

Fluorescence of Crowned Butadienyl Dye and Its Metal Complexes

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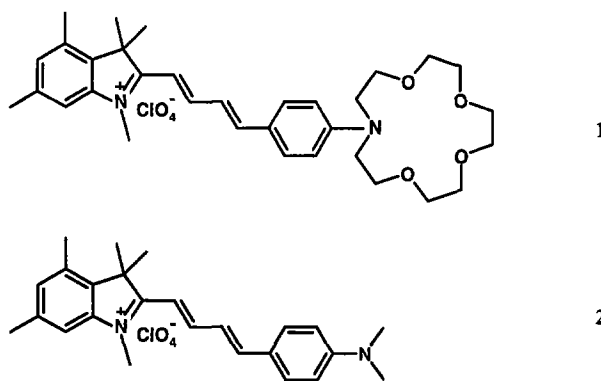
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The absorption and fluorescence spectra of complexes of butadienyl dye (**1**) with lithium, sodium, magnesium, and calcium cations in MeCN were investigated. The addition of Li, Na, Mg, and Ca perchlorates to the solution of dye **1** in acetonitrile results in a significant (up to 5900-cm^{-1}) short-wavelength shift of the absorption spectrum and a small (about 200-cm^{-1}) short-wavelength shift of the fluorescence spectrum. The recoordination reaction in metal complexes of **1** takes place by intramolecular mechanism. The fluorescence quantum yield of 1Li^+ , 1Na^+ , and 1Ca^{2+} is approximately two times higher than that for **1**. It was supposed that Li^+ cation coordinates predominantly with oxygen atoms of macrocycle and, hence, influences weakly macrocycle nitrogen atoms conjugated with a molecule π -system.

KEY WORDS: Crown ether; metal complex; recoordination; excited state.

INTRODUCTION

Crowned dyes can change ion-binding ability on irradiation [1]. It was shown recently that in the excited state of crowned dyes, adiabatic recoordination takes place [2–7]. The reaction was observed in crowned stilbene [2], merocyanine dyes [3,4], and styryl dyes [5–7]. The mechanism of the reaction consists in excited-state breaking of the bond of the metal cation with the macrocycle heteroatom linked with the π -system of the dye [2,3, 5]. However, systematic investigation of cation influence on the photoreoordination reaction in metal complexes of crown ethers was not carried out. In present work the photoreoordination reaction in complexes of butadienyl dye (**1**)



with lithium, sodium, magnesium, and calcium cations is investigated.

RESULTS AND DISCUSSION

The analogue of a crowned dye (**2**) whose molecule does not contain a macrocycle fluoresces weakly in aceto-

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Table I. Characteristics of Buthadienyl Dyes **1** and **2** and Their Complexes with H⁺, Li⁺, Na⁺, Mg²⁺, and Ca²⁺ in MeCN

Dye	K_{abs} (M^{-1})	K_{fl} (M^{-1})	λ_{abs} (nm)	$\Delta\nu_{\text{abs}}$ (cm^{-1})	λ_{fl} (nm)	$\Delta\nu_{\text{fl}}$ (cm^{-1})	λ_{iso} (nm)	ϵ ($M^{-1}\text{cm}^{-1}$)	φ
2	—	—	585	—	702	—	—	53,700	0.013
2H⁺	16.2	—	406	7,360	—	—	470	33,900	<0.001
1	—	—	585	—	702	—	—	59,300	0.049
1H⁺	151	—	408	7,280	—	—	472	37,400	<0.001
1Li⁺	91.7	73.5	543	1,210	694	190	548	47,900	0.095
1Na⁺	24.9	23.8	519	1,970	699	30	535	41,200	0.087
1Mg²⁺	89.5	50.0	435	5,920	656	1,010	492	43,800	—
1Ca²⁺	188.5	123	450	5,060	691	260	504	40,800	0.079

nitrile (Table I). The absorption spectrum of dye **2** is practically not changed by the introduction of a crown-ether moiety to the dye molecule. The fluorescence spectrum is also not shifted but the fluorescence quantum yield (φ) increases substantially. The absorption and fluorescence spectra of crowned dye **1** in acetonitrile are given in Fig. 1.

The addition of alkali (Li, Na) and alkaline-earth (Mg, Ca) metal perchlorates to the solution of dye **1** in acetonitrile results in a significant (up to 5900-cm^{-1}) short-wavelength shift of the dye absorption spectrum and a small (about 200-cm^{-1}) short-wavelength shift of the dye fluorescence spectrum. The absorption and fluorescence spectra of **1** in the presence of different concentrations of calcium perchlorate are shown in Fig. 2. The complexation equilibrium constants (K_{abs}) for 1:1 complexes, the values of maxima of calculated absorption (λ_{abs}) and fluorescence (λ_{fl}) spectra of pure complexes corresponding to infinitely high concentrations of metal cations, and the values of shifts of absorption ($\Delta\nu_{\text{abs}}$) and

fluorescence ($\Delta\nu_{\text{fl}}$) spectra maxima of **1** at complexation are given in Table I. The protonation of nitrogen atoms of the molecules of both crowned dye **1** and analogue **2** without a macrocycle by trifluoroacetic acid results in a short-wavelength shift of absorption spectra maxima by about 7300 cm^{-1} . The value of K_{abs} of **1** is approximately one order higher than that for **2**. The distinction of basicities of **1** and **2** cannot be caused by breaking of dialkylamino group conjugation with the π -system on going from **1** to **2** because of twisting of this group or pyramidalization of nitrogen atoms since twisting and pyramidalization should result in a significant distinction of the absorption spectra of **1** and **2**. The protonated forms of **1** and **2** do not fluoresce in acetonitrile.

The fluorescence excitation spectra of **1** are shifted to the short-wavelength region by at least 1410, 2600, 5260, and 5050 cm^{-1} at Li, Na, Mg, and Ca perchlorate concentrations equal to 0.0573, 0.215, 0.122, and 0.0328 M , respectively. The shifts of fluorescence excitation spectra are close to those of absorption spectra. In analogy

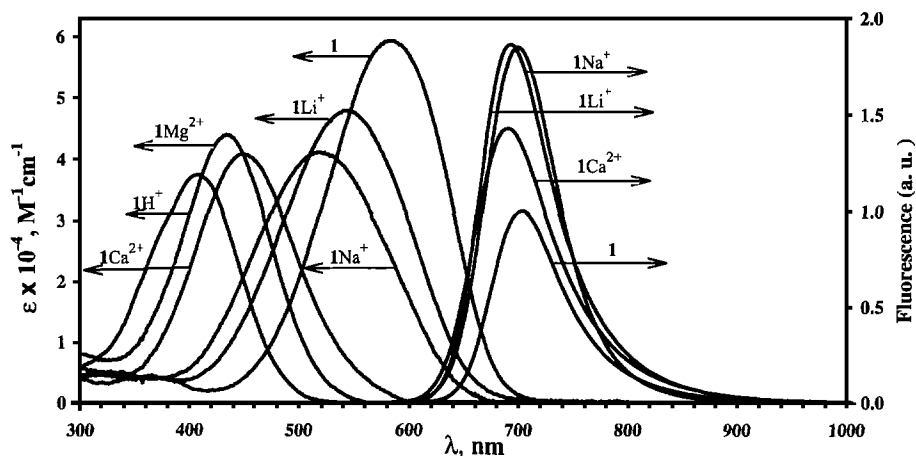


Fig. 1. Absorption and fluorescence spectra of butadienyl dye **1**, complexes of **1** with trifluoroacetic acid (**1H⁺**), lithium, sodium, magnesium, and calcium cations in acetonitrile at room temperature. The squares under the fluorescence spectrum of **1** and its complexes are proportional to their fluorescence quantum yields.

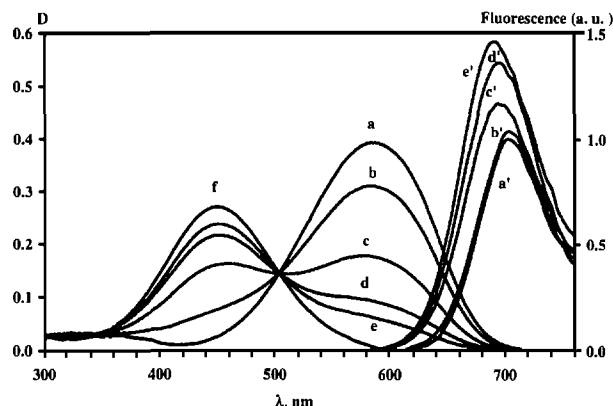


Fig. 2. Absorption (a, b, c, d, e, and f) and fluorescence (a', b', c', d', and e') spectra of butadienyl dye **1** in acetonitrile at room temperature. The concentration of $\text{Ca}(\text{ClO}_4)_2$ is equal to 0 M (a and a'), 0.00218 M (b and b'), 0.00739 M (c), 0.0169 M (d and c'), 0.00328 M (e and d'), and ∞ (f and e').

with early studied systems [4,7], the great difference in the values of absorption and fluorescence spectra maxima of metal complexes is explained by the photoinduced recoordination reaction in excited complexes. This reaction consists in the decreasing of strength or breaking of the metal cation bond with macrocycle nitrogen atoms and in the displacement of the cation from its equilibrium position in the ground state.

The recoordination reaction in metal complexes of **1** proceeds by an intramolecular mechanism. This is confirmed by the measurements of the fluorescence of **1** and 1Na^+ in a solid glassy butyronitrile matrix at 77 K, where diffusion is impeded. The shift of excitation fluorescence spectrum maxima on the complexation of **1** with Na^+ is significantly greater than that for the fluorescence spectrum (Fig. 3).

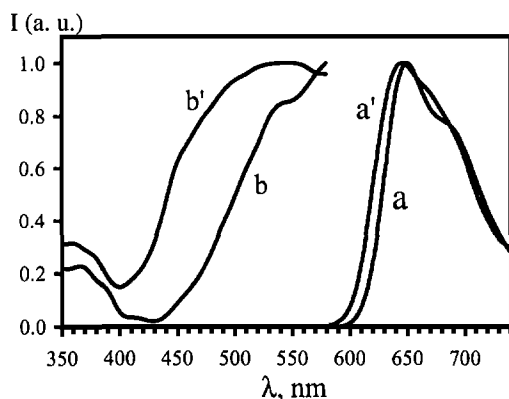


Fig. 3. Normalized-to-unity fluorescence (a and a') and fluorescence excitation (b and b') spectra of **1** in solid glassy butyronitrile at 77 K. The concentration of NaClO_4 is equal to 0 M (a and b) and 0.2 M (a' and b').

The complexation of **1** with Li^+ influences weakly the value of the absorption spectrum shift in comparison with Na^+ . This contradicts the results obtained for complexation of azacrowned 7-aminocoumarins with Li^+ and Na^+ [8] and the model according to which the value of the spectral shift on the formation of metal complexes of crowned dye is proportional to the ratio of the cation charge to its radius [8]. This contradiction could be caused by the fact that the lithium cation has a diameter approximately 1.5 times less than the size of the macrocycle cavity. It coordinates predominantly with oxygen atoms of the macrocycle and, hence, influences weakly macrocycle nitrogen atoms conjugated with a molecule π -system.

The complexation results in a change of the ϕ of dye **1**. The change in the fluorescence spectra of **1** in the presence of metal perchlorates can be described as a static fluorescence quenching owing to the formation of 1:1 complexes. The ϕ values of pure complexes were obtained on the base of the calculated limit fluorescence spectra ($[\text{M}^{n+}] \rightarrow \infty$). The fluorescence intensity of 1Mg^{2+} is less than that of **1**, but the fluorescence intensity of 1Li^+ , 1Na^+ , and 1Ca^{2+} is approximately two times higher than that of **1**. The equilibrium constants obtained from the analysis of fluorescence spectra (K_f) are close to the K_{abs} (Table I). Similar results were obtained for azacrowned merocyanine [9]. The results obtained provide additional evidence of the fact that the photoreoordination reaction is a fast intramolecular process, which proceeds in a time domain shorter than the lifetime of the excited state.

Together with the complexation, the changes in absorption and fluorescence spectra could be caused also by a salt effect. In order to check this possibility we obtained the absorption and fluorescence spectra of dye **2**, which cannot form a complex with metal salts in the presence of magnesium perchlorate (the magnesium cation has maximum charge density among considered cations). The absorption and fluorescence spectra of dye **2** are changed insignificantly at a $\text{Mg}(\text{ClO}_4)_2$ concentration equal to 0.1 M. The extinction coefficient of dye **2** increases by approximately 2%; the fluorescence quantum yield increases by approximately 15%, $\Delta\nu_{\text{abs}} \approx 70 \text{ cm}^{-1}$, $\Delta\nu_{\text{fl}} \approx 0 \text{ cm}^{-1}$. This points out that the influence of salt on the absorption and fluorescence spectra **1** can be neglected.

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