in solution there exists a narrow distribution of associates with various n; the peak is at $n = 3$. Therefore, the averaged effective volume of associates is

$$V = \sum_{n=0}^{N} P_n V(n) \tag{13}$$

where $V(n)$ are calculated and $N = 5$ is enough for convergence. For data presented in Table 3 this formula gives $V = 433$ Å^3, which is in reasonably good agreement with the effective volume obtained from fluorescence anisotropy experiment (see Table 2). The similar calculation for the inclusion complex dye **1**@CB[7] has revealed no stabilization of its associates with explicit water molecules.

4. CONCLUSIONS

The results obtained from steady-state absorption, fluorescence, and fluorescence anisotropy as well as time-resolved fluorescence studies indicate that styryl dye **1** produces the 1:1 inclusion complex with CB[7] (association constant $K = 1.0 \times 10^6$ M^{-1} in the range of CB[7] concentration up to 16 μM). Upon complexation the fluorescence intensity of dye **1** increases by a factor of ca. 5 that can be attributed to restrictions which are imposed on the dye intramolecular motion by the cavitand cavity. The comparison of the results of quantum-chemical calculations and data on the fluorescence anisotropy measurements confirms that dye **1** rotates as whole with CB[7] and with its hydration shell in the absence of CB[7].

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