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Influence of Structural Anisotropy on Mesogenity of Eu(III) Adducts and Optical Properties of Vitrified Films Formed on their Base

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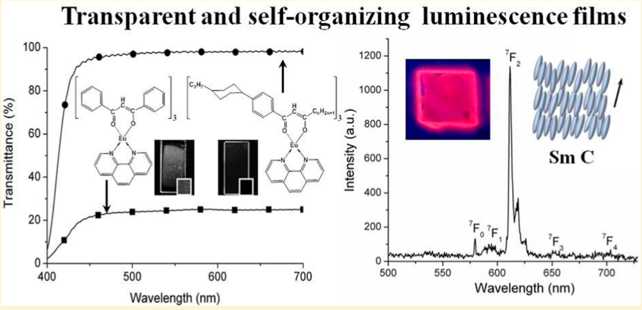
Supporting Information

ABSTRACT: A new series of europium adducts with the general formula Eu(CPDk$_{3\text{-CnH2n+1}}$)$_3$Phen, where CPDk$_{3\text{-CnH2n+1}}$ denotes β-diketones and Phen is 1,10-phenanthroline, was synthesized. The obtained mesogenic complexes were heated to the temperatures of the isotropic liquid state and then cooled. The complexes having short CH_3 and C_2H_5 substituents crystallized upon cooling, and the complexes with longer substituents from C_3H_7 to C_6H_{13} underwent a glass transition with the formation of optically transparent amorphous films. Inside the series the complexes with C_7H_{15} and C_8H_{17} substituents exhibited a unusual smectic C mesomorphism for lanthanidomesogens. On the basis of quantum-chemical simulations and the results of small-angle X-ray scattering the dependence between the anisotropy of Eu(III) complexes with various ligand environments and their supramolecular organization was found. The synthesized Eu(III) complexes in the solid state show intense red photoluminescence upon irradiation by ultraviolet light (λ_{max} − 337 nm).



■ INTRODUCTION

At present, many research groups are engaged in the synthesis and investigation of lanthanide complexes,[1,2] which have great potential as materials for optoelectronic devices, organic light emitting diodes, flat and flexible displays,[3−5] optical fiber components,[6,7] luminescent biological probes,[8,9] hybrid phosphors,[10] and solar batteries.[11,12]

Among coordination compounds of lanthanides, mesogenic lanthanide complexes or lanthanidomesogens are of particular interest due to their potential applications as advanced multifunctional materials.[13−16] Mesomorphic properties in these kinds of compounds are accompanied by anisotropy of their magnetic and optical properties, allowing one to create luminescent materials that emit polarized monochromatic light.[17,18] There is an interest in developing lanthanide-containing liquid crystals, mainly because of the unique magnetic properties of some of the trivalent ions of the lanthanide series.[19,20] As has been shown earlier,[21−25] lanthanidomesogens under the influence of external stimuli (magnetic fields, electric fields, and laser irradiation) or orienting agents are capable of forming homogeneous, supramolecularly organized media on the macroscopic scale. The important advantage of mesogenic lanthanide complexes is their increased solubility in organic solvents and capability to incorporate, in view of some structural resemblance, namely, the anisotropic form and the presence of terminal alkyl chains, into the structure of the conductive conjugated polymers.[26] It allows one to prepare hybrid film materials by the methods widely used in modern nanotechnologies, such as spin coating, vacuum deposition, and elaboration of molecular layers by the Langmuir−Blodgett method.

The anisotropic geometry of the molecules of mesogenic lanthanide complexes in combination with their glass-forming ability at ambient temperatures makes it possible to obtain a source of polarized luminescent light with controlled polarization and radiation intensity. The observed ability of mesogenic complexes to form optically transparent films could be used in the future in the development of components of transparent organic light-emitting diodes and light panels. In the present work, the syntheses of new coordination compounds of lanthanides with mesogenic properties are described; their liquid crystalline properties are discussed, and theoretical calculations of their molecular geometry with the purpose of understanding the mechanisms of self-organization in the mesophase are performed. We have determined that films of some of the obtained samples are transparent in the visible spectral range. The effects of the molecular geometry and the particular ways of intermolecular interactions and supramolecular self-assembly of the complexes on their luminescent and optical properties are investigated.

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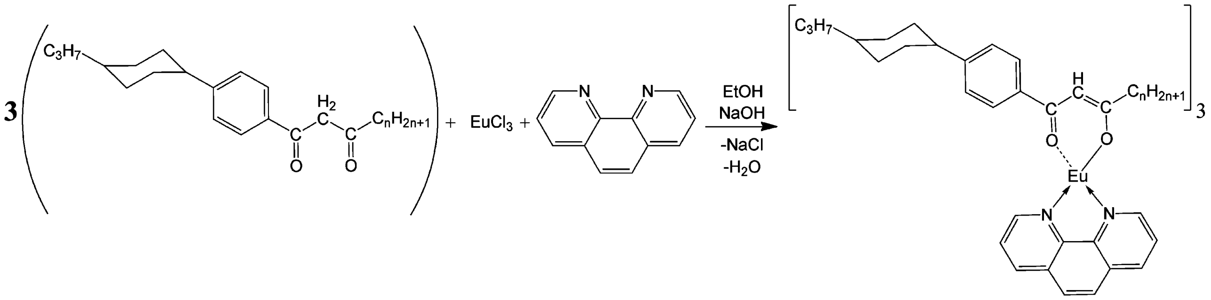
Scheme 1. Synthesis of Tris(β-diketonate) Europium Adducts with 1,10-Phenanthroline



RESULTS AND DISCUSSION

A new series of europium adducts with the general formula $Eu(CPDk_{3\text{-}CnH2n+1})_3Phen$, where $CPDk_{3\text{-}CnH2n+1}$ denotes β-diketones and Phen is 1,10-phenanthroline, have been synthesized in accordance with Scheme 1.

The special modifications of known methods have been applied to the synthesis of complexes, which have been developed earlier in our group[27] by taking into consideration the specific solubility of the initial ligands and reaction products containing long hydrocarbon chains. The composition and structure of the obtained compounds have been confirmed by data of elemental analysis and mass spectrometry and by the method of IR spectroscopy.

The obtained mesogenic complexes were heated to the temperatures of the isotropic liquid state, and then, depending on the length of alkyl substituents, complexes with short CH_3 and C_2H_5 substituents crystallized upon cooling and complexes with longer substituents from C_3H_7 to C_6H_{13} underwent a glass transition with the formation of optically transparent amorphous films. The obtained films are stable and remain transparent at room temperature over several months. Such kind of vitrified films have been described in the literature.[28] Complexes with C_7H_{15} and C_8H_{17} substituents exhibited smectic C mesomorphism (Figure 1). At the present time this is a unique example of an unusual Sc phase for lanthanidomesogens and the first example for β-diketonate adducts. In addition, attempts to obtain derivatives of lanthanide complexes exhibiting the Sc phase have been described in the literature.[13,16,29,30] Only two successful samples of complexes with Schiff bases are known (Table 1, entries 9–16).[31,32] As follows from Table 1, the mesophase exists without decomposition over a wider temperature range (ΔT = 80 °C). The new compounds have transition temperatures about 40 °C lower in comparison with literature data (Table 1).

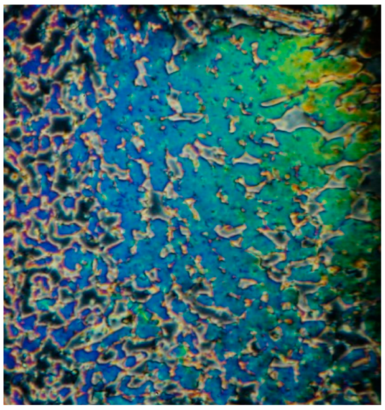


Figure 1. Schlieren texture of the smectic C mesophase of $Eu(CPDk_{3\text{-}C7H15})_3Phen$ at 130 °C (magnification 500×).

Phase transition temperatures of the synthesized lanthanide complexes and temperature ranges of the existence of mesophases (ΔT), which are determined by the polarizing polythermal microscopy, are given in Table 1.

As seen from the data in Table 1, an increase in the length of the alkyl substituent in β-diketone, starting from C_3H_7 in the complex $Eu(CPDk_{3\text{-}C3H7})_3Phen$, gives rise to a sharp decrease in the melting point and to the formation of amorphous products in the syntheses, rather than crystals. A further increase in the length of the alkyl substituent in the case of the C_7H_{15} and C_8H_{17} radicals promotes the formation of the smectic C mesophase and leads to an increase in the temperature of the isotropic liquid transition.

For determining relationships between the molecular structure of complexes and their supramolecular organization, the X-ray diffraction analysis data are quite helpful. However, the presence of a large number of long alkyl substituents in the structures of complexes does not allow one to grow a single crystal, since amorphous products are formed in the synthesis, as has been shown above. Therefore, we have tried preliminarily to estimate the sizes of molecules by quantum chemistry methods. A quantum-chemical simulation of Ln(III) complexes with various ligand environments makes it possible to foresee and afterward to synthesize compounds with obviously predictable mesomorphic properties. Such a prediction can be made on the basis of the value of geometric anisotropy: i.e., the ratio of the long inertial axis of a molecule to its short inertial axis in the ellipsoid of revolution (l/d).

The geometries of eight isomers of the studied complexes with different arrangements of β-diketones relative to the plane formed by the 1,10-phenanthroline ligand and europium ion were considered. Probable isomers of the europium complexes are represented in Table S1 in the Supporting Information for the example of the $Eu(CPDk_{3\text{-}C8H17})_3Phen$ complex. On the basis of the calculations of the equilibrium geometries for the isomer **5** with the energetically most advantageous arrangement of the ligands in the complex was chosen for further calculations of the geometric anisotropy values. In this isomer the long alkyl chains ($-C_8H_{17}$) in β-diketones have a crosswise arrangement and do not sterically hinder each other.

The highest contribution to the value of geometric anisotropy of a molecule is brought by the length of terminal alkyl substituents of ligands. While the anisometry of molecules in purely organic liquid crystals increases with an increase in the length of alkyl substituents, an increase in the length of alkyl substituents in the investigated complexes leads to a simultaneous increase in both the length and width, i.e. short

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Table 1. Values of Geometric Anisotropy of $Eu(CPDk_{3\text{-}CnH2n+1})_3Phen$ Molecules and Temperatures of Phase Transitions and Temperature Ranges of the Existence of Mesophases

entry	complex[a]	l, Å	d, Å	l/d	temp of phase transition,[b] °C
1	$Eu(CPDk_{3\text{-}CH3})_3Phen$	30.9	13.8	2.24	Cr 256 I
2	$Eu(CPDk_{3\text{-}C2H5})_3Phen$	30.9	13.9	2.22	Cr 221 I
3	$Eu(CPDk_{3\text{-}C3H7})_3Phen$	30.9	14.0	2.21	g 133 I
4	$Eu(CPDk_{3\text{-}C4H9})_3Phen$	30.8	15.3	2.01	g 114 I
5	$Eu(CPDk_{3\text{-}C5H11})_3Phen$	30.8	15.8	1.95	g 110 I
6	$Eu(CPDk_{3\text{-}C6H13})_3Phen$	30.9	16.4	1.88	g 78 I
7	$Eu(CPDk_{3\text{-}C7H15})_3Phen$	30.9	17.6	1.76	g 55 Sc 135 I
8	$Eu(CPDk_{3\text{-}C8H17})_3Phen$	30.8	19.4	1.59	g 55 Sc 113 I
9	$[La(LH)L_2(NO_3)]$[31]				Cr 94 Sc 161 dec
10	$[Pr(LH)L_2(NO_3)]$[31]				Cr 93 Sc 159 dec
11	$[Nd(LH)L_2(NO_3)]$[31]				Cr 93 Sc 166 dec
12	$[Eu(LH)L_2(NO_3)]$[31]				Cr 92 Sc 158 dec
13	$[Gd(LH)L_2(NO_3)]$[31]				Cr 93 Sc 158 dec
14	$[Ho(LH)L_2(NO_3)]$[31]				Cr 91 Sc 157 dec
15	$[Er(LH)L_2(NO_3)]$[31]				Cr 92 Sc 168 dec
16	$[Pr(L^1H_2)_3NO_3](NO_3)_2$[32]				Cr 113 Sf 173 Sc 240 dec

[a] L − 4-({3-hydroxy-4-[(octadecylimino)methyl]phenoxy}carbonyl)phenyl 4-(hexyloxy)benzoate; L^1 − *N,N′*-bis(4-hexadecyloxysalicylidene)-diaminoethane. [b] Legend: Cr, crystal; I, isotropic liquid; g, vitrified film; Sc, smectic C mesophase; Sf, smectic F mesophase; dec, decomposition;.

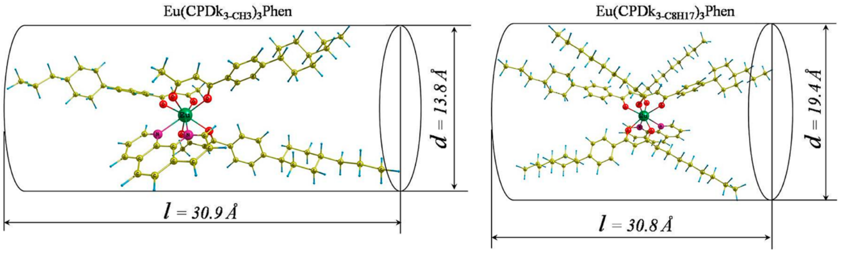

Figure 2. Optimized structures and geometry parameters of some $Eu(CPDk_{3\text{-}CnH2n+1})_3Phen$ complexes.

axis of the ellipsoid of rotation, of molecules. However, according to the results of quantum-chemical calculations, an increase in the length of alkyl substituents in *β*-diketones (Table 1) gives rise to a decrease in the anisometry of molecules of the complexes. In contrast to the complexes described earlier[33] with the $Bpy_{17\text{-}17}$ ligand (5,5′-dimethyl-2,2′-bipyridine), the length of which brings a crucial contribution to the overall geometric anisotropy of molecules of the complexes, the anisometry of the complexes with 1,10-phenanthroline depends on the molecular sizes of *β*-diketones to a greater extent. Though the l/d value for the majority of known organic calamitic liquid crystals lies in a range from 4 to 8, it reaches values of 1.76 and 1.59 in the case of the $Eu(CPDk_{3\text{-}C7H15})_3Phen$ and $Eu(CPDk_{3\text{-}C8H17})_3Phen$ complexes, respectively, and, in spite of this fact, they exhibit liquid crystalline phases in a rather broad temperature range. One of the possible explanations for such a difference in the behavior of lanthanide-containing metallomesogens and conventional organic liquid crystals is a participation in the lateral intermolecular interactions between complexes of lanthanide ions.[34] According to the computational data (Figure 2), the geometry of molecules becomes more branched on transition to the longer hydrocarbon radicals. This results in the reduction of intermolecular ligand−ligand and Ln−Ln interactions and, as follows from Table 1 data, the melting temperatures of complexes decrease as the substituent length grows. When the length of the substituent becomes longer (i.e., with the long alkyl chains $-C_7H_{15}$ and $-C_8H_{17}$), the relation between intermolecular attraction and anisometry become optimal for forming liquid crystal ordering; thus, mesophases can be formed at smaller anisometric values.

The phase transition temperatures determined by the POM method have been confirmed by the DSC method, as illustrated in Figure 3 on an example of the $Eu(CPDk_{3\text{-}C7H15})_3Phen$ complex. As seen from the given thermogram (Figure 3), two characteristic peaks corresponding to the transition from the crystal to a liquid crystalline phase (55 °C) and from the liquid crystalline phase to the isotropic liquid state (134 °C) appear

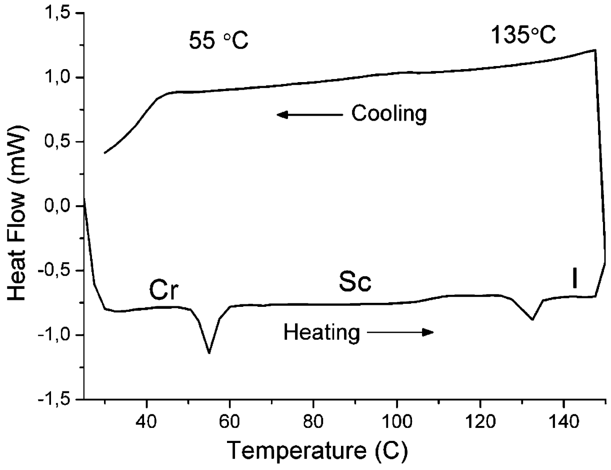

Figure 3. DSC thermogram of the $Eu(CPDk_{3\text{-}C7H15})_3Phen$ complex during heating and cooling.

upon heating of the sample. Upon cooling, the sample is vitrified with preservation of the molecular packing adopted in a mesophase (the molecular packing of the smectic C phase), as can be concluded from the absence of crystallization peaks on the thermogram.

Using the ability of the investigated adducts to form glasses with preservation of the molecular packing upon cooling, the vitrified phases of the Eu(CPDk$_{3\text{-CnH2n+1}}$)$_3$Phen complexes have been investigated by the method of small-angle X-ray scattering at ambient temperatures.

The X-ray diffraction pattern of a vitrified film of the Eu(CPDk$_{3\text{-C7H15}}$)$_3$Phen complex that is recorded at room temperature contains two peaks at $2\theta = 3.97°$ and $2\theta = 7.92°$ (Figure 4), which correspond to the first and second reflections of the interlayer spacing equal to 28.5 Å. The diffractogram is typical for a smectic C mesophase.[35] This is confirmed by preservation of the smectic C mesophase packing in a vitrified film of the complex, as can be observed by the polarizing optical microscopy method.

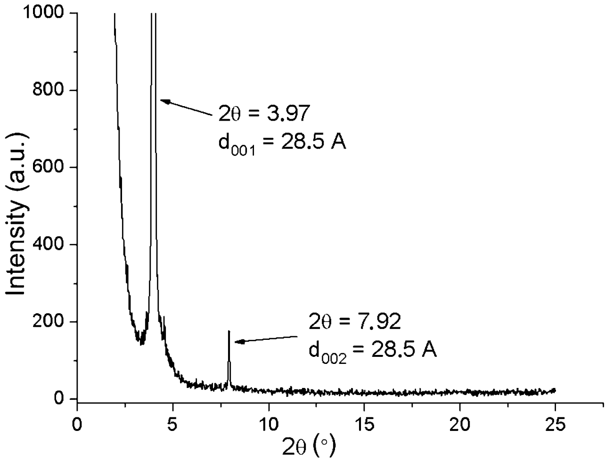

Figure 4. Diffractogram of Eu(CPDk$_{3\text{-C7H15}}$)$_3$Phen complex at 25 °C after cooling from an isotropic liquid.

Using the data of small-angle X-ray scattering (Figure 4), the packing of molecules in the smectic C phase was simulated. According to the performed calculations, the length of an Eu(CPDk$_{3\text{-C7H15}}$)$_3$Phen molecule equals 30.9 Å (Table 1) and exceeds the interlayer spacing distance (28.5 Å). Hence, it can be assumed that interpenetration of the alkyl substituents of β-diketone molecules belonging to neighboring layers takes place upon packing of the molecules in the mesophase (Figure 5).

The Eu(III) complexes with CPDk$_{3\text{-C3H7}}$–CPDk$_{3\text{-C6H13}}$ β-diketones are amorphous substances in the solid state at room temperature. As seen from the diffractogram (Figure 6), a film of Eu(CPDk$_{3\text{C6H13}}$)$_3$Phen upon cooling from the isotropic liquid state is vitrified at ambient temperatures with the formation of an amorphous low-ordered structure.

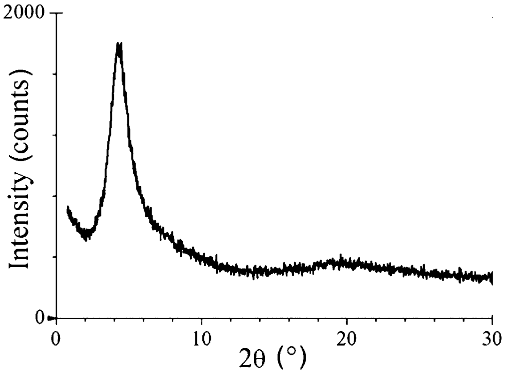

Figure 6. Diffractogram of Eu(CPDk$_{3\text{-C6H13}}$)$_3$Phen complex at 25 °C after cooling from an isotropic liquid.

Thin homogeneous films were prepared on the basis of Eu(CPDk$_{3\text{-C6H13}}$)$_3$Phen, by cooling the sample from its isotropic liquid state between quartz plates. The Eu(DBM)$_3$Phen complex (DBM = 1,3-diphenyl-1,3-propanedione) was used as the reference sample. The film thickness was about 10 μm. The photographic images of the prepared films are shown in Figure 7.

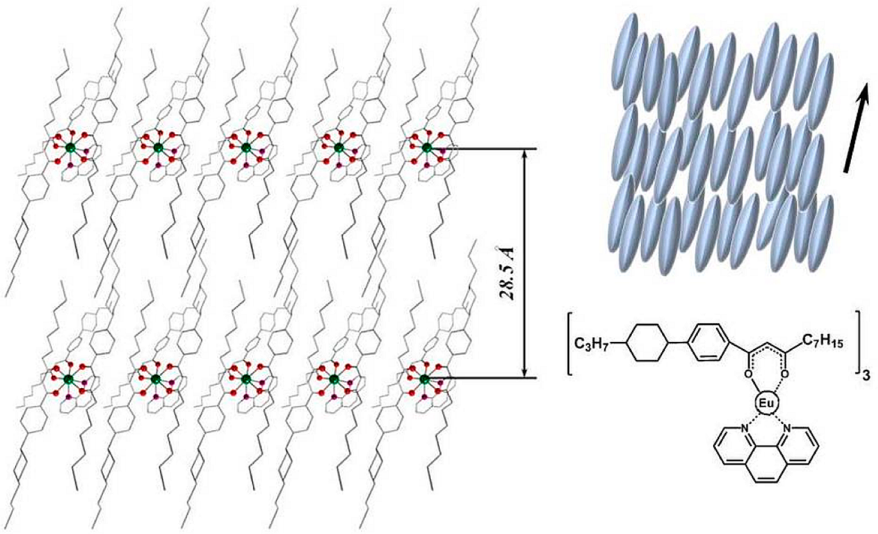

Figure 5. Model of packing of Eu(CPDk$_{3\text{-C7H15}}$)$_3$Phen according to quantum-chemical simulations (the length of the molecule) and small-angle X-ray diffraction (interlayer distance).

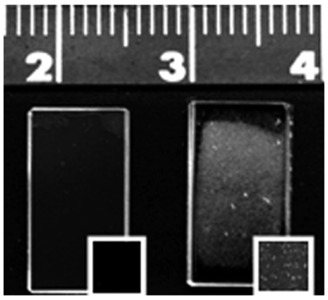

Figure 7. Photographic images of the prepared films of Eu($CPDk_{3\text{-}C6H13}$)$_3$Phen (left) and Eu(DBM)$_3$Phen (right) complexes between quartz plates (in cm).

The light absorption intensity data of a film of the Eu(DBM)$_3$Phen complex containing crystalline inclusions and of a vitrified Eu($CPDk_{3\text{-}C6H13}$)$_3$Phen film are given in Figure 8.

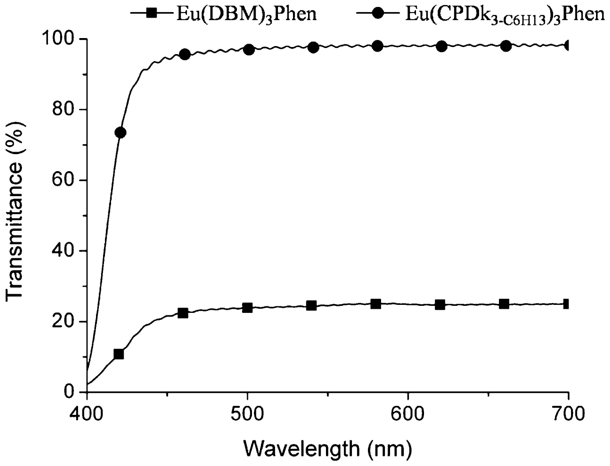

Figure 8. Light transmittance of Eu($CPDk_{3\text{-}C6H13}$)$_3$Phen and Eu(DBM)$_3$Phen complexes.

As seen from the spectra, the intensity of the transmitted light in the range from 400 to 700 nm strongly depends on the aggregate state of the substance in a film. The relative intensity of the transmitted light of a vitrified film of the amorphous Eu($CPDk_{3\text{-}C6H13}$)$_3$Phen complex reaches 98%, which exceeds by 5 times the same parameter for a film of the Eu(DBM)$_3$Phen complex containing crystalline inclusions.

The synthesized Eu(III) complexes in the solid state show intense red photoluminescence upon irradiation by ultraviolet light (λ_{max} 337 nm). The difference in structure and luminescence properties in the series of complexes under investigation are negligible. Typical excitation and emission spectra of the Eu($CPDk_{3C6H13}$)$_3$Phen adduct are shown in Figure 9 as an example. The maximum luminescence intensity corresponds to a wavelength of 612 nm.[36] The observed well-resolved peaks can be attributed to transitions from the $^5D_0$ level of the excited state to the ^7F_J sublevels of the ground-state multiplet (J = 0–4). The ratio of the electric dipole transition intensity to the magnetic dipole transition intensity (($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$)) is 11.5.[37] The complexes display relatively high luminescence efficiency among the Eu(III) mesogenic complexes with β-diketones; the absolute quantum yield is 30–32% and does not depends on the length of the alkyl chains. The values of the fluorescence lifetime (see Figure S1 in the Supporting Information) of synthesized lanthanide complexes are in the range 0.54–0.56 ms, which is typical for Eu(III) complexes with β-diketones.[38]

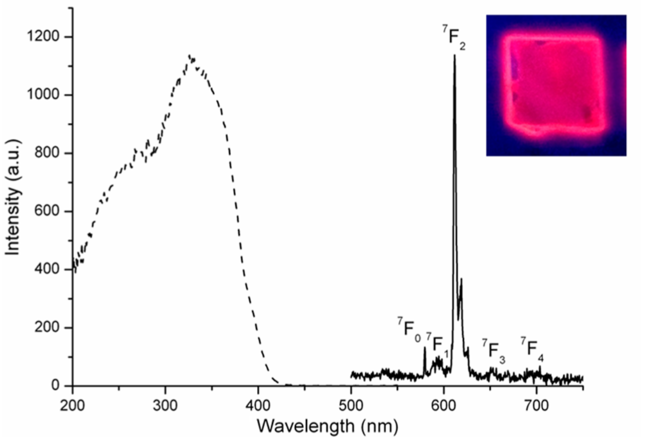

Figure 9. Excitation (dashed line) and emission (solid line) spectra of the film of the Eu($CPDk_{3C6H13}$)$_3$Phen adduct.

■ CONCLUSION

New mesogenic Eu(III) complexes containing ligands with multiple bonds have been synthesized. The obtained complexes are capable of undergoing a glass transition upon cooling from the isotropic liquid state with the formation of the supramolecularly organized media, which preserve the ordered arrangement of the Eu(III) ions created in the smectic C mesophase. By the methods of quantum chemistry and X-ray diffraction analysis, the relationship between the geometric anisotropy of molecules of the complexes, their intermolecular interaction, and supramolecular organization of the formed mesophases has been established. It is shown that some of the synthesized lanthanidomesogen entities are vitrified, forming optically isotropic films, which exhibit effective luminescence in the red spectral range.

■ EXPERIMENTAL SECTION

General Information. The optical textures and temperatures of phase transitions were determined on an Olympus BX-51 polarizing microscope equipped with a LINKAM high-precision heating system. The IR spectra were recorded on a Bruker-IFS66VIS spectrometer using samples suspended in Vaseline oil or in KBr tablets. ^{1}H NMR spectra were recorded with Bruker Avance 300 and Bruker Avance 400 spectrometers (operating at 300 and 400 MHz). The mass spectra were obtained using a Bruker Esquire LC-Ion Trap Mass Spectrometer. The X-ray diffraction studies were performed on a DRON-2 diffractometer using Fe Kα radiation with λ 1.93728 Å. DSC measurements were made on a Mettler-Toledo DSC 1 Star module in a heating–cooling mode at a scan rate of 10 K/min. The luminescence spectra were registered on a Varian Cary Eclipse spectrofluorimeter. The absolute quantum yield of the complexes in the solid state was determined following a standard technique using a specially designed setup equipped with an integrating sphere 105 mm in diameter coated with MgO, a light diode (380 nm, 10 mW) as an excitation source, and an FEU62 photomultiplier as a detector.[39]

Synthetic Procedures. The **β-diketone** ligands (abbreviated $CPDk_{3\text{-}R}$) with different lengths of the alkyl terminal substituents (R = CH_3–C_8H_{17}) were synthesized according to the method of Adams and Hauser.[40] To the stirred solution of the ketone (0.05 mol) in 100 mL of absolute ether, cooled to 10 °C, was added a suspension of sodium amide in toluene (0.1 mol). After 5 min the calculated amount of ester R-$COOC_2H_5$ (0.1 mol) in 100 mL of absolute ether was added over 20 min, and the stirring was continued for 6 h. After 20 mL of water was added, the mixture was neutralized with dilute hydrochloric acid and extracted with ether. The solvent was evaporated from the ether solution and the residue dissolved in the minimum volume of ethanol. The β-diketone was recrystallized twice from this ethanol solution. Yields, elemental analysis, and melting points have been described previously.[33]

Tris[1-(4-(4-propylcyclohexyl)phenyl)undecane-1,3-dionato](1,10-phenanthroline)europium(III): General Procedure. An alcoholic solution of $EuCl_3 \cdot 6H_2O$ (0.015 g, 0.04 mmol) was slowly dropped into a stirred hot alcoholic solution containing 0.078 g (0.12 mmol) of β-diketone, 0.008 g (0.04 mmol) of 1,10-phenanthroline, and 0.005 g (0.125 mmol) of KOH. The light yellow precipitate that formed was isolated by hot filtration, washed with hot alcohol, and dried under vacuum. Further, the product was dissolved in toluene, and the obtained solution was filtered off and evaporated to dryness under vacuum.

Theoretical Calculations. Quantum-chemical simulation of the equilibrium geometry of complexes was performed using the Priroda 06 software[41,42] by the DFT method with the PBE exchange correlation functional.[43] The properties of lanthanide-containing systems should be simulated by taking into account relativistic effects. Therefore, the rL11 relativistic basis set was applied for lanthanides and the rL1 basis set for other atoms,[44] which are analogues of the cc-pVDZ and cc-pCVDZ correlation-consistent double-ζ basis sets of Dunning, respectively. Calculations were carried out in the gas phase without symmetry constraints. The geometry of the coordination polyhedron of complexes was adopted from the Cambridge Structural Database, which contains the X-ray diffraction analysis data for similar compounds without alkyl substituents.[45−47]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01617.

> CHN analysis data and yields, optimized structures of isomers of the $Eu(CPDk_{3\text{-}C8H17})_3Phen$ complex, luminescence decay curves, and NMR and mass spectrometry data (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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