

# Mesogenic and Luminescent Properties of Lyotropic Liquid Crystals Containing Eu(III) and Tb(III) Ions

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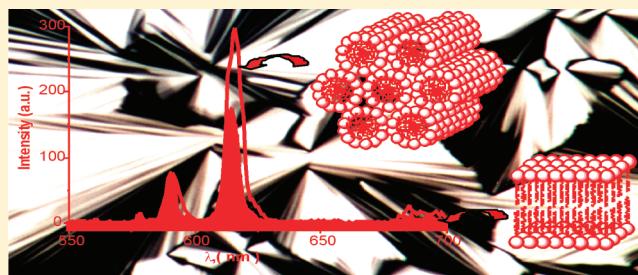
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 Supporting Information

**ABSTRACT:** Lyotropic metallomesogens containing trivalent rare-earth metal ions have unique attractive behavior due to the combination of some specific properties of the lanthanide ions with anisotropic supramolecular organization liquid crystal and provide new promises in biochemistry and materials science. In this article, we have studied the liquid crystal and luminescence properties of lyotropic systems containing Eu<sup>III</sup> and Tb<sup>III</sup> ions based on nonionic surfactants. The type, the structural parameters of the mesophases, and the structure of a liquid crystal complex have been investigated using polarized optical microscopy (POM), X-ray diffraction, and Fourier transform infrared. In addition, on the basis of the luminescence lifetime, the structure of the first coordination sphere was determined. The results obtained based on time-resolved spectroscopy data are discussed in the light of the influence ligand environment, ion type, and the type of supramolecular organization on the luminescence efficiency of lyotropic lanthanide containing systems. The first time was reported for Eu<sup>III</sup> complexes increasing the luminescence efficiency in the hexagonal phase compared to the lamellar mesophase.



## INTRODUCTION

liquid crystal systems with a strong response function to weak external stimuli have attracted a great deal of research interest owing to their wide application range including soft materials production.<sup>1–4</sup> In order to develop advanced materials, the application of liquid crystals has expanded from conventional optoelectronic devices to active matrices for synthesis and supramolecular organization of nanosized particles.<sup>5–8</sup> Recent papers<sup>9,10</sup> present a conceptually new approach to the application of nematic liquid crystalline phases to control the self-organization of nano- and microsized particles. This approach creates favorable conditions to design new chemosensitive colloidal architectures and easily convertible two-dimensional (2D) optical metamaterials. Moreover, a certain development can be observed in the synthesis of ordered nanomaterials through self-organizing processes in lyotropic liquid crystal (LLC) systems,<sup>11–14</sup> which regulate concentration, size, and architecture of colloidal structures at a macroscale, by selecting an organic ligand and the type and concentration of the solvent. The introduction of a metal ion into a mesomorphic system can significantly modify its properties and anticipate development of materials with unusual electrical, magnetic, and optical characteristics. In this regard, the ions of rare-earth elements are of

particular interest. The unique photophysical properties of lanthanides (Lns) find the most important applications. Thus, there appear many possibilities to synthesize multifunctional materials based on lanthanide ions, which are characterized by a narrow band of emission and a high quantum yield of luminescence. Lanthanide emission covers spectra ranging from UV (Ce<sup>III</sup> and Gd<sup>III</sup>), to visible (Tm<sup>III</sup>, Tb<sup>III</sup>, Dy<sup>III</sup>, Eu<sup>III</sup>, and Sm<sup>III</sup>), and to near-infrared (Yb<sup>III</sup>, Nd<sup>III</sup>, Ho<sup>III</sup>, and Er<sup>III</sup>) regions. This makes lanthanides potentially promising materials for the development of molecular electronics and for their use in organic light emitting diodes, organic lasers, optical amplifiers, and biomedical analysis as bioprobes and bioimaging for noninvasive methodologies.<sup>15–19</sup> However, along with their advantages, lanthanides have a significant disadvantage, they suffer from weak light absorption. The trivalent lanthanide ions have very low molar absorption coefficients (typically  $\epsilon < 1–10 \text{ mol}^{-1} \text{ cm}^{-1}$ ) due to the forbidden character of their intra-4f transitions, and the population of the excited states of the emitting metal ion by direct excitation in the 4f levels is consequently inefficient. For lanthanide

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**Table 1.** Liquid Crystal Properties and Geometries of Lyotropic Mesophases

system	mesophase type	mesophase–isotropic phase transition temperature, $T_{LLC-1}$ (°C)	temperature range of mesophase existence, $\Delta T$ (°C)	interplanar distance, $d_{100}$ (Å)	parameter of elementary cell, $a$ (Å)
$C_{12}EO_{10}/Eu^{III}$ (1:2 mol)	hex	95.0	80.0	46.00	53.00
$C_{12}EO_{10}/Tb^{III}$ (1:2 mol)	hex	80.2	65.2	48.20	55.70
$C_{12}EO_{10}/Eu^{III}/H_2O$ (1:2 mol)	hex	78.8	63.5	48.92	56.48
$C_{12}EO_{10}/Eu^{III}/D_2O$ (1:2 mol)	hex	71.4	56.4	49.08	56.64
$C_{12}EO_{10}/Tb^{III}/H_2O$ (1:2 mol)	hex	64.8	49.8	50.48	58.29
$C_{12}EO_{10}/Tb^{III}/D_2O$ (1:2 mol)	hex	69.1	54.1	48.81	56.36
$C_{12}EO_{10}/Eu^{III}/H_2O$ (1:1 mol)	hex	47.2	32.2	49.41	57.05
$C_{12}EO_{10}/Eu^{III}/D_2O$ (1:1 mol)	hex	44.6	29.6	51.10	60.00
$C_{12}EO_4/Eu^{III}/D_2O$ (1:1 mol)	lam	129.3	114.3	48.51	
$C_{12}EO_4/Eu^{III}/H_2O$ (1:1 mol)	lam	123.0	108.0	47.50	
$C_{12}EO_4/Tb^{III}/D_2O$ (1:1 mol)	lam	100.1	85.1	55.21	
$C_{12}EO_4/Tb^{III}/H_2O$ (1:1 mol)	lam	90.1	75.1	51.96	
$C_{12}EO_4/Tb^{III}/D_2O$ (1:2 mol)	lam	124.5	109.5	54.53	
$C_{12}EO_4/Tb^{III}/H_2O$ (1:2 mol)	lam	118.4	103.5	63.60	

<sup>a</sup>  $(NO_3)_3$  and 6H<sub>2</sub>O groups omitted for clarity. H<sub>2</sub>O and D<sub>2</sub>O: extra 5% weight.

complexes, the problem has been solved by selecting organic ligands to achieve an effective energy transfer from the ligand to the emitting ion.<sup>20–22</sup> Luminescence of lanthanide complexes is related to electron excitation due to energy transfer from the ligand triplet level followed by electron transition to the lower allowed states. In this case, the so-called antenna effect is observed.<sup>15</sup> Thus, the critical mission in the search for lanthanide luminescence intensification methods is the appropriate ligand selection. Of all the lanthanide coordination compounds, adducts of lanthanide  $\beta$ -diketonates show the most effective luminescence. The preparation of lanthanide  $\beta$ -diketonate adducts with mesogenic properties has been shown in ref 23. Because of the combination of the liquid crystal properties of these aggregates and high anisotropy of the magnetic susceptibility, single-domain environments with effective polarized luminescence can be obtained.<sup>24</sup> The application range of these systems is slightly limited by existing temperature intervals of mesophases. The approaches to development of luminescent hybrid materials by introducing lanthanide complexes into channels of mesoporous silica templates<sup>25–27</sup> have been proposed, but the question of even distribution of emitting ions remains open. One of the most promising research lines is the use of the template approach to the nanoorganization of lanthanide ions via the lyotropic LC state, therein complexes of Ln ions and amphiphilic molecules develop directly, followed by mesophase formation. The expected isolation of fluorescent clusters by a nanostructured matrix with uniaxially ordered molecule orientation can result in the reduction of the self-quenching effect that leads to a significant enhancement of optical properties.<sup>28</sup> The overviews in the field of molecularly designed lyotropic metellomesogens, their lyotropic behavior has been given in ref 29. The first lyotropic mesophases were reported<sup>30</sup> for some trivalent rare-earth dodecylsulfates in the presence of the ethylene glycol, water, and a mixture of both solvents. In our earlier papers, we first discussed synthesis of lanthanide containing LLC systems, based on nonionic surfactants made up of decaethylene glycol monododecyl ether and tetraethylene glycol monododecyl ether, which are stable over a wide range of temperatures (including room temperature) and concentrations. Self-organizing processes in

solutions and mesophases were investigated.<sup>31–34</sup> It was shown that the luminescence efficiency depends on the liquid crystal phase orientation. The luminescence efficiency demonstrated a 7-fold increase when a transition from unoriented samples to oriented samples occurred.<sup>31</sup> The objective of this article, as an extension of the previous research, is to present a comprehensive study of several factors, such as ligand environment, ion type, supramolecular organization method, and their effect on luminescence efficiency of lanthanide containing lyotropic systems.

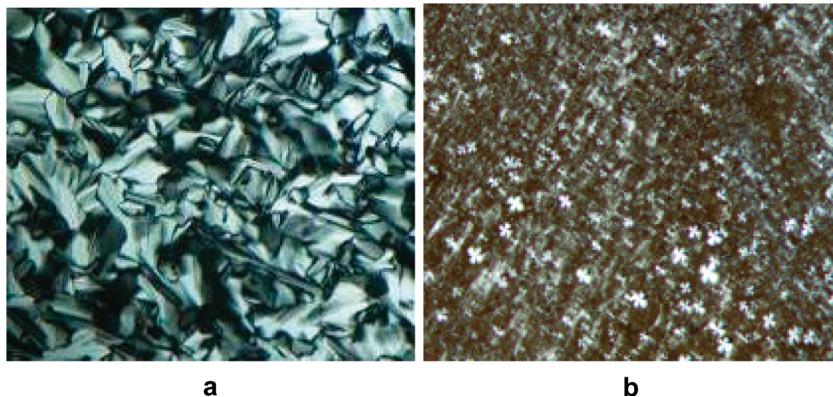
## EXPERIMENTAL SECTION

Systems on the basis of nonionic surfactants, decaethylene glycol monododecyl ether  $C_{12}H_{25}O(CH_2CH_2O)_{10}H$  ( $C_{12}EO_{10}$ ), tetraethylene glycol monododecyl ether  $C_{12}H_{25}O(CH_2CH_2O)_4H$  ( $C_{12}EO_4$ ), and hydrated lanthanide nitrates,  $Eu(NO_3)_3 \cdot 6H_2O$  and  $Tb(NO_3)_3 \cdot 6H_2O$  (Aldrich), were objects of the investigation.

Lyotropic liquid crystal (LLC) systems were synthesized according to the method described previously.<sup>31</sup> The surfactant/Ln ratio was 1:1 and 1:2. The complexes  $C_{12}EO_{10}/Eu(NO_3)_3 \cdot 6H_2O$ ,  $C_{12}EO_{10}/Tb(NO_3)_3 \cdot 6H_2O$ ,  $C_{12}EO_4/Eu(NO_3)_3 \cdot 6H_2O$ , and  $C_{12}EO_4/Tb(NO_3)_3 \cdot 6H_2O$  contain 11 wt %, 11 wt %, 15 wt %, and 15 wt % of H<sub>2</sub>O, respectively. For investigation of the structure of the first coordination spheres Ln-containing complexes by the Horrocks–Sudnick equation,<sup>35,36</sup> we need to compare the lifetime of H<sub>2</sub>O and D<sub>2</sub>O containing systems. For preparing good quality lyotropic liquid crystal systems, we add 5% weight extra of water (H<sub>2</sub>O or D<sub>2</sub>O).

The liquid crystal (LC) properties of the LLC system were studied by the polarization optical microscopy method (POM) on an Olimpus DX 51 polarization microscope equipped with a Linkam hot system. The accuracy of the temperature measurements was  $\pm 0.2$  °C.

The X-ray phase studies were performed on an automated D8 Advance X-ray diffractometer (Bruker) equipped with a Vario setup and a Vantec linear coordinate detector. The CuK $\alpha_1$  radiation monochromated by the curved Johansson monochromator ( $\lambda = 1.5406$  Å) was used, and the performance mode of the X-ray tube was 40 kV, 40 mA. Experiments were carried out at



**Figure 1.** Textures of hexagonal (a) and lamellar (b) lyotropic mesophases (polarization microscope,  $\times 96$ ).

room temperature in the Bragg–Brentano geometry on a plane sample. The LC sample was deposited on a glass plate.

The infrared (IR) spectra for the  $C_{12}EO_{10}/Eu^{III}/H_2O$  and  $C_{12}EO_4/Eu^{III}/H_2O$  systems were taken on Bruker Tensor-27 and Bruker IFS-113v spectrometers in the frequency range of  $4000\text{--}500\text{ cm}^{-1}$  and  $700\text{--}100\text{ cm}^{-1}$ , respectively.

The luminescence properties of the obtained compounds were studied on an original setup in the  $90^\circ$  geometry. A nitrogen LGI-21 laser ( $\lambda=337\text{ nm}$ ,  $f=50\text{ Hz}$ , duration = 10 ns, and  $P=60\text{ kW}$ ) was used as a source of the excitation. The experiment was performed in a specially designed quartz cell,  $58\text{ }\mu\text{m}$  thick, thermostatically controlled in the temperature range of  $23\text{--}80\text{ }^\circ\text{C}$ . The luminescence spectra presented in the work were taken at the delay of  $25\text{ }\mu\text{s}$ , the luminescence kinetics were recorded at the wavelengths of  $\lambda_{max}=612\text{ nm}$  (for  $Eu^{III}$ ) and  $\lambda_{max}=544\text{ nm}$  (for  $Tb^{III}$ ).

## ■ DISCUSSION OF RESULTS

**LC Properties.** The surfactant structure considerably affects the supramolecular organization of molecules in the mesophase. Surfactants with different numbers of oxyethylated groups with lanthanide nitrates form different types of lyotropic mesophases. According to the POM data, it was established in the studies of a thin layer of a sample in the polarized light that the systems on the basis of  $C_{12}EO_{10}$  have a fan texture and form a hexagonal mesophase (Figure 1a). A Maltese cross texture was observed in the crossed polaroids with the increase in the number of the oxyethylene groups in the lyotropic system with the  $C_{12}EO_4$  ligand (Figure 1b). This characterizes the supramolecular organization of molecules in the mesophase as a lamellar one. The parameters of the liquid crystal and structural properties of the systems studied in this work are given in Table 1.

The data analysis showed that the temperature interval of the existence depends considerably on the surfactant/Me mole ratio in the europium-containing systems forming the hexagonal mesophase. In the triple systems, at the surfactant/Me ratio of 1:1 the  $\Delta T$  value decreases on the average by  $30\text{ }^\circ\text{C}$  in comparison with the systems containing metal in the amount of 1:2. The systems forming the lamellar phases have wider temperature intervals of the existence of the mesophase than those forming the hexagonal phases in the cases of both  $Eu^{III}$  and  $Tb^{III}$  ions. To further estimate the amount of coordinated water and its effect on the efficacy of luminescence, mesophases containing deuterated water were obtained. For lamellar mesophases, the substitution of

water by the deuterated solvent leads to the increase in the temperature interval of the mesophase on the order of  $10\text{ }^\circ\text{C}$ , this dependence is not traced for the hexagonal phases. It should be noted that the  $C_{12}EO_4/Eu^{III}/H_2O-D_2O$  systems at the surfactant/Me molar ratio of 1:2 were thermodynamically unstable, and the crystallization of the salt was observed in 10 days. At the same time, the systems with the  $Tb^{III}$  ion under the analogous conditions exhibited more stable thermostable phases keeping the textures and temperatures of the phase transitions upon several heating and cooling cycles.

To confirm the identification of the mesophases and to determine their geometric parameters, the data of small-angle X-ray diffraction were used. Four well-resolved reflections at  $2\theta = 1.81^\circ, 3.64^\circ, 5.46^\circ$ , and  $7.28^\circ$  corresponding to the (100), (200), (300), and (400) planes of the lamellar symmetry with the interlayer distances  $d = 48.51, 24.26, 16.17$ , and  $12.13\text{ \AA}$  in the ratio of 1:1/2:1/3:1/4 were observed in the diffractograms of the  $C_{12}EO_4/Eu^{III}/D_2O$  system (Figure 2a). The diffraction of the  $C_{12}EO_{10}/Eu^{III}/H_2O$  sample with a fan texture (Figure 2b) is characterized by the Bragg peaks at  $2\theta = 1.79^\circ, 3.10^\circ, 3.57^\circ$ , and  $4.73^\circ$  corresponding to the (100), (110), (210), and (220) planes of the  $P6mm$  symmetry. The interplane distances  $d_{100} = 49.41\text{ \AA}$ ,  $d_{110} = 28.50\text{ \AA}$ ,  $d_{210} = 24.69\text{ \AA}$ , and  $d_{220} = 18.66\text{ \AA}$  in accord with the ratio of  $1:1/(3)^{1/2}:1/2:1/(7)^{1/2}$  characterize the studied system as a 2D hexagonal liquid crystal structure. The geometric parameters of the studied systems are given in Table 1. The presence of the extra solvent in the amount of 5 wt % in the system leads to the slight increase in the interlayer distance  $d$  in comparison with the binary system. The analysis of the  $C_{12}EO_{10}/Ln^{III}/H_2O-D_2O$  systems shows that the change of the solvents and the change of the surfactant/Ln mole ratio almost do not affect the geometric parameters of hexagonal mesophases. The analogous pattern is observed in the lamellar phases of  $C_{12}EO_4/Eu^{III}/H_2O-D_2O$ ; however, the interlayer distance increases by  $12\text{ \AA}$  in the  $C_{12}EO_4/Tb^{III}/H_2O$  system with increase in the mole ratio. By analyzing the phase behavior of the metal-containing systems versus binary systems  $C_{12}EO_4/H_2O$ <sup>37</sup> and  $C_{12}EO_{10}/H_2O$ , it can be concluded that, in general, types of lyomesophases are preserved, but the presence of  $Ln^{III}$  ions significantly increases the transition temperature mesophase-isotropic liquid and extends the concentration range of the mesophase's existence.

**Determination the Structure of the LLC Complex.** To obtain information about the structure of the complex upon the formation of the lyotropic mesophases, IR spectra in the LC film

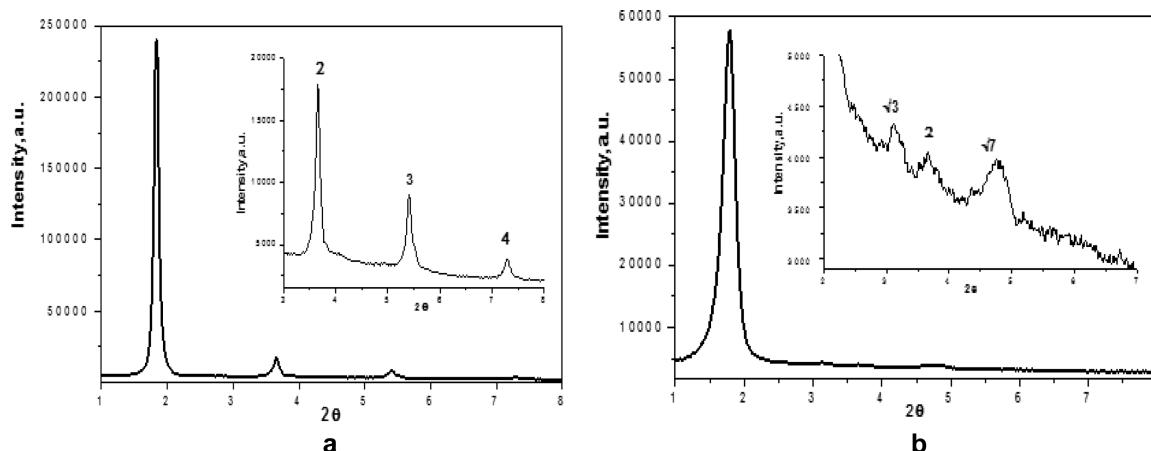


Figure 2. Diffractograms of the  $\text{C}_{12}\text{EO}_4/\text{Eu}^{\text{III}}/\text{D}_2\text{O}$  system (1:1 mol) (a) and  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  system (1:1 mol) (b).

were recorded (Figures S1–S5, Supporting Information). The shift of the bands of the valence vibrations of the O–H and C–O groups to the low-frequency range in the spectra of the complex in comparison with the ligand spectrum (from 3405 to 3378  $\text{cm}^{-1}$  and 1114 to 1077  $\text{cm}^{-1}$ ) indicates the coordination of the oxygen of the oxyethylated group with the lanthanum ion in the LC complex by hydrogen bonds. The observed changes in the region of 3000–2800  $\text{cm}^{-1}$  occurring at complexing (band shift from 2923 to 2924  $\text{cm}^{-1}$  and 2856 to 2854  $\text{cm}^{-1}$ ) and the appearance of the band at 1326  $\text{cm}^{-1}$  favor the gauche conformation of the  $(-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-)$  structural unit, the geometry of which provides the coordination of the lanthanide ion. This result is not contrary to relevant data found at the formation of LC mesophases between the oligo(ethylene oxide) surfactant and transition metal aqua complexes.<sup>38</sup> There are peaks at 1037 and 736  $\text{cm}^{-1}$  characteristic for bidentate  $\text{NO}_3^-$  and also strong bands of 1762, 1458, 1326, 819  $\text{cm}^{-1}$  inherent for the absorption of the free  $\text{NO}_3^-$  ion in the spectrum of the liquid crystal system. In the region 100–600  $\text{cm}^{-1}$ , the peaks of the medium intensity at 307 and 220  $\text{cm}^{-1}$  and 309 and 220  $\text{cm}^{-1}$ , respectively, due to the vibrations of the Eu–O bond are observed in the  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}$  spectra. The appearance of the 267 and 200  $\text{cm}^{-1}$  bands in the  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}$  system and the 290 and 205  $\text{cm}^{-1}$  bands in the  $\text{C}_{12}\text{EO}_4/\text{Eu}^{\text{III}}$  system are related to the coordination of the oxygen of the oxyethylated group by the lanthanum ion.<sup>39</sup> Thus, according to the obtained data, the formation of the liquid crystal complex occurs by the intermolecular interactions with participation of both water molecules and nitrate ions in a bidentate manner coupled with lanthanum ions. In a series of Dag and co-workers' publications, the structure and mesogenic behavior of transition metal complexes with nonionic surfactants has been investigated. Liquid crystal binary and ternary systems formed between oligo(ethylene oxide) $-\text{C}_n\text{EO}_m$  and aqua complexes of transition metals,  $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ ,  $[\text{Ni}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ ,  $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ ,  $[\text{Cd}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ , and  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ <sup>40,41</sup>. According to ref 38, the lyotropic LC-phase is formed by water molecules via the polar–nonpolar interaction with the metal salt dissolved in the hydrophilic domain lyomesophases. As well as in our case, there is the coordination of the nitrate ion to the metal ion.

To specify the structure of the first coordination sphere, in particular the hydration extent of the  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  ions, the lifetimes of luminescence in water and  $\text{D}_2\text{O}$  were studied.

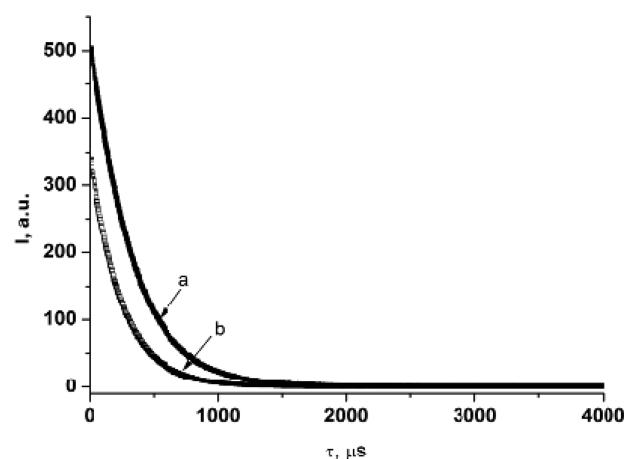


Figure 3. Kinetic luminescence curves corresponding to the  ${}^5\text{D}_0 - {}^7\text{F}_2$  transition for the systems:  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{D}_2\text{O}$  (a) and  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  (b).

According to the Horrocks–Sudnick equations,<sup>35,36</sup> the difference between the constants of the luminescence decay of the water and deuterated solutions of the lanthanide ions is proportional to the number of the coordinated water molecules in the first coordination sphere

$$q = A(\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1}) \quad (1)$$

where  $q$  is the number of water molecules coordinated to the metal ion,  $\tau$  is the lifetime of luminescence, and  $A$  is the constant reflecting the physical–chemical features of the interaction between the metal ion and the ligand environment; for the  $\text{Eu}^{\text{III}}$  ion,  $A = 1.05$ , and for the  $\text{Tb}^{\text{III}}$  ion,  $A = 4.2$ .

Later<sup>40,43</sup> the relationship in eq 1 was modified and eqs 2 and 3 were proposed

$$q(\text{Eu}^{\text{III}}) = 1.11(\Delta k - 0.31) \quad (2)$$

$$q(\text{Tb}^{\text{III}}) = 5.0(\Delta k - 0.06) \quad (3)$$

where  $\Delta k = \tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1}$ .

However, it was shown in ref 18 that these relationships are restrictedly applicable to different classes of ligands. Although this methodology was successfully used for studies of processes

of the association of the Eu<sup>III</sup>, Tb<sup>III</sup>, and Ce<sup>III</sup> ions with micelles of the cation surfactant sodium dodecyl sulfate in water solutions,<sup>44</sup> a series of lanthanide chelates,<sup>45</sup> a series of anions, and cation and neutral Eu, Tb, and Yb complexes.

For the first time, we attempted to estimate the hydration extent of the coordination site of the lanthanide ion in the quite condensed, organized liquid crystal state. Data on the luminescence kinetics of the systems on the basis of europium ions containing water and deuterated solvent are given in Figure 3.

A monoexponential dependence of the kinetics of the luminescence decay is characteristic for all studied systems (Figures S6 and S7, Supporting Information). The values of the luminescence lifetime and the values of the number of the coordinated water molecules in the complex calculated according to eqs 2 and 3 are summarized in Table 2.

The luminescence lifetime increases on the average by 50–170  $\mu$ s when the H<sub>2</sub>O solvent is substituted for D<sub>2</sub>O. This agrees with the literature data; according to ref 43, the O–H oscillators are more effective luminescence quenchers than the O–D oscillators since there is a considerable nonradiation deactivation of the radiative states of the lanthanide ions due to the O–H vibrations of the coordinated water molecules. It should be noted that the luminescence lifetime of the systems on the basis of the Tb<sup>III</sup> ion is higher than that for the systems with the Eu<sup>III</sup> ion. According to ref 46, the energy gap between the radiative and ground state for the Tb<sup>III</sup> ion is 15 000 cm<sup>-1</sup>, and

**Table 2. Luminescence Lifetimes, Number of Coordinated Water Molecules, and Intensity Ratios of the Main Energy Transitions in the Systems under Study**

system	$\tau$ ( $\mu$ s)	$q$	$\eta$
C <sub>12</sub> EO <sub>10</sub> /Eu <sup>III</sup> /H <sub>2</sub> O (1:2 mol)	242	0.8	4.1
C <sub>12</sub> EO <sub>10</sub> /Eu <sup>III</sup> /D <sub>2</sub> O (1:2 mol)	321		4.7
C <sub>12</sub> EO <sub>10</sub> /Tb <sup>III</sup> /H <sub>2</sub> O (1:2 mol)	594	0.9	3.5
C <sub>12</sub> EO <sub>10</sub> /Tb <sup>III</sup> /D <sub>2</sub> O (1:2 mol)	696		3.2
C <sub>12</sub> EO <sub>10</sub> /Eu <sup>III</sup> /H <sub>2</sub> O (1:1 mol)	184	2.0	3.1
C <sub>12</sub> EO <sub>10</sub> /Eu <sup>III</sup> /D <sub>2</sub> O (1:1 mol)	298		3.5
C <sub>12</sub> EO <sub>4</sub> /Tb <sup>III</sup> /H <sub>2</sub> O (1:2 mol)	554	1.9	3.3
C <sub>12</sub> EO <sub>4</sub> /Tb <sup>III</sup> /D <sub>2</sub> O (1:2 mol)	731		2.5
C <sub>12</sub> EO <sub>4</sub> /Eu <sup>III</sup> /H <sub>2</sub> O (1:2 mol)	152	1.4	2.3
C <sub>12</sub> EO <sub>4</sub> /Eu <sup>III</sup> /D <sub>2</sub> O (1:2 mol)	198		3.4
C <sub>12</sub> EO <sub>4</sub> /Tb <sup>III</sup> /H <sub>2</sub> O (1:1 mol)	344	3.8	3.0
C <sub>12</sub> EO <sub>4</sub> /Tb <sup>III</sup> /D <sub>2</sub> O (1:1 mol)	477		2.7

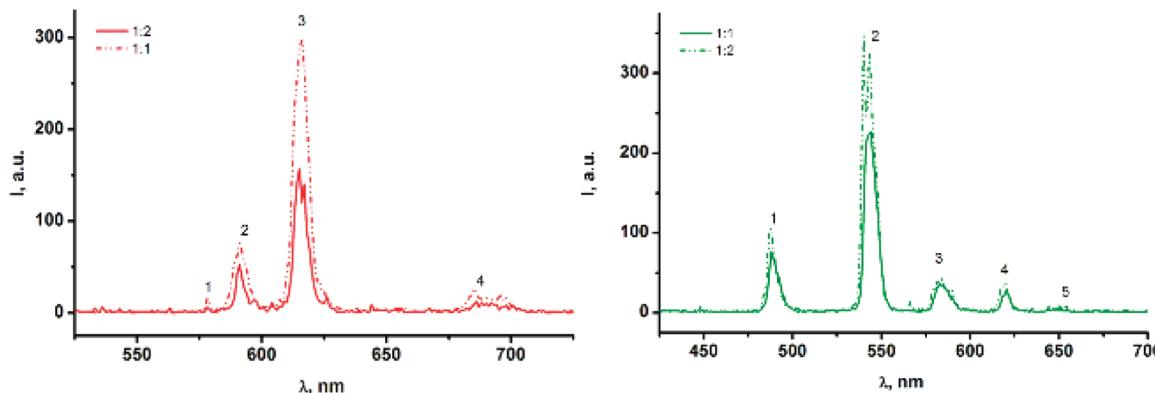
for the Eu<sup>III</sup> ion, it is 12 000 cm<sup>-1</sup>. This considerably weakens the nonradiative relaxation via the vibration levels of the coordinated water molecules. Therefore, the luminescence of the Tb<sup>III</sup> ions is less sensitive to the O–H oscillators coordinated to the metal ion of water molecules in comparison with the luminescence of the Eu<sup>III</sup> ion.

The analysis of data in Table 2 showed the effect of the surfactant/Ln mole ratio and the structure of the organic ligand on the hydration extent of the coordination site of the lanthanide ion. Liquid crystal complexes of the europium and terbium ions with the C<sub>12</sub>EO<sub>10</sub> ligand at the mole ratio of 1:2 contain one water molecule in the first coordination sphere and two molecules upon the decrease in the mole ratio to 1:1. Liquid crystal complexes with the C<sub>12</sub>EO<sub>4</sub> ligand having a smaller number of oxyethylated groups contain about two water molecules at the mole ratio of 1:2. The number of water molecules increases to four in the Tb<sup>III</sup> complex upon the decrease in the surfactant/Ln mole ratio. The luminescence lifetime decreases naturally.

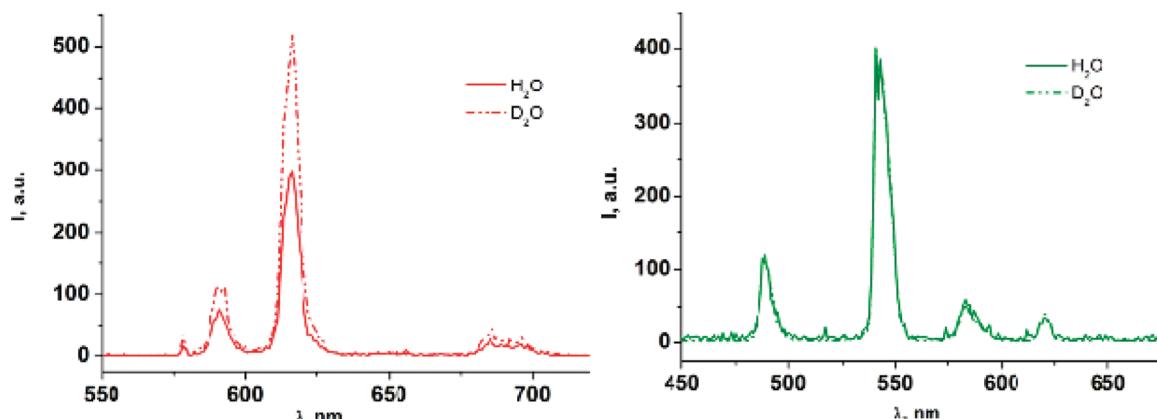
**Luminescence Properties.** To establish the relationship between the structure of the coordination site of the ion and the luminescence efficacy, data of time-resolved luminescence were analyzed. Considering the obtained experimental results, one should single out the effect of three parameters on the luminescence efficiency: the surfactant/Ln mole ratio, the type of the solvent, and the type of the supramolecular organization of ions in the mesophase determined by the ligand structure.

Luminescence spectra of the samples of the C<sub>12</sub>EO<sub>10</sub>/Ln<sup>III</sup>/H<sub>2</sub>O systems at different mole ratios are shown in Figure 4.

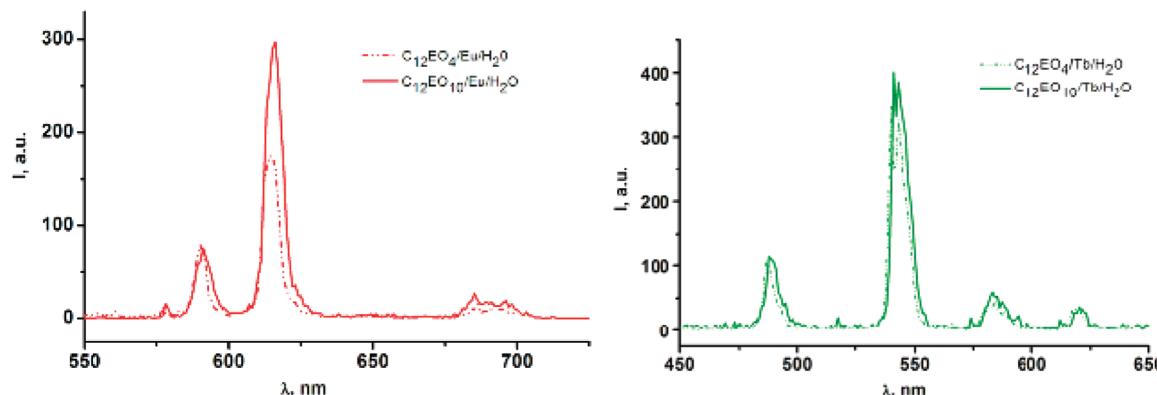
Narrow bands corresponding to the radiative transitions of the Eu<sup>III</sup> ion: (1)  $^5D_0 \rightarrow ^7F_0$ , (2)  $^5D_0 \rightarrow ^7F_1$ , (3)  $^5D_0 \rightarrow ^7F_2$ , and (4)  $^5D_0 \rightarrow ^7F_4$  are observed in the luminescence spectra of the samples of the C<sub>12</sub>EO<sub>10</sub>/Eu<sup>III</sup>/H<sub>2</sub>O system. The most intense band with the radiation maximum at 612 nm corresponds to the  $^5D_0 \rightarrow ^7F_2$  transition providing red luminescence of the complex. The analysis of the intensity ratios of the main  $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)-\eta$  transitions (Table 2) of systems with different surfactant/Eu mole ratios showed that the highest intensity is observed in the LC complex at the mole ratio of 1:2. The  $^5D_0 \rightarrow ^7F_1$  transition has a magnetic-dipole character and weakly depends on the coordination sphere, i.e., the ligand field.<sup>47</sup> On the contrary, the electric-dipole  $^5D_0 \rightarrow ^7F_2$  transition is very sensitive to the symmetry of the coordination sphere. It was established<sup>48</sup> that the intensity ratios of the  $^5D_0 \rightarrow ^7F_2$  and  $^5D_0 \rightarrow ^7F_1$  transitions are a criterion of the symmetry of the first coordination sphere of the Eu<sup>3+</sup> ion. The magnetic-dipole  $^5D_0 \rightarrow ^7F_1$  transition



**Figure 4.** Comparative luminescence spectra of (a) the C<sub>12</sub>EO<sub>10</sub>/Eu<sup>III</sup>/H<sub>2</sub>O system and (b) the C<sub>12</sub>EO<sub>4</sub>/Tb<sup>III</sup>/H<sub>2</sub>O system; molar ratio surfactant: Ln = 1:1 and 1:2.



**Figure 5.** Comparative luminescence spectra of (a) the  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{H}_2\text{O}-\text{D}_2\text{O}$  system and (b) the  $\text{C}_{12}\text{EO}_{10}/\text{Tb}^{\text{III}}/\text{H}_2\text{O}-\text{D}_2\text{O}$  system; molar ratio = 1:2.



**Figure 6.** Comparative luminescence spectra of (a) the  $\text{C}_{12}\text{EO}_4/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  system (Lam) and the  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  system (Hex); (b) the  $\text{C}_{12}\text{EO}_4/\text{Tb}^{\text{III}}/\text{H}_2\text{O}$  system (Lam) and the  $\text{C}_{12}\text{EO}_{10}/\text{Tb}^{\text{III}}/\text{H}_2\text{O}$  system (Hex); molar ratio = 1:2.

dominates in the central symmetric environment, and the distortion of the symmetry around the ion leads to the increase in the intensity of the electric-dipole  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition. This indicates that the  $\text{Eu}^{3+}$  ion in these compounds has an asymmetric coordination sphere. The ratio of the intensities of the transitions  $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$  may also be a criterion of the luminescence monochromaticity of different europium(III) complexes. The high color purity is characterized by a rather high  $\eta$  value. For example, this  $\eta$  value varies in the range of 6.6–27.6 for different  $\beta$ -diketonate europium(III) complexes.<sup>49</sup> The maximum value  $\eta = 4.7$  obtained in our case is due to the presence of water molecules in the coordination site. This result provides prerequisites for the modification of the studied complex, for example, the introduction of a coagent substituting the water molecules in the first coordination sphere. This will be studied in a further research.

Luminescence spectra of the samples of the  $\text{C}_{12}\text{EO}_4/\text{Tb}^{\text{III}}/\text{H}_2\text{O}$  system in which the following radiative transitions of the  $\text{Tb}^{\text{III}}$  ion are observed: (1)  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ , (2)  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ , (3)  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$ , (4)  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$ , and (5)  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_2$  are shown in Figure 4b. Luminescence at the wavelength  $\lambda_{\text{max}} = 544$  nm corresponding to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  transition provides the green emission of the samples.

Since it was not possible to obtain a stable LC  $\text{C}_{12}\text{EO}_{10}/\text{Tb}^{\text{III}}/\text{H}_2\text{O}$  system at the mole ratio of 1:1, the comparative analysis of the effect of this parameter is presented by the example of the

$\text{C}_{12}\text{EO}_4/\text{Tb}^{\text{III}}/\text{H}_2\text{O}$  system. It is seen from the data of Figure 4b and Table 2 that the highest luminescence intensity is observed at the high surfactant/ $\text{Tb}$  mole ratio.

Luminescence spectra of the samples of the LC systems with different solvents are presented in Figure 5. The luminescence intensity increases considerably upon the transition from  $\text{H}_2\text{O}$  to  $\text{D}_2\text{O}$  for the systems with the  $\text{Eu}^{\text{III}}$  ion. When water molecules are substituted for the deuterated ones, luminescence quenching decreases, and the emission for the europium ion levels increases. The  $\text{C}_{12}\text{EO}_{10}/\text{Tb}^{\text{III}}$  systems are indifferent to the change of solvents. This agrees with the literature data given above.

To study the effect of the type of the supramolecular organization on the luminescence efficacy due to the structure of the  $\text{C}_{12}\text{EO}_{10}$  and  $\text{C}_{12}\text{EO}_4$  ligands, luminescence spectra of the systems forming different types of lyotropic mesophases, hexagonal and lamellar, were obtained (Figure 6). The analysis showed that the luminescence intensity depends on the type of the supramolecular organization, and the type of the ion also determined this dependence. The intensity ratios of the main energy transitions in the lamellar phase was  $\eta = 2.2$ , and in the hexagonal phase,  $\eta = 4$  for the europium ion. A less considerable difference is observed for the terbium ion: at the lamellar organization,  $\eta = 3.3$ , and at the hexagonal organization,  $\eta = 3.5$ .

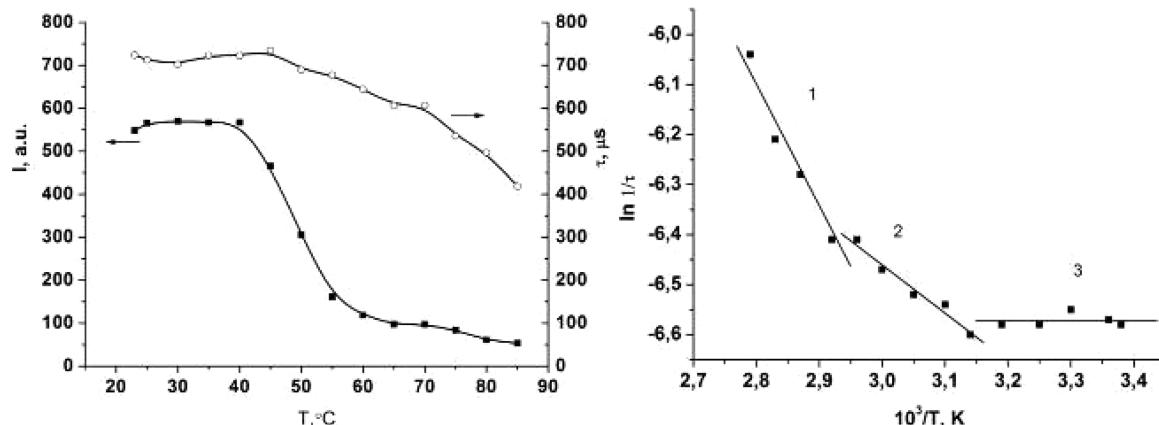


Figure 7. Temperature-dependent emission and luminescence lifetime ( $\lambda_{\text{max}} = 544$  nm) of the  $\text{C}_{12}\text{EO}_{10}/\text{Tb}^{\text{III}}/\text{H}_2\text{O}$  system; mole ratio = 1:2.

To study the effect of the liquid crystal state on the luminescence efficiency, time-resolved spectra were obtained at different temperatures. Generally, increasing the temperature induces more nonradiative deactivation of the excited state and consequently, both the luminescence intensity and lifetime are expected to decrease according to an exponential law (4):<sup>47</sup>

$$y = y_0 e^{-C/RT} \quad (4)$$

The studies were performed in the LC state, the region of the phase transition from the mesophase to the isotropic liquid where exist two phases, the mesophase and the isotropic liquid, and in the isotropic state. The temperature-dependent emission of the samples of the  $\text{C}_{12}\text{EO}_{10}/\text{Tb}(\text{III})/\text{H}_2\text{O}$  system is presented in Figure 7. It is vividly seen that the phase transition intrinsically affect on luminescence parameters. The intense excitation corresponds to the thermodynamically stable lyotropic mesophase. The luminescence intensity decreases, and the emission tends to zero with the temperature increase and approach to the phase transition (according to the POM data  $T_{\text{Hex}-1} = 64.6$  °C) when the supramolecular organization of the system is destroyed, and the sample is an isotropic liquid. A symbiotic change of the lifetime is observed. It is important to note that in the region of the isotropic state ( $T = 65–85$  °C) a small emission is observed indicating a partial conservation of the coordination site of the terbium ion.

The dependence of the luminescence decay constant on the inverse absolute temperature presented in the logarithmic coordinates (Figure 6b) allowed us to calculate the activation energy of the process of the temperature luminescence quenching of the  $\text{Tb}^{\text{III}}$  ion. Two regions corresponding to the isotropic state and pretransition mesogenic state with the values  $E_1 = 21.82$  kJ/mol and  $E_2 = 8.56$  kJ/mol are distinguished in the curve. The activation energy temperature luminescence quenching is close to zero in the stable LC state.

## CONCLUSIONS

Thus, the liquid crystal properties of the lyotropic systems containing  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  ions on the basis of a nonionic surfactant with different numbers of oxyethylated groups were studied. It was shown that the  $\text{C}_{12}\text{EO}_{10}/\text{Ln}^{\text{III}}/\text{H}_2\text{O}-\text{D}_2\text{O}$  systems form hexagonal mesophases, and the  $\text{C}_{12}\text{EO}_4/\text{Ln}^{\text{III}}/\text{H}_2\text{O}-\text{D}_2\text{O}$  systems form lamellar mesophases. Their geometric parameters were determined. It was established from the IR

spectroscopy data that the formation of the liquid crystal complex of the lanthanide ion occurs by the intermolecular interactions with the oxyethylated groups of the surfactant molecule, both with the participation of the water molecules and nitrate ions in a bidentate manner coupled with the lanthanum ions. The hydration extent of the first coordination sphere of the  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  ions in the liquid crystal state were estimated from the luminescence lifetime data. It was established that there is one water molecule in the complexes with the  $\text{C}_{12}\text{EO}_{10}$  ligand at the surfactant/Ln mole ratio of 1:2; at the ratio of 1:1, the number of coupled water molecules increases to two. When the number of the ligand oxyethylated groups decreases, there are from two to four water molecules in the coordination site. Time-resolved luminescence spectroscopy data were used to study the effect of the following factors: the ligand environment, the type of the ion, and the type of supramolecular organization on the luminescence efficacy of the lyotropic lanthanide-containing systems. It was found that in the europium complexes the type of the supramolecular organization of the mesophase provides the considerable contribution: the luminescence efficiency is 2-fold in the hexagonal phase. These systems are also more sensitive to the change of solvents, and the effect of the surfactant/Ln mole ratio in them is expressed to a higher extent than that in the terbium complexes. The relationship between the phase transition and the optical properties of the lyotropic systems is presented on the basis of the data on the temperature-dependent emission and the decay constants. This result demonstrates that the mesogenic phase transition in lanthanide-containing liquid crystals can be used to accurately monitor a temperature in biosystem analogues with the lyotropic liquid-crystals.

In conclusion, the presented findings and the patterns of the lanthanide-containing lyotropic mesophases formation can be utilized for the synthesis of a new lyotropic metallomesogens and for a luminescence organized media creation.

## ASSOCIATED CONTENT

**S Supporting Information.** FT-IR spectra in the 100–600  $\text{cm}^{-1}$  region of the samples of systems  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  (Figure S1),  $\text{C}_{12}\text{EO}_4/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  (Figure S2) molar ratio surfactant/Ln 1:1, and crystalline hydrate  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Figure S3); FT-IR spectra in the 600–4000  $\text{cm}^{-1}$  region of the samples of systems  $\text{C}_{12}\text{EO}_{10}/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  (Figure S4),  $\text{C}_{12}\text{EO}_4/\text{Eu}^{\text{III}}/\text{H}_2\text{O}$  (Figure S5), the luminescence kinetics

of the lyotropic liquid crystal systems  $C_{12}EO_{10}/Eu^{III}/H_2O$ ,  $C_{12}EO_{10}/Eu^{III}/D_2O$  (Figure S6), and  $C_{12}EO_4/Tb^{III}/H_2O$ ,  $C_{12}EO_4/Tb^{III}/D_2O$  (Figure S7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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