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Lanthanide Tris-2-(quinolyl-8-iminomethyl)phenolates: Synthesis and Structures

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Abstract—The reactions of sodium 2-(quinolyl-8-iminomethyl)phenolate with rare-earth element chlorides afford homoleptic mononuclear complexes [Ln{2-(8-quinolyl)N=CH–C_6H_4O}$_3$] (Ln = La (**I**), Nd (**II**), Eu (**III**), and Tb (**IV**)) with the nonacoordinated rare-earth element ion. All synthesized complexes are similar in structure, and complexes **II**, **III**, and **IV** are isostructural (CIF files CCDC nos. 2124365 (**I**), 2124364 (**II**), 2124366 (**III**), and 2124367 (**IV**)). Compounds **III** and **IV** exhibit no luminescence, and characteristic luminescence in the near-IR range is observed for complex **II**.

Keywords: rare-earth elements, ONN-donor ligands, X-ray diffraction

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INTRODUCTION

The majority of rare-earth elements Ln^{3+} with an open 4*f*-electron shell are capable of luminescing and demonstrate characteristic narrow lines in the luminescence spectra [1–3].

Rare-earth element (REE) ions luminesce due to forbidden 4*f*–4*f* transitions and, hence, they are characterized by low luminescence quantum yields. In order to enhance the luminescence quantum yield, an indirect excitation of the REE ion is used via absorption bands of the coordinated organic ligand that can efficiently absorb electromagnetic radiation followed by the excitation transfer to the REE ion. This use of an organic ligand is named the “antenna” effect [1, 4]. Heterocyclic organic compounds coordinated to a lanthanide cation by a heteroatom are frequently applied as such ligands [5–7]. Organic ligands in the coordination sphere of the REE ion also prevent contacts with solvent molecules thus avoiding luminescence quenching due to nonradiative relaxation owing to vibrations of the O–H, N–H, and C–H groups. In this respect, it seems most efficient to use polydentate organic ligands bearing several donor atoms (N, O) capable of coordinating with the REE cation, especially condensed aromatic compounds that can act as antenna ligands [1, 3, 4]. Possible interligand interactions between bulky ligands in the coordination sphere of the REE complex and their influence on the photophysical properties are of special interest. These interactions can lead to the formation of “induced” charge-transfer states [8] involved in processes of luminescence sensitization, and the control of these processes can be considered as a new method for designing luminescent materials with specified properties.

The purpose of this work is to reveal coordination possibilities of the tridentate ONN-donor 2-(quinolyl-8-iminomethyl)phenolate ligands in the REE complexes and to study the photophysical properties of these compounds.

EXPERIMENTAL

All synthetic manipulations were carried out under prepurified argon in anhydrous solvents using an argon–vacuum line and Schlenk technique. Tetrahydrofuran (THF) was dried over NaOH and distilled over potassium benzophenone. Hexane was distilled over a potassium–sodium eutectic and benzophenone. Toluene was distilled over sodium benzophenone. Compounds $LnCl_3(THF)_x$ were synthesized using a known procedure [9]. NMR spectra were recorded on a Bruker AM-300 instrument. Direct complexonometric titration with a solution of Trilon B using xylenol orange as the indicator was used to determine the lanthanide content in a sample. Elemental analysis was carried on a Perkin-Elmer automated CHN microanalyzer.

Synthesis of [La(C_9H_6N–N=CH–C_6H_4–O)$_3$]-(THF) (I). A solution of sodium 2-(quinolyl-8-iminomethyl)phenolate, which was prepared by the reaction of 2-(quinolyl-8-iminomethyl)phenol (0.818 g, 3.3 mmol) and a 0.85 M solution (3.88 mL) of sodium methylate (3.3 mmol) in methanol, was added to a solution of anhydrous lanthanum chloride (0.270 g, 1.1 mmol) in anhydrous methanol (25 mL). The prepared mixture was stirred for 10 h. The mixture was evaporated to dryness, and THF (20 mL) and CH_3OH (5 mL) were added to the residue. The solution was separated from the precipitate, and the precipitate was extracted with THF. The combined extract was evaporated three times, and crystals precipitated during staying for a week were dissolved in THF (15 mL) and methanol (5 mL) on heating (T = 60°C). Hexane was carefully added to the mixture, and the mixture was left to stay for two weeks. The formed crystals were separated from the mother liquor and dried in vacuo. The yield of compound **I** was 0.48 g (46%).

For $C_{52}H_{41}N_6O_4La$

Anal. calcd., %	La, 14.60	C, 65.56	H, 4.31	N, 8.82
Found, %	La, 14.72	C, 65.16	H, 3.81	N, 9.27

The crystals suitable for X-ray diffraction (XRD) were obtained by the slow diffusion of hexane into a solution of compound **I** in THF.

^{1}H NMR ($CDCl_3$; δ, ppm): 1.80 m (8H), 3.75 m (8H), 6.00 d (3H), 6.2 t (3H), 6.7 m (6H), 6.90 m (3H), 7.15 m (6H), 7.25 m (3H), 7.87 m (3H), 8.02 m (3H), 9.01 d (3H). ^{13}C NMR ($CDCl_3$; δ, ppm): 112.3, 117.4, 121.3, 123.0, 123.0, 124.1, 127.0, 128.4, 134.0, 135.3, 136.7, 143.4, 149.0, 152.5, 164.8, 169.6.

Synthesis of [Nd(C_9H_6N–N=CH–C_6H_4–O)$_3$]-($CHCl_3$) (II) was carried out by the method similar for complex **I** from $NdCl_3$·1.8THF (1.40 g, 3.69 mmol), 2-(quinolyl-8-iminomethyl)phenol (2.75 g, 11.07 mmol), and a solution of sodium methylate (13.02 mL, 0.85 M, 10.47 mmol). Crystalline compound II was isolated by recrystallization from chloroform with the slow addition of hexane. The yield of compound II was 2.63 g (80%). Found, %: Nd 14.12; for $C_{49}H_{34}N_6O_3Cl_3Nd$ anal. calcd., %: Nd 14.33.

Synthesis of [Eu(C_9H_6N–N=CH–C_6H_4–O)$_3$]-($CHCl_3$)$_2$ (III) was carried out by the method similar for complex **I** from $EuCl_3$·2THF (0.39 g, 0.96 mmol), 2-(quinolyl-8-iminomethyl)phenol (0.71 g, 2.88 mmol), and a solution of sodium methylate (2.32 mL, 1.24 M, 2.88 mmol). Crystalline compound **III** was isolated by recrystallization from chloroform with the slow addition of hexane. The yield of compound **III** was 0.24 g (78%).

For $C_{50}H_{35}N_6O_3Cl_6Eu$

Anal. calcd., %	C, 53.00	H, 3.09	N, 7.42
Found, %	C, 53.18	H, 3.39	N, 7.37

Synthesis of [Tb(C_9H_6N–N=CH–C_6H_4–O)$_3$]-($CHCl_3$) (IV) was carried out by the method similar for complex **I** from $TbCl_3$·3THF (0.61 g, 1.26 mmol), 2-(quinolyl-8-iminomethyl)phenol (0.94 g, 3.78 mmol), and a solution of CH_3ONa (2.58 mL, 1.464 M, 3.78 mmol). Crystalline compound **IV** was isolated by recrystallization from chloroform with the slow addition of hexane. The yield of compound **IV** was 0.75 g (58%).

For $C_{49}H_{34}N_6O_3Cl_3Tb$

Anal. calcd., %	Tb, 15.60	C, 57.70	H, 3.33	N, 8.23
Found, %	Tb, 16.77	C, 58.12	H, 3.40	N, 7.79

According to the XRD data, crystalline lattices of unit cells of single crystals of all studied compounds contain solvate molecules of the solvent (four $CHCl_3$ molecules per formula unit (**II**–**IV**) and three THF molecules (**I**)). Some solvate molecules were lost upon drying in vacuo to a constant weight.

XRD of complexes **I**–**IV** was carried out on a Bruker Quest D8 diffractometer (MoK_α radiation, graphite monochromator, ω scan mode). The structures were solved by a direct method and refined by least squares in the anisotropic full-matrix approximation for F^2_{hkl}. An absorption correction was applied semiempirically by equivalent reflections. Restraints for the atomic shift parameters and positional parameters (DFIX and EADP) were used in the refinement of disordered solvate molecules. In all structures, hydrogen atoms were calculated and refined by the riding model. All calculations were performed using the SHELXL-2014/2017 software. Selected crystallographic data and refinement parameters for compounds **I**–**IV** are given in Table 1.

The coordinates of atoms and other structural parameters for compounds **I**–**IV** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2124364–2124367, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

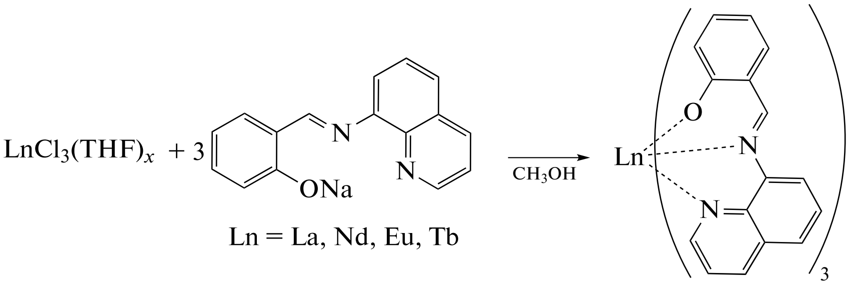
RESULTS AND DISCUSSION

The lanthanum, neodymium, europium, and terbium complexes with the 2-(quinolyl-8-iminomethyl)phenolate anion of the general formula LnL_3 (Ln = La (**I**), Nd (**II**), Eu (**III**), and Tb (**IV**); L is {2-(8-quinolyl)N=CH–C_6H_4O}) were synthesized by

Table 1. Selected crystallographic data and refinement parameters for compounds **I–IV**

Parameter	Value			
	La (**I**)	Nd (**II**)	Eu (**III**)	Tb (**IV**)
Empirical formula	$C_{60}H_{56}N_6O_6La$	$C_{52}H_{37}N_6O_3Cl_{12}Nd$	$C_{52}H_{37}N_6O_3Cl_{12}Eu$	$C_{52}H_{37}N_6O_3Cl_{12}Tb$
FW	1096.01	1363.51	1371.23	1378.19
T, K	120	120	120	120
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	8	4	4	4
a, Å	18.421(2)	12.6867(11)	12.6119(5)	12.6223(5)
b, Å	20.032(2)	19.3960(16)	19.4608(7)	19.4964(8)
c, Å	27.301(3)	22.6510(19)	22.6466(8)	22.6394(9)
α, deg	90	90	90	90
β, deg	90	96.933(2)	97.0460(10)	97.0108(9)
γ, deg	90	90	90	90
V, Å^3	10074(2)	5533.0(8)	5516.4(4)	5529.7(4)
ρ_{calc}, g cm^{-3}	1.445	1.637	1.651	1.655
μ, cm^{-1}	9.08	15.67	17.67	19.08
F(000)	4504	2716	2728	2736
$2\theta_{max}$, deg	56	64	61	63
Number of measured reflections	111184	80320	74312	80683
Number of independent reflections	12164	9451	16843	25466
Number of reflections with $I > 2\sigma(I)$	6624	16160	12630	18671
Number of refined parameters	654	742	742	742
R_1	0.0493	0.0401	0.0438	0.0464
wR_2	0.1312	0.1073	0.1114	0.1152
GOOF	0.956	1.033	1.018	0.930
Residual electron density (max/min), e Å^{-3}	0.966/–1.064	1.940/–2.059	2.071/–1.821	2.094/–1.910

the reactions of solutions of $LnCl_3(THF)_x$ in absolute methanol with sodium salt of the ligand, which was synthesized by the treatment of 2-(quinolyl-8-iminomethyl)phenol with a solution of sodium methylate in methanol (Scheme 1). Single crystals of the complexes were obtained by recrystallization from chloroform (**II–IV**) or by the slow addition of petroleum ether to a solution of the complex in THF (**I**).



Scheme 1.

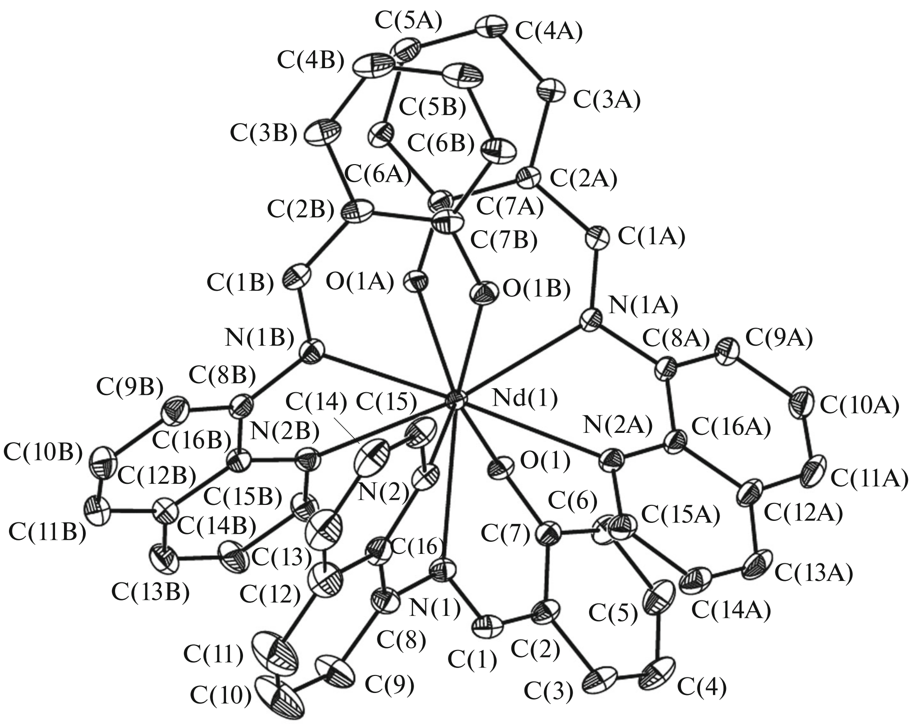


Fig. 1. General view of complexes **I**–**IV** exemplified by the Nd(**II**) complex in representation of atoms by thermal ellipsoids (p = 50%).

The structures of compounds **I**–**IV** were determined by XRD (Fig. 1, Table 2).

The neodymium, europium, and terbium complexes (**II**–**IV**) are isostructural (space group $P2_1/c$) and crystallize as solvates with four $CHCl_3$ molecules, whereas the lanthanum complex (**I**) was obtained as a solvate with three THF molecules and belongs to the space group *Pbca*. In spite of differences in the number and type of solvate molecules, the structures of the complexes are nearly the same.

In complexes **I**–**IV**, the REE cations are coordinated by two nitrogen atoms and one oxygen atom of each of three ligands. The coordination environment of the lanthanide cation is a "one-capped" tetragonal antiprism. Thus, the coordination number of the metal atom is nine. The coordination mode and geometry of the coordination polyhedron result in a substantial distortion of planarity of the ligands: the angle between the iminoquinoline and hydroxyphenyl fragments varies in a narrow range of 34°–40°. An interesting specific feature of this complex is the mutual arrangement of π systems of adjacent ligands. All the three complexes exhibit three different types of dimers in which stacking interactions can be assumed,

Table 2. Selected structural parameters of complexes **I**–**IV**

Parameter	La (**I**)	Nd (**II**)	Eu (**III**)	Tb (**IV**)
Ln–O (Å)	2.389(3)– 2.400(3)	2.342(2)–2.355(2)	2.309(2)–2.324(2)	2.285(2)–2.302(2)
$Ln{-}N_{imino}$	2.683(4)–2.791(4)	2.616(2)–2.675(2)	2.581(3)–2.641(3)	2.564(2)–2.617(2)
$Ln{-}N_{quinoline}$	2.716(3)–2.822(4)	2.687(2)–2.751(2)	2.649(3)–2.726(3)	2.628(2)–2.719(2)
C(7)...C(8a)	3.338(4)	3.390(4)	3.343(4)	3.323(3)
C(7)...C(16a)	3.306(4)	3.193(4)	3.164(4)	3.155(3)
C(1)...C(15a)	3.365(4)	3.254(4)	3.229(4)	3.218(3)
C(7a)...C(7b)	3.357(4)	3.234(4)	3.226(4)	3.198(3)
C(8b)...C(16)	3.499(4)	3.418(4)	3.369(4)	3.363(3)
C(16b)...C(8)	3.447(4)	3.418(4)	3.408(4)	3.390(3)
N(2b)...N(1)	2.956(40	2.932(4)	2.911(4)	2.881(3)

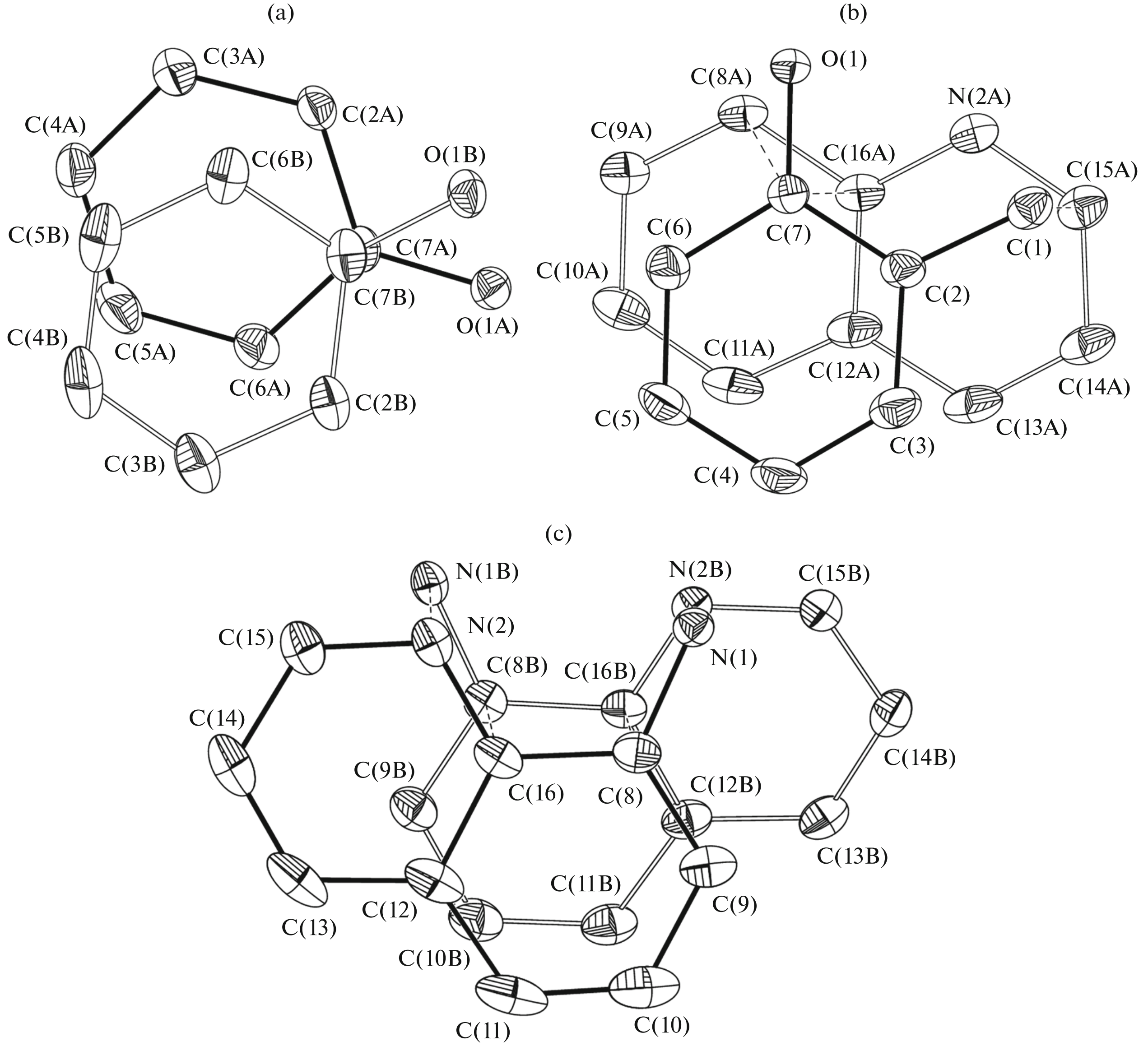


Fig. 2. Fragments of the crystal structures of compounds **II**–**III** illustrating the arrangement of the π systems in possible stacking dimers (scheme of superimposition of (a) phenoxy...phenoxy, (b) phenoxy...iminoquinoline, and (c) iminoquinoline...iminoquinoline fragments).

namely, hydroxyphenyl...hydroxyphenyl, hydroxyphenyl...iminoquinoline, and iminoquinoline...iminoquinoline. In the indicated dimers, the π systems are not parallel and are inclined toward the metal. However, in all cases, very short contacts, which can be considered as a possible "channel" of charge transfer, are observed (see Fig. 2, Table 2). In fact, in this system the interatomic distances are comparable with similar contacts in [2.2]paracyclophane [10, 11]. However, unlike the latter, the contacts in the studied complexes occur also between the cycles different in size and electronic characteristics. It is important that these intramolecular contacts depend slightly on the nature of both the metal and solvate molecules (crystal packing effect).

Therefore, it could be expected that these contacts can result in the formation of the charge-transfer states that substantially affect the sensitization of REE luminescence [12, 13]. The performed TD-DFT calculations (PBe1PBE, 6-311G* for C, H, O, and N and f-in-core pseudo-potential for europium) confirmed our assumption about the low-lying charge-transfer state corresponding to the interaction of the ligands in the coordination sphere of REE. According to the calculation, the energy of the lowest triplet is 632 nm. As shown by an analysis of the molecular orbitals, this state together with a series of close in energy transi-

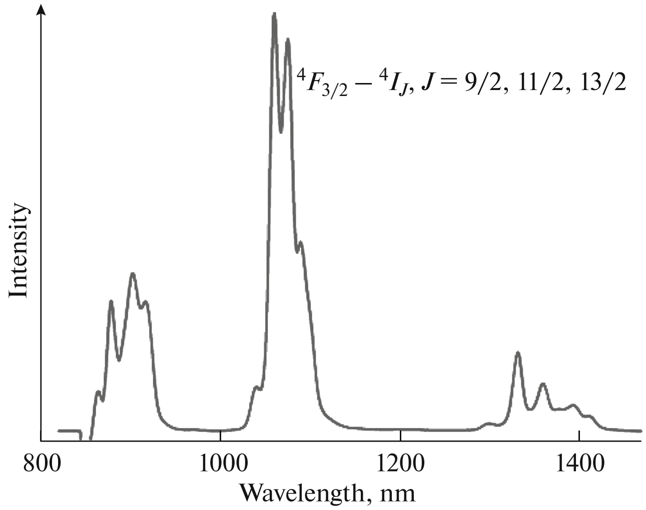


Fig. 3. Luminescence spectrum of compound **II** at 300 K.

tions corresponds to the transfer from one of the ligands to another ligand within the range characteristic of the dimers described above.

If the energy of the excited state is so low indeed, it is reasonable to assume that among the complexes considered only the neodymium complexes would exhibit luminescence. In fact, the resonance level of the Nd^{3+} ion is substantially lower (870 nm (11 500 cm^{-1})) than that of the Tb^{3+} ion (490 nm (20 410 cm^{-1})). Our preliminary studies distinctly showed no luminescence for the europium and terbium complexes, whereas characteristic luminescence in the near-IR spectral range was detected for the neodymium complex (Fig. 3).

Since the observed geometry of the complexes depends slightly on the metal nature, it can be assumed that this ligand system bearing low-lying states of intramolecular charge transfer will be potentially interesting for other REE demonstrating luminescence in the IR range, which will further be studied.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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