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Luminescence of Bound Forms of Schiff Bases in a Perfluorosulfonic Membrane

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Abstract—Perfluorosulfonic membranes were modified by Schiff bases by sorption of molecules on sulfonic groups of the membranes and by coordination attachment to preliminarily implanted La^{3+} cations. The fixation of the molecules in nanosized cavities of membranes is responsible for their luminescence at room temperature in a violet-blue spectral range. The choice of guest molecules of bases and the mode of their immobilization in a membrane provides certain possibilities of regulating the position of the de-excitation band of film luminophores.

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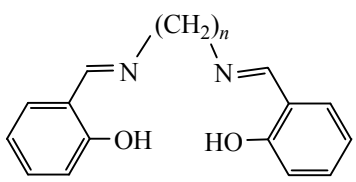
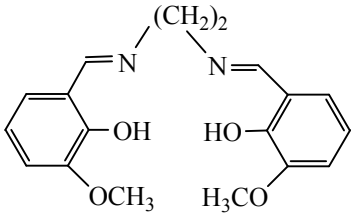
Perfluorosulfonic membranes possessing nanosized canals and cavities [1, 2] are used to obtain and stabilize in them a wide set of guest materials [3–5]. In essence, the membranes fulfill the functions of nanoreactors with a size specificity of the corresponding processes and properties of resulting materials. The transparence of membranes in a wide spectral range gives rise to a special interest to optical properties of nanocomposites based on them. Fixation of the protonated form of 4,7-diphenyl-1,10-phenantroline on the walls of cavities of a perfluorosulfonic membrane provides a bright blue luminescence at room temperature [6]. This feature opens an opportunity of obtaining a series of film luminophores with light emission parameters determined by the nature of guest molecules and by the character of their interaction with the carrying agent. In the present work we have studied sorption of a series of organic bases **I–VII** by an MF-4SK membrane manufactured in Russia and also luminescent-spectral properties of the resulting composites.

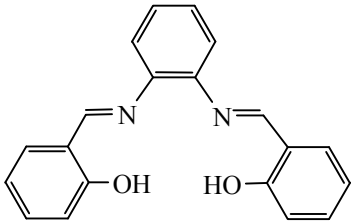


I–III

n = 2 (**I**), 3 (**II**), 4 (**III**)



IV



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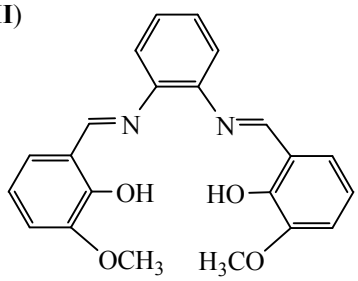
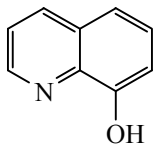


VI



VII

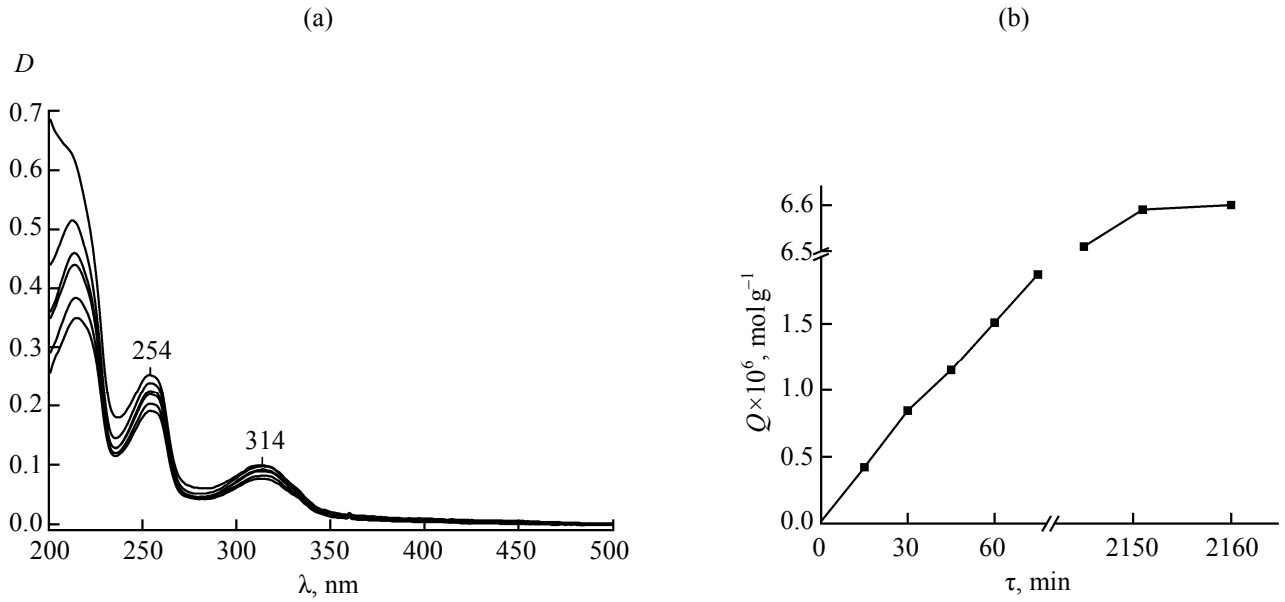


Fig. 1. (a) Decrease in the intensity of the spectra of 10^{-5} M acetonitrile solution of compound **I** during its contact with a membrane and (b) sorption kinetics; membrane weight 0.05 g, solution volume 10 ml.

The MF-4SK membranes are porous polymeric films containing functional sulfo groups located inside cavities of a fluorocarbon framework. The cavities have an effective diameter of ~4 nm and are connected with each other by narrow canals of ~1 nm in diameter [1, 2]. On dipping the membranes in acetonitrile solutions of Schiff bases **I–VI** and 8-hydroxyquinoline **VII** the course of the sorption is reliably recorded by a decrease in the intensity of absorption bands (Fig. 1). The photometric monitoring points to a slow process hampered by diffusion in narrow canals of the membranes; values of sorption close to equilibrium are reached only after a day (Fig. 1).

It is not excluded that the prolonged character of the sorption is caused by "thickening" redistribution of large guest molecules in nanosized space of membrane cavities alongside with the diffusion inhibition. It is highly probable that Schiff bases B strongly fixed and firmly kept on washing off are forms protonated by nitrogen atoms [6] [Eq. (1)].

$$2(-SO_3H) + B \rightarrow 2(-SO_3^-)\cdots 2H^+\cdots B. \quad (1)$$

The found values of sorption (see the table) in all cases appear more than by an order of magnitude lesser than the concentration of sulfo groups in a membrane ($[-SO_3H] = 0.84\times10^{-3}$ mol g^{-1} [6–8]), which is not surprising in view of large sizes of molecules and steric hindrances in their arrangement in narrow cavities of the carrying agent. In this connection attention should be given to a significant, comparable in the order of magnitude with the concentration of sulfo groups, value of sorption of a rather small molecule **VII**, which is also sorbed due to protonation. The action of a steric factor in the case of sorption concentrating large guest molecules is of a specific character: a decrease in the sorption is absent though it is expected upon elongation of the hydrocarbon bridge in the series of compounds **I–III**, moreover, the a slight trend to its increase is observed. At the same time, a significant inhibition of the sorption is observed for bases **IV, VI** with methoxy groups in a benzene ring and at the replacement of a methylene bridge by a phenylene bridge.

In the luminescent spectra of the modified membranes well-pronounced wide bands in the region of 400–500 nm (Fig. 2) are reliably detected at room temperature; a sorbed form of compound **IV**, which practically does not show light emission, and compound **VI** with a stretched poorly resolved spectrum make an exception. It is important to emphasize that the luminescence of bases **I–VII** in solutions is absent, whereas in polycrystalline samples of the studied substances it can be detected only for compound **III**. It suggests that this is the bound state which is responsible for a perturbation of electronic structure of molecules of the bases in a membrane and for both the luminescence appearance and its character at room temperature.

Value of sorption (Q) and optical properties of molecules of bases in acetonitrile solutions and in bound states in the initial and La-substituted forms of an MF-4SK membrane

Base no.	Solution	Membrane in H-form			Membrane in La-substituted form			
	λ_{abs}, nm	$Q\times10^6$, mol g^{-1}	λ_{lum}, nm	I, rel. units	$Q\times10^6$, mol g^{-1}	λ_{abs}, nm	λ_{lum}, nm	I, rel. units
I	213	43.5	449	26	4.0	228	445	27
	255					273		
	315					376		
II	–	73.9	446	28	3.2	234	446	18
	255					287		
	314					358		
III	–	60.4	444	53	2.8	234	445	48
	254					287		
	314					357		
IV	221	50.0	515	22	3.1	228	458	2
	263					279		
	330					380		
V	208	43.5	467	7	2.6	228	376	69
	269					297		
	330					323		
VI	223	11.1	398	16	2.1	228	405	4
	278					–		
	330					305		
VII	202	163.1	480	16	8.2	265	472	6
	–					318		
	308					357		

Unusual shape of the absorption spectra consisting of wide intensive bands practically unresolved and displaced in the long-wavelength region corresponds to the features of the luminescence of the modified membranes. The spectrum typical for all systems of encapsulated molecules **II** is given in Fig. 3 in comparison to the spectrum of their acetonitrile solution. The observed broadening of bands and practically continuous absorption can be caused not only by protonation, but also by essential and various in extent

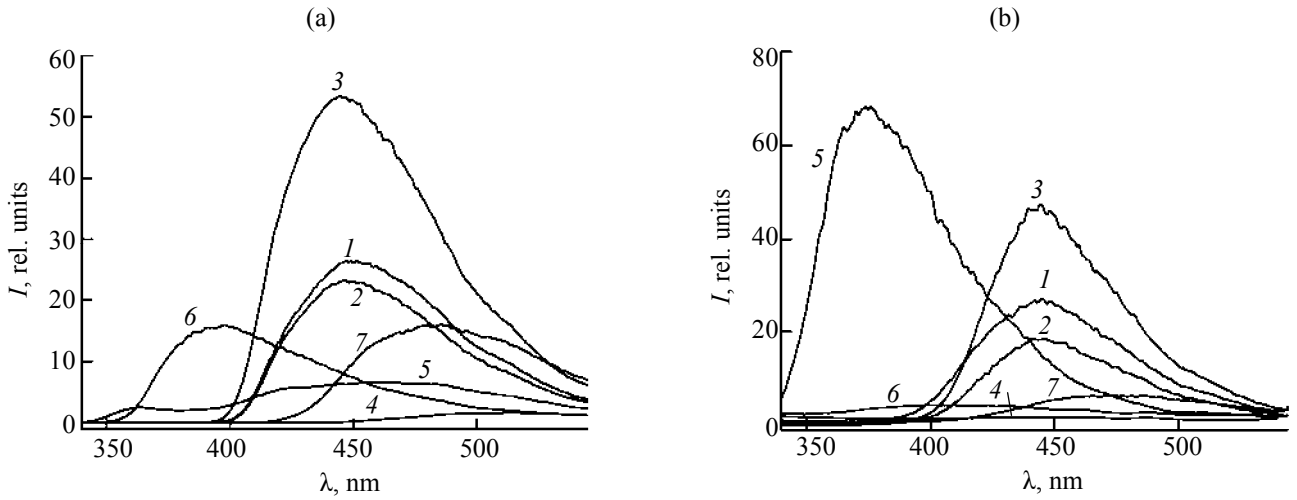


Fig. 2. (*1*–*7*) Luminescence of sorbed forms of bases **I–VII** on (a) hydrogen and (b) La-substituted forms of the membrane.

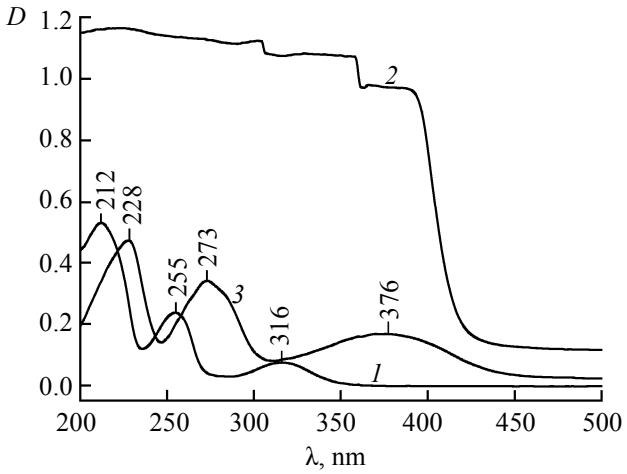


Fig. 3. Absorption spectra of compound **I** in (*1*) 10^{-5} M acetonitrile solution and in a bound state on (*2*) hydrogen- and (*3*) La-substituted forms of a membrane.

and character distortions of geometrical parameters of molecules on their sterically hampered sorption on sulfo groups in nanosized cavities of a membrane.

To elucidate the influence of the nature and content of sorption centers on spectral-luminescent properties of fixed molecules, the alternative mode of modification of membranes by them [6, 8] can be used, which consists in preliminary ion-exchange fixation of cations having no proper luminescence with the subsequent replacement of water in their coordination sphere by molecules of bases as ligands. The treatment of the membrane by an aqueous $LaCl_3$ solution results in practically complete replacement of protons of membrane sulfo groups by La^{3+} cations [6–8] (2).

$$3(-SO_3H) + LaCl_3 + nH_2O \rightarrow (-SO_3-)_3La(H_2O)_n + 3HCl. \quad (2)$$

As a result of ion-exchange modification a significant reduction of the number of sorption centers is reached, as almost limiting filling the accessible surface area of the membrane by cations ($[La^{3+}] = 2.8\times10^{-4}$ mol g^{-1}) corresponds to the substitution of lanthanum for protons of three sulfo groups [6–8]. As a result the values of the subsequent coordination sorption of bases on the membrane appear essentially less than on its initial hydrogen form (see the table). Modified membranes do not demand washing off by a solvent, as the excess content of guest molecules (Q_{exc}) in the porous space is insignificant compared to the sorption value: at the concentration of working solutions of the bases 10^{-5} M and at the known volume of membrane pores (V_p 0.20 cm^3 g^{-1} [9]) $Q_{exc} = cV_p = 2\times10^{-9}$ mol g^{-1}.

The conservation of the implanted complexes on the prolonged washing of membranes by acetonitrile points to stability of lanthanum anchor bonds with the carrying agent. In the absorption spectra of modified membranes well-resolved bands are recorded (Fig. 3), which, most likely, reflect a uniform mode of the fixation of guest molecules on sorption centers and a decrease in the steric hindrances to their arrangement. Polarization of molecules in the bound state is confirmed by a significant long-wave shift and redistribution of the intensity of absorption bands in relation to the spectrum of the "free" state in solutions (Fig. 3). It gives rise to the luminescence reliably detected at room temperature in the case of several implanted complexes (Fig. 2). Comparison of the spectra of bases **I–III, VII** fixed in the initial and La-substituted forms of the membrane reveals their similarity, whereas for three other bases **IV–VI** sharp differences are observed: on passing from the protonated to the coordinated states the weak wide luminescence band of compound **V** is unexpectedly strongly exhibited in the short-wave region (λ_{max} 376 nm), whereas well-pronounced luminescence bands of compounds **VI, VII** are practically completely leveled down.

In spite of difficulties in interpretation of the observed behavior of the obtained systems, there are some common features in it. The appearance of luminescence of molecules of the bases at room temperature, obviously, is connected with a significant perturbation of their electronic structure owing to strong fixation and polarization in nanosized cavities of the membrane. It is probable that in the bound state of organic molecules the vibration relaxation process proceeds more actively, and as a result an additional stabilization of radiative triplet states [10] is reached. Finally, the choice of guest molecules of bases and of the mode of their immobilization in the membrane provides certain possibilities of regulating the position of the de-excitation band of the film luminophores in the violet-blue spectral region.

EXPERIMENTAL

The absorption spectra of the modified membranes and solutions were recorded on a Shimadzu UV-2550 spectrophotometer; luminescence was recorded at room temperature using a Flyuorat-02-Panorama spectrometer.

Perfluorosulfonic MF-4SK membranes of 0.25 mm width were purified by boiling in concentrated HNO_3 over 2.5–3 h with the subsequent washing by distilled water up to the absence of acid reaction. When a direct modification mode was used the value of sorption of bases **I–VII** was determined by photometry from decrease in concentrations of their 10^{-5} M acetonitrile solutions during their contact with membranes in the initial H-form.

To realize the second implantation mode of the bases, the membranes were preliminary modified by the ion-exchange with La^{3+} cations. To do this, the membranes were held in a $LaCl_3$ 10^{-3} M aqueous solution up to reaching an equilibrium monitored by measuring pH. Then the excess salt was removed from the pore space by careful washing with water. In the following stage La-containing membranes were immersed in 10^{-5} M acetonitrile solutions of the bases and held there up to reaching an equilibrium determined by a photometer monitoring of the sorption.

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