

Article

Anisometric Ln(III) Complexes with Efficient Near-IR Luminescence

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Abstract: Recent studies in development of near-infrared luminophores focus on overcoming their disadvantages such as low quantum efficiency, limited emission power, and broad emission spectra. Rare earth (RE) elements are promising compounds in this respect as they offer a unique set of optical properties that provide narrow emission spectra and large Stokes shifts. This work reports the results of synthesis and characterization of new anisometric complexes of lanthanide(III) tris(b-diketonates) and 1,10-phenanthroline. These complexes possess light emitting-properties in the near-infrared range. Due to their structural features, these complexes allow production of homogeneous films by spin coating. These films are transparent in the visible and near-infrared ranges (transmission up to 99%). This paper demonstrates advantages of Yb(III), Er(III), and Nd(III) complexes as potential components of highly efficient light-transforming NIR coatings.

Keywords: lanthanide complexes; NIR luminescence; light-transforming coatings



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1. Introduction

Infrared radiation (IR) attracts the sustained attention of scientists due to growing opportunities for its practical applications [1–6]. Most of these applications rely on the results of research in physics, chemistry, pharmacy, medicine, cosmetics, food sciences, and agriculture [1]. Various IR light sources are represented by tungsten halogen lamps, Globars, and light-emitting diodes with luminophore conversion (PC light emitting diodes) [7]. Selection of a proper IR luminophore depends primarily on its emission wavelength, full width at half maximum (FWHM), efficiency, service life, and thermal stability. Today, PC LEDs are popular near-infrared (NIR) light sources that are used as components of remote control devices, automobile sensors, traffic enforcement cameras, ocular scanners, spectrometers, optic fiber devices, and biological analysis instruments [8–18]. Near-infrared PC LEDs demonstrate a longer service life of up to 100,000 h. They are cost-effective devices due to their small size [7].

Recent research activities in development of near-infrared luminophores focus on overcoming their disadvantages such as low quantum efficiency, limited emission power, and broad emission spectra [19–22]. Rare earth (RE) elements make a substantial contribution to solving these problems because they offer a unique set of optical properties such as narrow emission spectra and large Stokes shifts [23]. With the exception of lanthanum and lutetium, Ln³⁺ ions generate stable long-life *f-f*-emissions in response to a direct photoexcitation within absorption wavelengths of metals. The advantages of lanthanide complexes as components of optoelectronic devices are their narrow emission bands and broad light color options offered by lanthanide ions: Tm(III)—blue, Tb(III)—green, Eu(III)—red, Dy(III)—yellow, Sm(III)—orange, Nd(III), Er(III) and Yb(III)—infrared. By combining these complexes with various ions, we can generate emission of virtually any color such as a white color emission. However, molar absorption coefficients of inorganic Ln³⁺ compounds

are usually very small ($\epsilon = 0.01\text{--}10 \text{ L}/(\text{mol} \times \text{cm})$). They are limited by parity-forbidden *f-f*-transitions [24]. Compounds allowing one to overcome these limitations are organic ligands with absorbing chromophore groups. These groups transmit energy to the emission level of a metal ion (an antenna effect) [25]. They should satisfy the following two criteria. Firstly, a suitable chromophore should be a good sensitizer of Ln^{3+} ions [17]. Secondly, the resulting compounds should be thermally and chemically stable and possess good mechanical properties for possible practical applications in molecular electronics [26]. Ligands represented by β -diketonates possess strong broadband absorption properties. They are among the most studied chromophores for neutral tris(β -diketonate) [27] or anionic tetrakis(β -diketonate) Ln^{3+} complexes [28]. These compounds perform an efficient transfer of energy to the Eu^{3+} and Tb^{3+} ions and generate a relatively high first excited state ($^5\text{D}_0$ for Eu^{3+} is $17,286 \text{ cm}^{-1}$ and $^5\text{D}_4$ for Tb^{3+} is $20,545 \text{ cm}^{-1}$, respectively) [29,30]. On the other hand, less detailed studies are reported for complexes of lanthanide β -diketonates generating emissions in the near-infrared range [31,32]. Due to their monochromatic NIR luminescence properties, such substances exhibit potential for applications in telecommunications, biology, and laser technologies [24,33–35].

In addition to these peculiar features, lanthanide materials demonstrate less intensive NIR light scattering in biological systems. The emission band of such materials is, therefore, within the biological transparency window ($\lambda = 700\text{--}1100 \text{ nm}$), so they are particularly attractive for generation of detailed images of thick tissues with time synchronization [36–39]. Thus, synthesis and characterization of new rare earth coordination compounds with IR luminescence properties represent an urgent problem of modern science.

This work reports the results of synthesis and characterization of new anisometric complexes of lanthanide(III) tris(β -diketonates) and 1,10-phenanthroline that possess light emitting-properties in the near-infrared range.

2. Results and Discussion

Ligands represented by β -diketonates possess strong broadband absorption properties. Such ligands are among the most studied chromophores for the synthesized neutral tris- β -diketonate [27] or anionic tetrakis- β -diketonate Ln^{3+} -complexes [28]. Efficient sensitization of visible light luminescence is reported for Eu^{3+} and Tb^{3+} ions with relatively high first excited states ($^5\text{D}_0$ for Eu^{3+} is $17,286 \text{ cm}^{-1}$ and $^5\text{D}_4$ for Tb^{3+} is $20,545 \text{ cm}^{-1}$) [29,30,40]. There is, however, an unresolved problem of synthesis of a suitable β -diketonate ligand with a relatively lower triplet energy level that matches the first excited state of NIR-luminescent Ln^{3+} ions [41,42] ($^4\text{F}_{3/2}$ for Nd^{3+} is $11,257 \text{ cm}^{-1}$; $^2\text{F}_{5/2}$ for Yb^{3+} is $10,400 \text{ cm}^{-1}$, and $^4\text{I}_{13/2}$ for Er^{3+} is 6610 cm^{-1}). According to the literature data, ligands with the triplet energy levels from $18,000 \text{ cm}^{-1}$ to $21,000 \text{ cm}^{-1}$ are used to synthesize β -diketonate lanthanide complexes with the NIR-emission properties (Table 1). A possible approach to intensifying luminescence in the near-infrared range and minimizing a non-radiative deactivation is to use β -diketonate ligands that contain fluorine [43,44]. Another approach is to reduce the triplet energy level of a ligand by adding conjugated bonds [45].

Previously, the authors synthesized a large number of β -diketonates with various substituents that allow alteration of the triplet level of a ligand (Table 1). In the earlier works, however, these β -diketonates were used to synthesize lanthanide(III) complexes, which possess visible light emission properties. The triplet level of a ligand was, therefore, selected to efficiently sensitize the visible light luminescence of the Eu^{3+} , Sm^{3+} , or Tb^{3+} ions with relatively high first excited states [46,47]. In this work, the structures of β -diketonates were selected according to the following criteria: (a) matching the triplet level energy values of similar compounds, which are known to be used for coordinating NIR-luminescent Ln^{3+} ions; (b) demonstrating good solubility in organic solvents; (c) possessing an amorphous structure provided by long hydrocarbon or cyclohexane substituents that allows fabrication of homogeneous and defectless films. Compounds that satisfy these criteria can be potential components of film coatings for PC light-emitting diodes.

Table 1. Structures and triplet levels of some β -diketones.

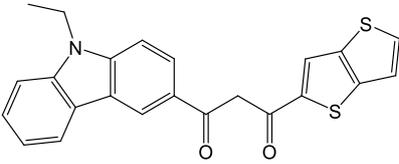
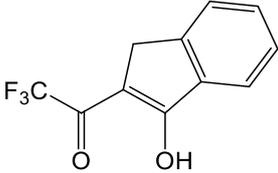
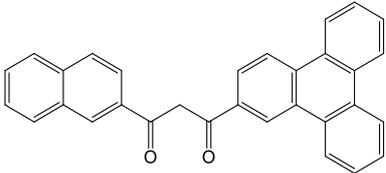
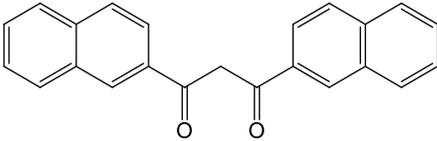
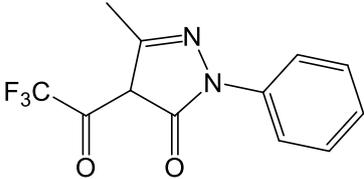
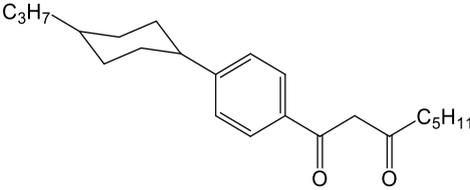
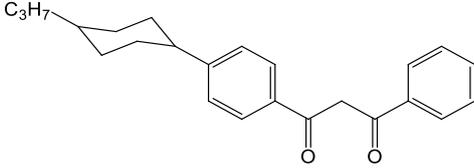
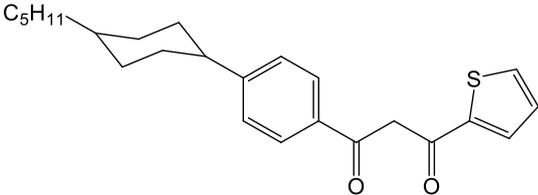
#	Structure of β -Diketone	${}^3T_1, \text{cm}^{-1}$	Reference
1		19,230	[48]
2		19,607	[49]
3		19,300	[50]
4		19,300	[50]
5		18,975	[31]
6		20,200	In this paper
7		19,200	[51]
8		18,200	[52]

Table 1. Cont.

#	Structure of β -Diketone	3T_1 , cm^{-1}	Reference
9		19,160	[53]
10		19,200	[54]

We synthesized complexes of lanthanide (III) tris(β -diketonates) and 1,10-phenanthroline. The molecular structure of these complexes has an anisometric geometry (Figure 1) [55–57]. Original β -diketonates and 1,10-phenanthroline were used as the ligands. Their triplet levels perform efficient energy transfer to the emitting levels of the Ln^{3+} ions. The composition and structure of these complexes were confirmed by elemental analysis and mass spectrometry. The synthesized compounds are amorphous powders due to their anisotropy and long hydrocarbon substituents at molecular edges. The anisometric molecular structure of such complexes was confirmed by previous quantum chemistry calculations and X-ray diffraction characterization performed by the authors for similar Eu(III) complexes. These powders demonstrate good solubility in nonpolar or low-polar organic solvents.

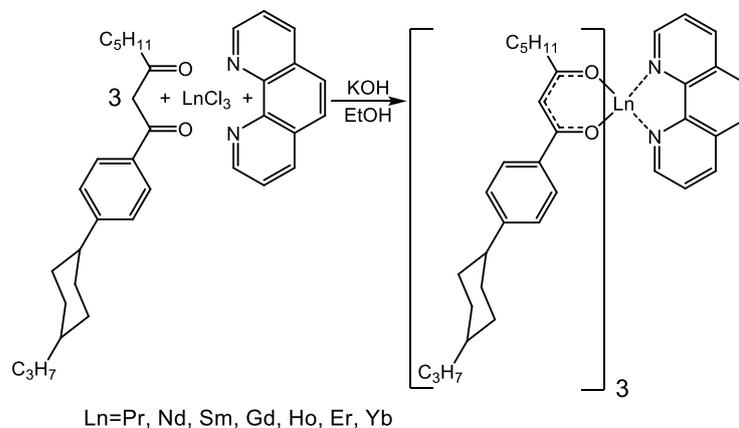


Figure 1. Synthesis of tris(β -diketonate) lanthanide(III) complexes with 1,10-phenanthroline.

The solutions of these complexes in toluene (1×10^{-3} mol/L) were used to fabricate films with the thickness of 100 ± 5 nm by spin coating [51]. We characterized optical properties of both solutions and films that contained La(III) complexes. The maximums of the UV/VIS absorption spectra obtained for the Ln(III) complexes dissolved in hexane ($c = 1 \times 10^{-5}$ mol/L, Figure 2a) are similar to the maximums observed for the individual ligands. Due to their structural features, these complexes allow production of homogeneous films by the spin coating deposition from their solutions. These films are transparent in the visible and near-infrared ranges (light transmission up to 99%) (Figure 2b).

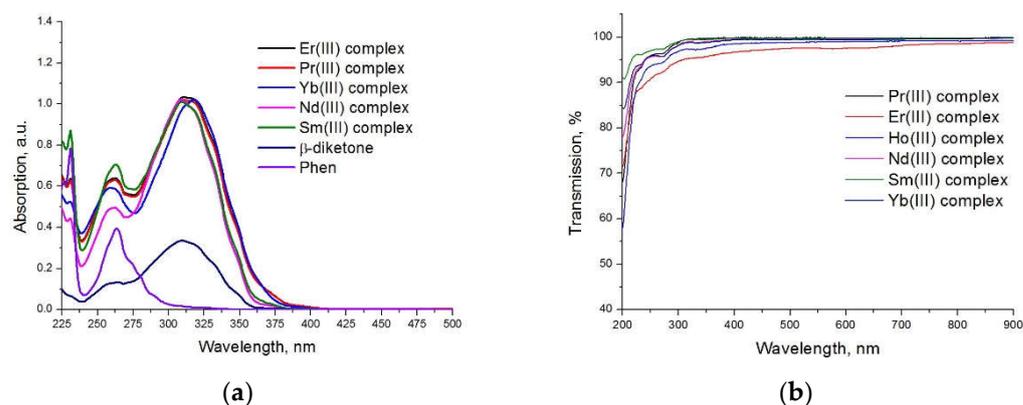


Figure 2. (a) Absorption spectra of lanthanide(III) complexes and ligands dissolved in hexane with the concentration of 10^{-5} mol/L; (b) transmittance spectra of the films containing lanthanide(III) complexes.

To determine the energy levels of the ligand environment, we studied the luminescent properties of the gadolinium Gd(III) complexes that were incorporated into thin films by spin coating at the temperature of liquid nitrogen ($T = 77$ K) (Figure 3). A Gd^{3+} ion does not emit light because its first excited ${}^6P_{7/2}$ -level ($32,000\text{ cm}^{-1}$) is above the lower triplet level of the majority of known organic ligands. According to the literature data, most β -diketonate Gd(III) complexes exhibit only phosphorescence at 77 K due to their efficient intercombinational conversion [58]. The central ion does not exert a substantial impact on the excited energy levels of the ligands. Similar energy levels can be, therefore, observed for other Ln(III) ions.

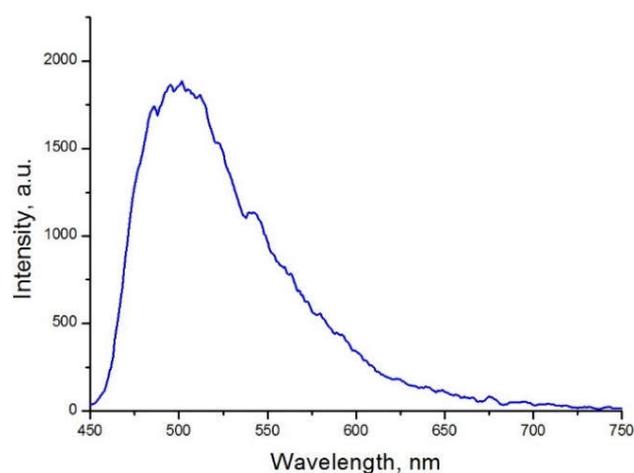


Figure 3. Luminescence spectrum of the films with the Gd(III) complexes at $T = 77$ K.

The experimental phosphorescence spectrum of Gd(III) allowed attainment of the value of the β -diketonate triplet level equal to approximately $20,200\text{ cm}^{-1}$. The triplet levels of the ligands and the emission transitions of the lanthanide ions are summarized in the energy level diagram that represents the energy transfer processes occurring in the synthesized complexes. This diagram is shown in Figure 4.

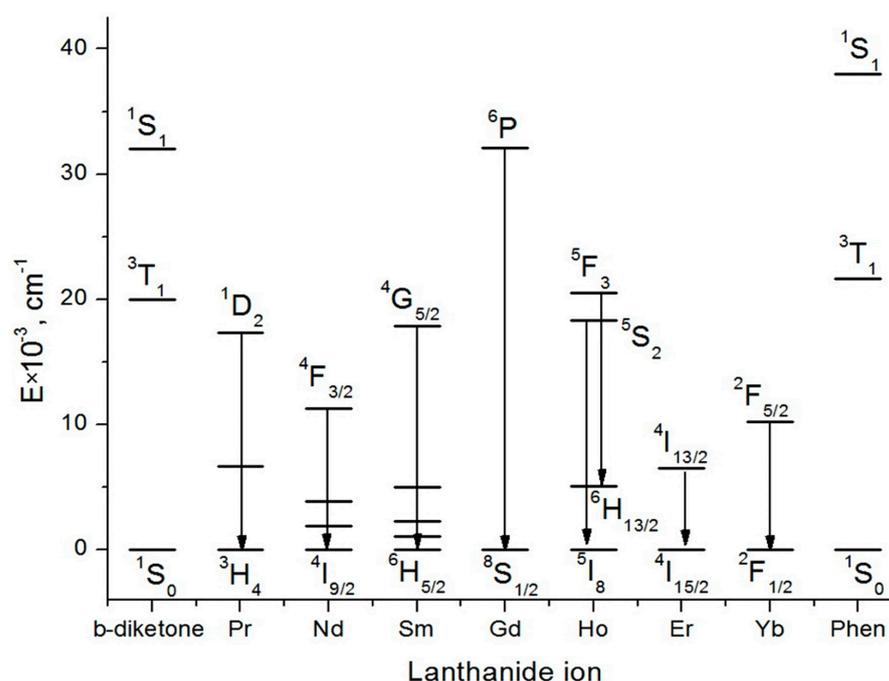


Figure 4. Energy levels of the synthesized complexes.

We can see in this diagram that the triplet energy levels of the β -diketone and the Lewis base are slightly higher than the resonance levels of virtually all the lanthanide ions discussed in this work. Such properties should favor the transfer of energy (an antenna effect) and efficient luminescence in the near-infrared range [59,60].

To evaluate applicability of the synthesized complexes to producing conversion coatings for PC-LEDs, we obtained the luminescence spectra of the films by using a 408 nm blue light emitting diode as the source of the excitation light. The emission spectra of the Sm(III) complexes obtained at room temperature show the characteristic samarium ion transition bands at the wavelengths of 800–1400 nm. The observed high-resolution peaks represent the transitions from the $^4G_{5/2}$ level of the excited state to the 6H_j sub-levels of the main multiplet. The maximum intensities of the characteristic peaks at the wavelengths of 887, 909, 927, 952, and 1036 nm correspond to the transitions from the $^4G_{5/2}$ level of the excited state to the 6F_j sub-levels of the main multiplet ($J = 1/2, 3/2, 5/2, 7/2,$ and $9/2$) (Figure 5a). The peaks at the wavelengths of 1130, 1210, and 1300 nm correspond to the second harmonic of the transitions from the $^4G_{5/2}$ level of the excited state to the 6H_j sub-levels of the main multiplet ($J = 5/2, 7/2, 9/2$).

The emission spectrum of the Yb(III) complex contains several intensive lines at 976 nm with the lifetime $\tau = 11 \mu\text{s}$, which correspond to the Stark splitting of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition (Figure 5b) and fit the middle of the first biological transparency window ($\lambda = 700\text{--}1100 \text{ nm}$). In combination with a two-photon excitation technique, such compounds of Yb(III) become attractive substances for biological research techniques [61]. The Nd(III) complex shows three luminescence peaks that correspond to the $^4F_{3/2} \rightarrow ^4I_j$ transitions ($J = 9/2, 11/2, 13/2$) with the lifetime $\tau = 9 \mu\text{s}$ (Figure 5c).

The luminescence spectra of the Er(III) complexes contain a single line corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition at 1530 nm in the near-infrared range of the spectrum with the lifetime $\tau = 3 \mu\text{s}$ (Figure 5d) that can be used in laser technologies and telecommunications. The Pr(III) complex demonstrates a relatively low characteristic peak corresponding to the $^1D_2 \rightarrow ^3H_4$ transition at 1060 nm (Figure 5e). The Ho(III) complex exhibits a noise-level IR luminescence. The spectra reveal that the luminescence intensity of the films that contain the Yb(III) и Nd(III) complexes is almost two times higher than that of the films containing the Er(III) and Sm(III) compounds and six times higher than the luminescence intensity

of the films containing the Pr(III) complex. Therefore, the most intensive luminescence is demonstrated by the compounds that contain Yb(III), Er(III), or Nd(III) ions.

This work, therefore, demonstrates a potential of using Yb(III), Er(III) and Nd(III) complexes as components of highly efficient light-transforming NIR coatings for PC light emitting diodes.

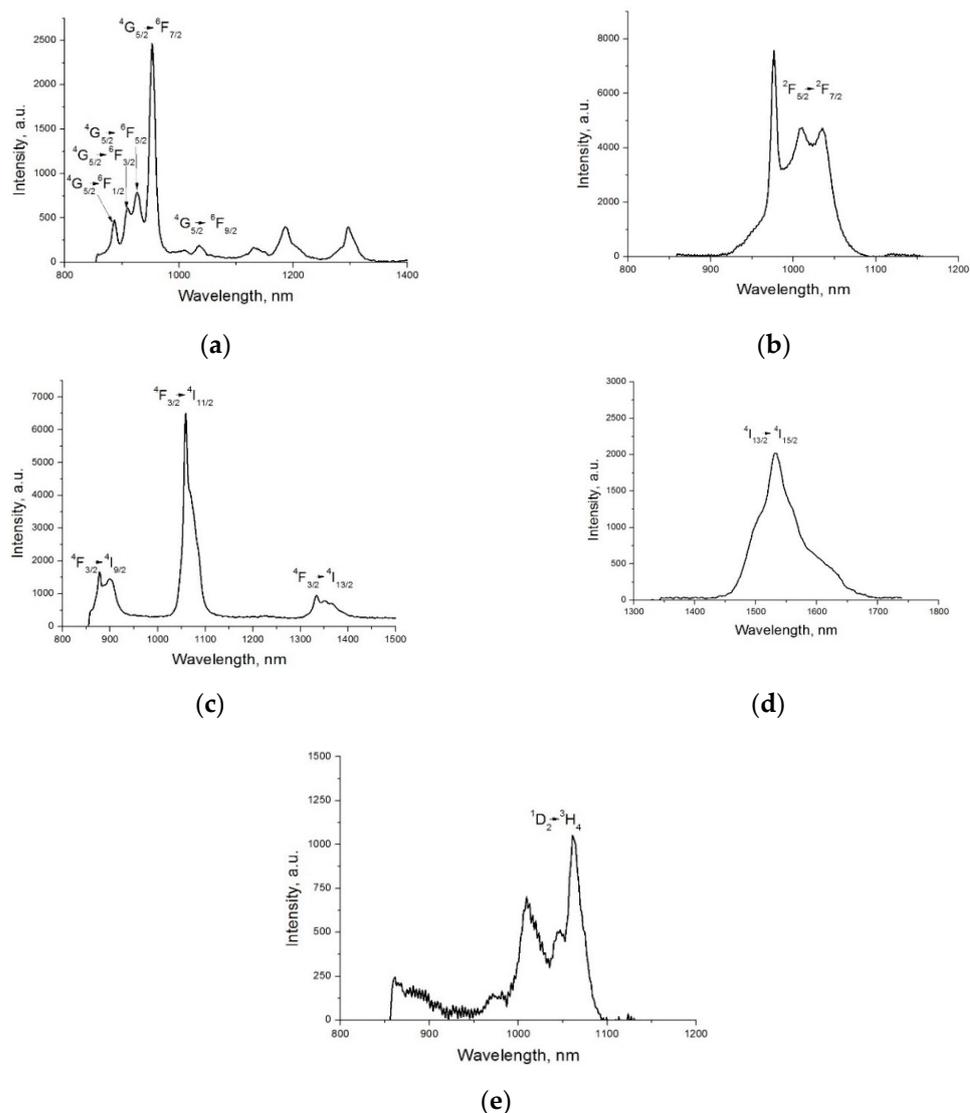


Figure 5. Luminescence spectra of the films containing (a) Sm(III), (b) Yb(III), (c) Nd(III), (d) Er(III) and (e) Pr(III) complexes in the near IR range.

3. Materials and Methods

3.1. Materials

Praseodymium(III) chloride hexahydrate (99.9%), neodymium(III) chloride hexahydrate (99.9%), samarium(III) chloride hexahydrate (99.99%), gadolinium(III) chloride hexahydrate (99.999%), holmium(III) chloride hexahydrate (99.9%), erbium(III) chloride hexahydrate (99.9%), ytterbium(III) chloride hexahydrate (99.9%), and 1,10-phenanthroline (99%) were purchased from Sigma-Aldrich.

3.2. Characterization Techniques

CHN elemental microanalysis was performed with a Delta V Plus isotope mass spectrometer (Thermo Fisher Scientific, Braunschweig, Germany). X-ray fluorescence analysis was performed with a Bruker M4 «Tornado» spectrometer. The mass spectra data were

obtained by a Bruker Esquire LC-Ion Trap Mass Spectrometer. Absorption and transmission spectra were measured by a Perkin–Elmer Lambda-35 UV/Vis spectrophotometer. Luminescence spectra of the produced films were recorded by an Ocean optics NIR Quest 512 spectrofluorimeter (Bridge Tronic Global Inc, Costa Mesa, CA, USA). The excitation wavelength was set to 408 nm.

3.3. Synthesis of Complexes

The 1-[4-(4-propylcyclohexyl)phenyl]-octane-1,3-dione ligand was synthesized according to the modified procedures reported in the literature [52,62].

Ln(III) complexes [63] were synthesized according to the following general procedure: ethanol solutions of $\text{LnCl}_3 \times 6\text{H}_2\text{O}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Ho}, \text{Er}$ or Yb) (0.1 mmol) were added dropwise to a stirred hot ethanol solution that contained β -diketone (1-[4-(4-propylcyclohexyl)phenyl]-octane-1,3-dione) (0.3 mmol), 1,10-Phenanthroline (0.1 mmol), and KOH (0.35 mmol). The resulting light-yellow precipitates were filtered from their solutions, washed by hot alcohol, and dried under vacuum. The dry product was dissolved in toluene, filtered again, and dried under vacuum (Table 2).

Table 2. The results of the analysis of synthesized Ln(III) complexes.

Lanthanide Ion	Yield, %	Elemental										ESI-MS (m/z)
		C, %		H, %		N, %		O, %		Ln, %		
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Pr	75	72.30	72.01	8.01	8.17	2.08	2.05	7.13	7.22	10.47	10.45	1368 (M + Na) ⁺
Nd	73	72.12	71.98	7.99	8.06	2.08	2.05	7.12	7.26	10.69	10.81	1370 (M + Na) ⁺
Sm	78	71.79	71.59	7.96	8.12	2.07	2.04	7.08	7.23	11.10	11.47	1377 (M + Na) ⁺
Gd	74	71.43	71.25	7.92	8.15	2.06	2.04	7.05	7.27	11.55	11.63	1385 (M + Na) ⁺
Ho	71	71.03	70.87	7.87	8.11	2.05	2.02	7.01	7.42	12.04	12.16	1391 (M + Na) ⁺
Er	72	70.91	70.78	7.86	8.05	2.04	2.02	7.00	7.22	12.19	12.03	1394 (M + Na) ⁺
Yb	73	70.61	70.48	7.83	8.02	2.03	2.01	6.97	7.16	12.56	12.41	1399 (M + Na) ⁺

4. Conclusions

This paper reports synthesis of new anisotropic lanthanide(III) complexes that possess near-infrared luminescence properties. Due to their structural features, these complexes can be incorporated into homogeneous films by spin coating deposition from their solutions. The resulting films are transparent in the visible and near-infrared ranges (transmission up to 99%). The synthesized Yb(III), Er(III) and Nd(III) compounds demonstrate efficient luminescence in the near-infrared range. By varying lanthanide(III) ions, we can control emission wavelengths of the produced films. Thus, this work demonstrates a possibility to use Yb(III), Er(III) and Nd(III) complexes for making highly efficient light-transforming NIR coatings for PC light emitting diodes. The emission bandwidth of the Yb(III) and Nd(III) complexes is within the biological transparency window ($\lambda = 700\text{--}1100\text{ nm}$). Therefore, these complexes are attractive for biomedical applications such as performing a comprehensive study of thick tissues of the majority of living organisms. In its turn, the luminescence emission of the Er(III) compounds fits the third transparency window of optic fibers ($\lambda \approx 1550\text{ nm}$) and highlights potential applications of such compounds in the telecommunications industry.

Author Contributions: This work is the collaborative development of all the authors. Conceptualization, A.A.K. and Y.G.G.; methodology, A.A.K. and Y.G.G.; software, A.S.K.; validation, A.A.K., A.S.K. and Y.G.G.; formal analysis, A.S.K.; investigation, A.A.K., A.S.K. and Y.G.G.; resources, Y.G.G.; data curation, A.A.K. and Y.G.G.; writing—original draft preparation, A.A.K. and A.S.K.; writing—review and editing, Y.G.G.; supervision, A.A.K. and Y.G.G. All authors have read and agreed to the published version of the manuscript.

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