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Modulating the Near-Infrared Luminescence of Neodymium and Ytterbium Complexes with Tridentate Ligands Based on Benzoxazole-Substituted 8-Hydroxyquinolines

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An improved synthesis of 2-(2′-benzothiazole)- and 2-(2′-benzoxazole)-8-hydroxyquinoline ligands that combine a tridentate N,N,O-chelating unit for metal binding and extended chromophore for light harvesting is developed. The 2-(2′-benzoxazole)-8-hydroxyquinoline ligands form mononuclear nine-coordinate complexes with neodymium, [Nd(κ^3-ligand)$_3$], and an eight-coordinate complex with ytterbium, [Yb(κ^3-ligand)$_2$·(κ^1-ligand)·H_2O], as verified by crystallographic characterization of five complexes with four different ligands. The chemical stability of the complexes increases when the ligand contains 5,7-dihalo-8-hydroxyquinoline versus an 8-hydroxyquinoline group. The complexes feature a ligand-centered visible absorption band with a maximum at 508−527 nm and an intensity of (7.5−9.6) × 10^3 $M^{-1}\cdot cm^{-1}$. Upon excitation with UV and visible light within ligand absorption transitions, the complexes display characteristic lanthanide luminescence in the near-infrared at 850−1450 nm with quantum yields and lifetimes in the solid state at room temperature as high as 0.33% and 1.88 μs, respectively. The lanthanide luminescence in the complexes is enhanced upon halogenation of the 5,7- positions in the 8-hydroxyquinoline group and upon the addition of electron-donating substituents to the benzoxazole ring. Facile modification of chromophore units in 2-(2′-benzoxazole)-8-hydroxyquinoline ligands provides means for controlling the luminescence properties of their lanthanide complexes.

Introduction

Near-infrared (NIR) luminescent materials have potential application in biochemical analysis[1,2] and in optical telecommunication devices.[1,3,4] Certain fluorescent organic dyes,[5] metal complexes,[6] and phosphorescent d-transition metal complexes[7] emit in the NIR at ambient conditions. However, the former exhibit short luminescence lifetimes and small Stokes shifts, while the latter are susceptible to quenching by oxygen and display low quantum yields.

Lanthanide ions (Ln) that emit NIR luminescence from metal-centered f states combine a lack of sensitivity to oxygen quenching, large Stokes shifts upon excitation into

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10.1021/ic8020468 CCC: $40.75

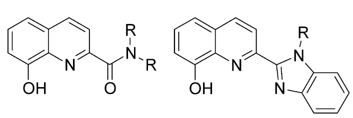
the ligand states, long excited-state lifetimes, and high quantum yields, especially in inorganic materials and in the solid state.[1,8] However, lanthanide ions do not absorb light efficiently, and in order to achieve bright emission, inorganic or organic "sensitizer" ligands are commonly used to absorb excitation light and transfer energy to the lanthanide.[1,8]

For example, recently reported inorganic polynuclear lanthanide clusters[3b−f] display very long NIR luminescence lifetimes, and their intrinsic quantum yields calculated from lifetime data can be as high as 41% for the Nd^{III} ion.[3f] However, these clusters often display air and moisture sensitivity, and it is difficult to predict a priori that a particular type of cluster would result from a particular combination of reagents. In addition, they lack strong ligand-centered absorption bands in the near UV and visible spectral ranges for efficient excitation of ligand-sensitized lanthanide luminescence.

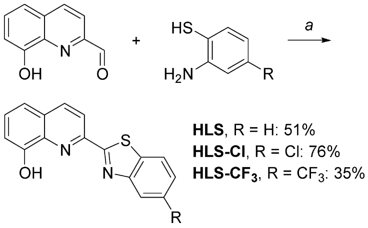
Efficient NIR emission of lanthanide ions is achieved in inorganic systems,[3] but switching to organic materials is problematic[9] due to the quenching of excited states of lanthanides by high-energy oscillators, for example, O−H, N−H, and C−H bonds.[1,8] Therefore, the design of NIR-emitting lanthanide complexes with organic ligands aims at avoiding O−H and N−H oscillators in the inner coordination sphere and replacing the ubiquitous C−H bonds with C−F bonds (or possibly C-D bonds), which possess less energetic vibrations.[10] For example, the organic complex of neodymium with a perfluorinated benzenethiolate ligand $[(DME)_2Nd(SC_6F_5)_3]$ displays an impressive 9% calculated intrinsic quantum yield.[3d] However, it lacks intense ligand-centered UV−vis absorption bands to sensitize lanthanide emission.

Among organic ligands, 8-hydroxyquinolines[11] are considered to be good candidates for the design of luminescent lanthanide materials because they form stable metal complexes and absorb light in the UV−vis spectral range.[12−15] Recently, we, and others, have developed tridentate 8-hydroxyquinoline ligands[16−18] which coordinate to lanthanide ions and sensitize their NIR emission (Chart 1). Herein, we investigate the ability of 2-(2′-benzothiazole)- and 2-(2′-benzoxazole)-8-hydroxyquinoline ligands[19] to form NIR-emissive lanthanide complexes. These ligands attracted our attention because they advantageously combine a monoanionic rigid tridentate N,N,O-chelating unit for metal binding and an extended chromophore for light harvesting (Schemes 1 and 2) and thus can potentially provide metal complexes with interesting optical properties. We report the first synthetic, structural, and photophysical study of their metal complexes as well as discuss the influence of halogen substituents on the NIR luminescence of their Nd^{III} and Yb^{III} chelates.

Chart 1. Tridentate 8-Hydroxyquinoline Ligands Known to Form Lanthanide Complexes[16−18]



Scheme 1. Synthesis and Structures of Benzothiazole-Substituted 8-Hydroxyquinolines[a]



[a] Reaction conditions: (a) DMSO, under N_2, 130 °C. 2-Aminothiophenol can be used in the form of hydrochloride salt.

Results and Discussion

Synthesis of Ligands and Precursors. Although the synthesis of ligands HLS and HL was recently reported,[19] we have developed a new, more convenient, synthetic route to these compounds.

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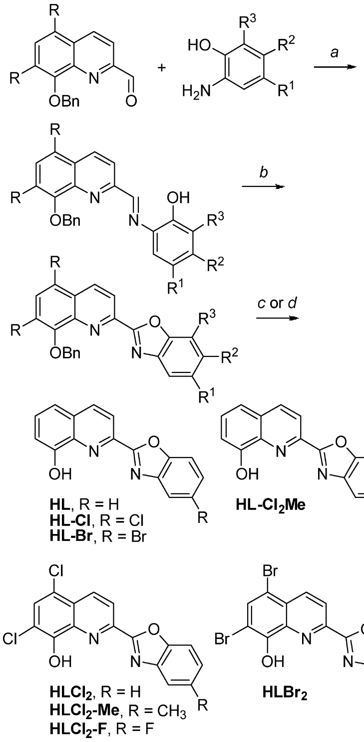
Scheme 2. Synthesis and Structures of Benzoxazole-Substituted 8-Hydroxyquinolines[a]

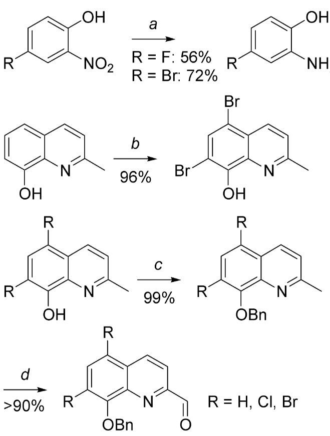


[a] Reaction conditions: (a) ethanol or dioxane/ethanol, under N_2, 80 °C; (b) DDQ, CH_2Cl_2, under N_2, rt 40 °C; (c) ammonium formate, Pd/C, THF, under N_2, 90 °C; (d) BBr_3, CH_2Cl_2, under N_2, rt.

Benzothiazole ligands were prepared by reacting 8-hydroxyquinoline-2-carboxaldehyde with 2-aminothiophenols (or their hydrochloride salts) in DMSO at 130 °C followed by chromatography and recrystallization from ethanol/CH_2Cl_2 (Scheme 1). This is a general synthesis of benzothiazole rings,[20] and it does not require protection of the hydroxyl group in 8-hydroxyquinoline. Its disadvantages are the limited commercial availability of 2-aminothiophenols, their malodorous nature, and their instability toward oxidation. The latter two problems can be partially resolved by using the hydrochloride salts of 2-aminothiophenols, which are less volatile and more resistant to oxidation.

Benzoxazole ligands were prepared in a three-step procedure (Scheme 2) starting from benzyl-protected 8-hydroxyquinoline precursors. In the first step, 8-benzyloxyquinoline-2-carboxaldehyde[21] was reacted with 2-aminophenol to give the Schiff base in quantitative yield. In the second step, the Schiff base was oxidized to benzoxazole with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[22] In the third step, the benzyl group was removed either with BBr_3[23] or by hydrogenation with ammonium formate/Pd/C.[24] Finally, the ligands were recrystallized from ethanol/CH_2Cl_2.

Scheme 3. Synthesis of Precursors[a]



[a] Reaction conditions: (a) $Na_2S_2O_4$, ethanol/H_2O, under N_2, 95 °C; (b) Br_2, $NaHCO_3$, methanol, under air, rt; (c) benzyl chloride, K_2CO_3, dry DMF, under N_2, 85 °C; (d) SeO_2, dioxane, under N_2, 80 °C.

Recrystallization played a crucial role in the purification of the ligands and their precursors because chromatography was often complicated by the coelution of inseparable impurities. The ligands had low solubility in ethanol and limited solubility in CH_2Cl_2, which complicated their extraction and chromatography but simplified their recrystallization. For instance, benzothiazole ligands were less soluble compared to benzoxazole ones, and solubility decreased significantly upon the introduction of 5,7-dichloro or 5,7-dibromo groups in 8-hydroxyquinoline. A further loss of solubility occurred when halogens were introduced to benzothiazole/benzoxazole rings, while the addition of a methyl group (as in ligand $HLCl_2$−Me) did not alleviate this problem.

Syntheses of precursors are shown in Scheme 3. Bromination of 2-methyl-8-hydroxyquinoline provided 5,7-dibromo-2-methyl-8-hydroxyquinoline in quantitative yield.[25] 2-Aminophenols were obtained by the reduction of 2-nitrophenols with $Na_2S_2O_4$ in ethanol/H_2O. 8-Benzyloxyquinoline-2-carboxaldehydes were prepared by the benzylation of 2-methyl-8-hydroxyquinolines with benzyl chloride/K_2CO_3/DMF, followed by oxidation with SeO_2 in dioxane.[21] All of these reactions were high-yielding, could be performed on a multigram scale, and did not require extensive purification of the products.

All organic compounds were identified by ^1H NMR spectroscopy (Figures S1−S28, Supporting Information); the ligands were also characterized by elemental analysis.

Synthesis of Lanthanide Complexes. This study focused on the synthesis and photophysical investigation of Nd^{III} and Yb^{III} complexes, which are among the most efficient NIR emitters within the lanthanide series.[1]

The lanthanide complexes were obtained as air- and moisture-stable intensely colored dark red solids from THF/water solutions starting from a stoichiometric 3:3:1 molar ratio of the ligand, base (NaOH or NEt_4OH), and

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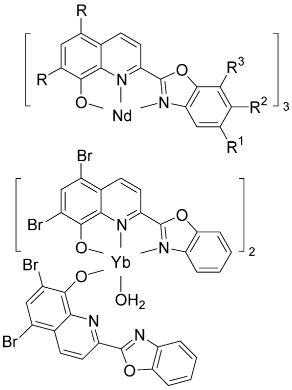
Chart 2. Structure of the New Lanthanide Complexes



$LnCl_3 \cdot nH_2O$ (Ln = Nd and Yb). The choice of NEt_4OH as a base was prompted by the insolubility of the sodium salts of some ligands in organic solvents or their mixtures with water. Besides, as a word of caution, we would recommend using noncoordinating organic bases, such as $(NEt_4)OH$, instead of NaOH, because the combination of NaOH with certain ligands and lanthanides results in the formation of mixed metal complexes containing both sodium and lanthanide, instead of tris complexes. The complexes were identified by CHN-elemental analysis, by chemical microanalysis with energy dispersive X-ray spectrometry (EDX) on a scanning electron microscope (SEM), and, whenever possible, by X-ray crystallography.

The reactions of Nd^{III} or Yb^{III} with benzothiazole ligands (HLS, HLS−Cl, and HLS−CF_3) have not produced the expected tris complexes for any of the metal and ligand combinations (the details are provided in the Supporting Information). As a result, the 2-(2′-benzothiazole)-8-hydroxyquinoline ligands and their complexes will not be discussed further in this work.

On the other hand, the reaction of Nd^{III} with benzoxazole ligands in every case produced tris complexes in good yield. The Nd^{III} ion is nine-coordinated by three κ^3 ligands in all of these complexes, as verified by crystal structure determinations (Chart 2, Figures 1 and 2).

In contrast, the reaction of Yb^{III} with the benzoxazole ligand $HLBr_2$ produced a “tris complex” containing an eight-coordinate Yb^{III} ion, according to crystal structure analysis (Chart 2, Figure 3). In this complex, one of the ligands is coordinated only via the phenolate oxygen, and a water molecule is bound to the metal ion. It should be stressed that it is difficult to distinguish between the $[Yb(\kappa^3\text{-}LBr_2)_3]$ and $[Yb(\kappa^3\text{-}LBr_2)_2 \cdot (\kappa^1\text{-}LBr_2)_3 \cdot H_2O]$ species using elemental analysis alone. The observed difference in the reactivity of benzoxazole ligands toward Nd^{III}/Yb^{III} ions may be explained by the smaller ionic radius of Yb^{III}, which prevents simultaneous κ^3-coordination of three rigid tridentate ligands and results in an eight-coordinate Yb^{III} center. As a consequence of the isolation of this hydrated eight-coordinate complex, no attempt to prepare tris complexes of Yb^{III} with other benzoxazole ligands was made.

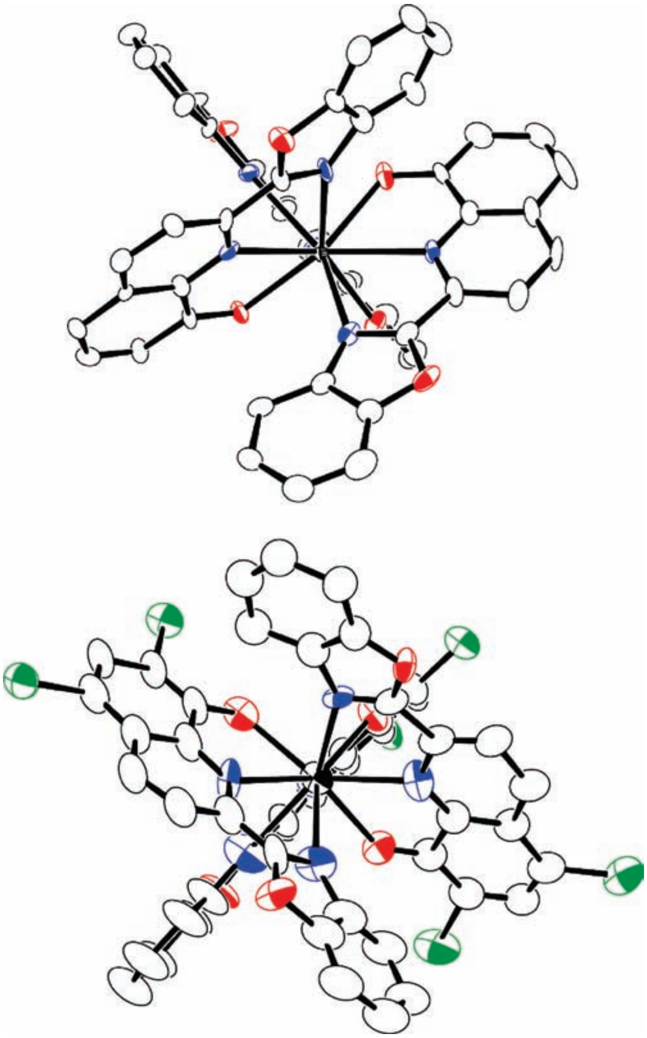


Figure 1. Structures of complexes $[Nd(L)_3]$ (top) and $[Nd(LBr_2)_3]$ (bottom) (50% probability ellipsoids, H atoms and cocrystallized solvent molecules omitted). Heteroatom color codes: O, red; N, blue; Br, green; Nd, black. Only one of the two independent molecules is shown for $[Nd(L)_3]$ (**1**). The plane containing the N atoms of the quinoline rings that occupy the capping positions of the idealized tricapped trigonal prismatic coordination polyhedron is horizontal and perpendicular to the plane of the paper.

X-Ray Structural Studies. The crystal and molecular structures of the Nd^{III} complexes with ligands HL, $HLCl_2$, $HLCl_2$−Me, and $HLBr_2$ and of the Yb^{III} complex with ligand $HLBr_2$ were determined by X-ray diffraction.

The Nd^{III} complexes feature the following structural properties (Figures 1 and 2, Table 1): (i) The Nd^{III} ion is nine-coordinated by three κ^3 ligands arranged in an “up−up−down” fashion around the metal center. (ii) The coordination environment around Nd^{III} can be described as a distorted tricapped trigonal prism,[26] with the N atoms of quinoline (quin) rings in capping positions (these N atoms lay in-plane with the Nd atom). (iii) The introduction of an electron donating and bulky methyl group in the benzoxazole (bzox) ring results in a shortening of the Nd−O bond because the O atom becomes more basic and in a lengthening of

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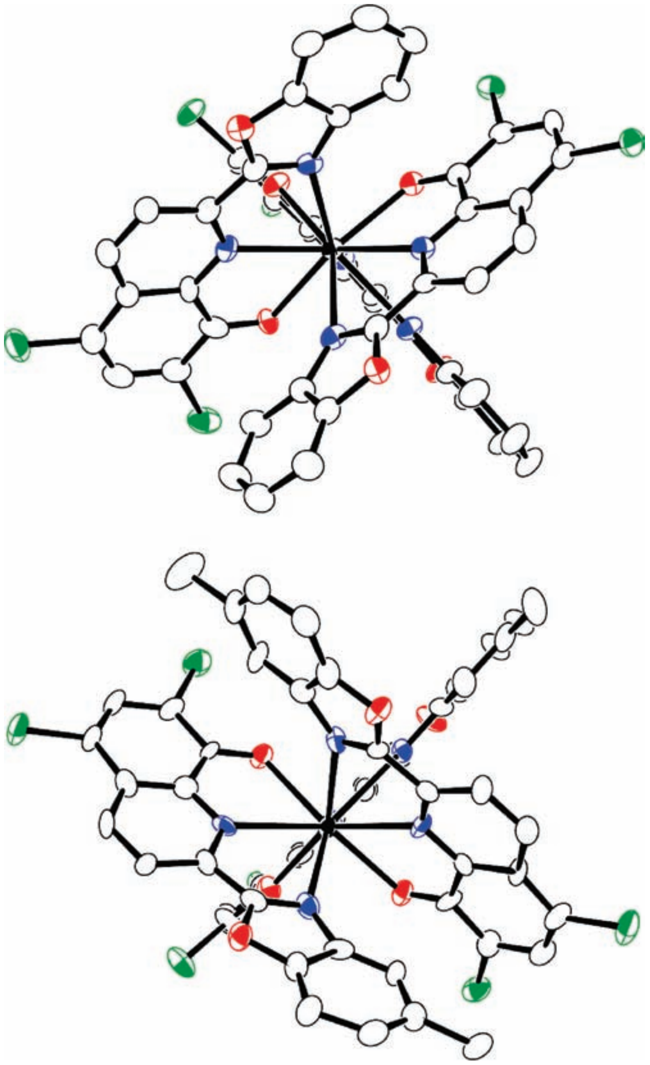

Figure 2. Structures of complexes [Nd(LCl_2)$_3$] (top) and [Nd(LCl_2-Me)$_3$] (bottom) (50% probability ellipsoids, H atoms and cocrystallized solvent molecules omitted). Heteroatom color codes: O, red; N, blue; Cl, green; Nd, black. Only one of the two independent molecules is shown for [Nd(LCl_2)$_3$] (**1**). The plane containing the N atoms of the quinoline rings that occupy the capping positions of the idealized tricapped trigonal prismatic coordination polyhedron is horizontal and perpendicular to the plane of the paper.

the Nd−N bonds, the latter probably resulting from unfavorable steric effects; compare the complexes with $HLCl_2$ and $HLCl_2$−Me. (iv) The introduction of electron-withdrawing 5,7-dihalo substituents on 8-hydroxyquinoline leads to an elongation of Nd−O bonds because the O atom becomes less basic, while no obvious trend is observed for Nd−N bonds; compare the complexes with HL, $HLCl_2$, and $HLBr_2$.

The Yb^{III} ion in the complex [Yb(κ^3-LBr_2)$_2$•(κ^1LBr_2)$_3$•H_2O] is eight-coordinate: two of the ligands are bound to the metal ion in a tridentate fashion, while the third ligand is bound only via the phenolate oxygen (Figure 3). In addition, the metal center is coordinated to a water molecule which, at the same time, is most likely hydrogen-bonded to the N atoms of the κ^1 ligand. The hydrogen atoms of the water molecule could not be located, but the corresponding N•••O distances are <3 Å. As a result, a water molecule is "squeezed" between the Yb^{III} ion and the κ^1 ligand. It appears that the κ^3-coordination of the benzoxazole ligands comes at a cost of longer metal−ligand bonds compared to κ^1-coordination. In fact, the Nd−O bond is shorter by 0.15 Å for the κ^1 ligand compared to that for the κ^3 ligand (Table 1); the rigidity of the benzoxazole ligands may be partly responsible for this effect. The coordination environment around Yb^{III} can be described as a distorted trigonal dodecahedron with D_{2d} symmetry, the pairs of N atoms spanning its *a* edges.[26]

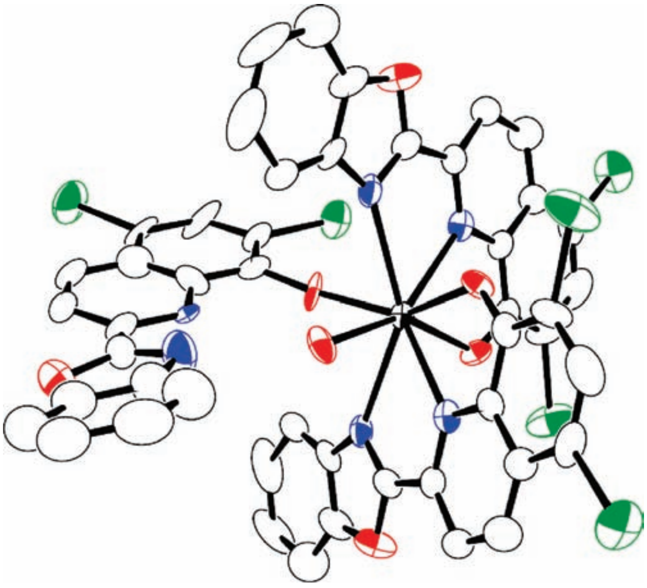

Figure 3. Structure of complex [Yb(κ^3-LBr_2)$_2$•(κ^1-LBr_2)$_3$•H_2O] (50% probability ellipsoids, H atoms and cocrystallized solvent molecules omitted). Heteroatom color codes: O, red; N, blue; Br, green; Yb, black. The molecule lies on a symmetry site (2-fold axis along *c*) which generates from the asymmetric unit (half of the molecule) the missing ligand(s), one being disordered, as well as the bound water molecule. The κ^1 ligand and H_2O molecule are disordered over two positions related by symmetry, and only one of these two is shown.

The common structural features for Nd^{III} and Yb^{III} complexes can be summarized as follows: (i) The ligands within one complex are nearly planar, with dihedral angles between quinoline and benzoxazole groups < 14°. (ii) The nonplanarity of the ligands arises both from the rotation and the "folding" of the quinoline and benzoxazole groups, with respect to each other, along and across the connecting C−C bond. (iii) The lanthanide ion is bound to a N atom[27] of the benzoxazole ring and not to an O atom.[28] (iv) The three ligands are not equally strongly bonded to the lanthanide, as reflected in the different respective sets of bond lengths. (v) The lanthanide ion is preferentially bound to the 8-hydroxyquinoline, while bonding to the benzoxazole is relatively weak, which is reflected in longer Ln−N(bzox) bond lengths and their wider variation in range, for example, in the Nd^{III} complexes: Nd−O, 2.369−2.449 Å (Δ = 0.080Å); Nd−N(quin), 2.574−2.677 Å (Δ = 0.103 Å); Nd−N(bzox), 2.702−2.872 (Δ = 0.170 Å) (Table 1). (vi) The metal−metal distances in the complexes are >8.7 Å,

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Table 1. Selected Structural Parameters for the Lanthanide Complexes[a]

	bond lengths (Å)[b]			angle (deg)	
complex	Ln−O	Ln−N (quin)	Ln−N (bzox)	bzox−quin[c]	Ln−Ln (Å)[d]
$[Nd(L)_3]$ (**1**)[e]	2.374(7)	2.584(9)	2.738(9)	7.22	8.779
	2.375(8)	2.594(9)	2.720(9)	3.50	
	2.402(8)	2.677(9)	2.872(9)	9.98	
	2.384	**2.618**	**2.777**	**6.90**	
$[Nd(L)_3]$ (**2**)[e]	2.380(8)	2.574(10)	2.702(9)	4.20	
	2.395(8)	2.676(10)	2.862(10)	11.76	
	2.412(9)	2.647(9)	2.760(10)	2.74	
	2.396	**2.632**	**2.775**	**6.23**	
$[Nd(LCl_2)_3]$ (**1**)[e]	2.396(6)	2.600(7)	2.754(7)	3.35	9.733
	2.398(6)	2.630(7)	2.799(7)	7.55	
	2.427(6)	2.650(7)	2.819(7)	9.81	
	2.407	**2.627**	**2.791**	**6.90**	
$[Nd(LCl_2)_3]$ (**2**)[e]	2.382(6)	2.591(7)	2.724(8)	5.32	
	2.423(6)	2.609(8)	2.794(7)	9.06	
	2.429(7)	2.662(7)	2.810(8)	12.55	
	2.411	**2.621**	**2.776**	**8.98**	
$[Nd(LCl_2\text{-}Me)_3]$	2.369(7)	2.613(9)	2.790(8)	4.37	9.467
	2.419(7)	2.655(9)	2.837(9)	12.40	
	2.424(7)	2.664(8)	2.782(8)	13.62	
	2.404	**2.644**	**2.803**	**10.13**	
$[Nd(LBr_2)_3]$	2.389(12)	2.614(14)	2.71(2)	4.68	9.608
	2.403(14)	2.661(17)	2.794(15)	7.83	
	2.449(15)	2.660(12)	2.774(17)	13.22	
	2.414	**2.645**	**2.759**	**8.58**	
$[Yb(LBr_2)_3 \cdot H_2O]$[f]	2.244(6)	2.426(7)	2.598(7)	6.68	10.495
	2.244(6)	2.426(7)	2.598(7)	6.68	
	2.094(11)				
	2.194	**2.426**	**2.598**	**6.68**	

[a] Each line in the table corresponds to one and the same ligand in the complex. Numbers in bold are data averaged over the three ligands. [b] N(quin) and N(bzox) are nitrogen atoms of quinoline and benzoxazole rings, respectively. [c] Dihedral angle between planes of quinoline and benzoxazole groups. The planes were defined by C, N, and O atoms of core rings, that is, 10 and 9 atoms for quinoline and benzoxazole rings, respectively. [d] The shortest metal−metal distance in the structure. [e] Two independent molecules are present in the unit cell of these complexes. [f] The molecule lies on a symmetry site (2-fold axis along *c*) which generates from the asymmetric unit (half of the molecule) the missing ligand(s), one being disordered, as well as the bound water molecule. Bond length Yb−OH_2 is 2.289(14) Å. Dihedral angle bzox−quin for κ^1 ligand is 19.27°.

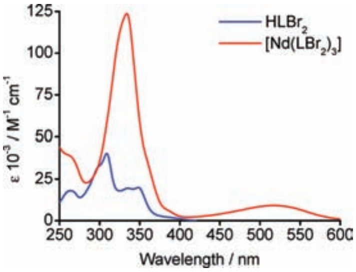

Figure 4. Absorption spectra of the ligand $HLBr_2$ (1.77×10^{-4} M) and its Nd^{III} complex (3.85×10^{-5} M) in CH_2Cl_2 solution. Absorption spectra for other ligands and complexes are provided in the Supporting Information.

which is likely to prevent significant interaction between metal centers.

Electronic Spectroscopy. The UV−vis absorption spectra of the ligands and their complexes, recorded in CH_2Cl_2 solution at room temperature, are depicted in Figure 4 and Figures S29−S37 (Supporting Information), and the main spectral features are summarized in Table 2.

The spectra of the ligands display several absorption bands in the range 250−400 nm. Upon deprotonation of the ligand and formation of a lanthanide complex, a new absorption band appears in the visible range with a maximum at 508−527 nm for the benzoxazole complexes, which determines their intense dark red color. The maximum of this transition is red-shifted by 7−11 nm when an electron-withdrawing group (F, Cl, Br) is present on the benzoxazole ring or in the 5,7- positions of the quinoline group. These changes point to an electronic communication between the quinoline and benzoxazole units within the ligand. We assign this band to an intraligand charge transfer transition (ILCT) wherein the phenolate and {quinoline + benzoxazole} moieties serve as an electron donor and acceptor, respectively. The molar absorption coefficient of this transition is $(2.5-3.2) \times 10^3$ $M^{-1}cm^{-1}$ per ligand and is typical for a metal-coordinated 8-hydroxyquinolate chromophore.[29]

Table 2. Absorption Spectra of the Ligands and Complexes[a]

compound	λ_{max}/nm (10^{-3} ε/M^{-1} cm^{-1})
HLS	350 (19), 337 (18), 301 (31), 259 (18)
HLS−Cl	351 (18), 339 (17), 300 (32), 290 (29), 258 (19)
$HLS-CF_3$	347 (19), 332 (17), 298 (32)
HL	343 (19), 332 (18), 301 (33), 255 (17)
HL−Cl	344 (21), 332 (19), 298 (27), 284 (27)
HL−Br	344 (22), 332 (20), 298 (27), 285 (28)
$HL-Cl_2Me \cdot (C_2H_5OH)_{0.5}$	346 (23), 335 (22), 301 (30), 260 (23)
$HLCl_2 \cdot (C_2H_5OH \cdot H_2O)_{0.5}$	347 (21), 335 (20), 308 (40), 260 (19)
$HLCl_2-Me \cdot C_2H_5OH$	350 (21), 308 (30), 261 (19)
$HLCl_2-F \cdot C_2H_5OH$	348 (19), 334 (19), 305 (32), 269 (18)
$HLBr_2 \cdot (C_2H_5OH \cdot H_2O)_{0.33}$	348 (20), 335 (19), 309 (40), 264 (18)
$[Nd(L)_3]$	508 (9.1), 326 (105)
$[Nd(L-Cl)_3]$	517 (9.6), 329 (104)
$[Nd(L-Br)_3]$	515 (9.3), 330 (101)
$[Nd(L-Cl_2Me)_3] \cdot 2H_2O$	509 (7.5), 330 (85)
$[Nd(LCl_2)_3]$	519 (8.7), 333 (118)
$[Nd(LCl_2-Me)_3]$	517 (8.8), 337 (109)
$[Nd(LCl_2-F)_3]$	527 (8.4), 334 (117)
$[Nd(LBr_2)_3]$	519 (9.1), 334 (124)
$[Yb(LBr_2)_3 \cdot H_2O]$	515 (8.4), 333 (114)

[a] Spectra were recorded in CH_2Cl_2 solution at room temperature in the spectral range 250−800 nm. Estimated errors are ±1 nm for λ_{max} and ±5% for ε. Concentrations of the samples were in the range $(1.59-3.09) \times 10^{-4}$ M for the ligands and $(3.85-5.67) \times 10^{-5}$ M for the complexes.

The absorption spectra of solutions of the Nd^{III} and Yb^{III} complexes with ligand $HLBr_2$ are similar with respect to ligand-centered transitions (Table 2; Figure S37, Supporting Information). This result is unexpected, considering that these complexes have different solid state structures, and it may indicate that they are fluxional and dissociate in solution.

Stability of the Complexes in Solution. The long-term stability of the complexes in dilute CH_2Cl_2 solution at $(3.85-5.67) \times 10^{-5}$ M was monitored by electronic spectroscopy. These solutions were neither dried nor degassed and were kept under air in closed vials stored in the dark. After six weeks of storage, the complexes with 2-(2′-benzoxazole)-5,7-*H*-8-hydroxyquinolines underwent partial decomposition (Figures S38−S39, Supporting Information), while complexes with 2-(2′-benzoxazole)-5,7-*dihalo*-8-hydroxyquinolines remained unchanged (Figures S40−S44, Supporting Information). Decomposition is revealed by bleaching of the visible absorption band and a change in the envelope of the UV band. It probably proceeds via hydrolysis of the complex by traces of water present in the solvent. These results

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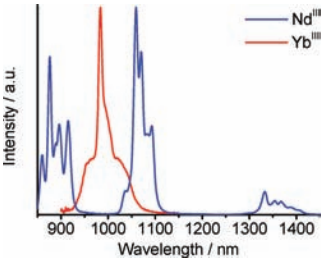

Figure 5. Corrected and normalized luminescence spectra of the Nd^{III} and Yb^{III} complexes with ligand $HLBr_2$ in the solid state at room temperature. Emission spectra were independent of excitation wavelength; emission slit was 5 nm. Emission spectra for other Nd^{III} complexes are similar and are provided in the Supporting Information.

show that complexes with 5,7-dihalo-8-hydroxyquinoline ligands are more resistant to hydrolysis compared to their nonsubstituted analogues, which may be explained by the increased acidity of the halogenated ligands.

Near-Infrared Luminescence of the Complexes. Because of the low solubility of the complexes in noncoordinating solvents and their possible dissociation, all photophysical experiments were conducted in the solid state only.

The Nd^{III} and Yb^{III} ions are known to emit luminescence from metal-centered f states.[1] For Nd^{III}, the emitting $^4F_{3/2}$ state is situated at 11 460 cm^{-1},[30] while for the Yb^{III}, the fluorescent $^2F_{5/2}$ state lies at 10 250 cm^{-1}.[31] The energy gap between the emitting level and the more energetic sublevel of the ground state is smaller in Nd^{III} compared to Yb^{III}, that is, 5300 cm^{-1} versus 10 250 cm^{-1}.[30,31] As a result, the excited state of Nd^{III} ion is more sensitive to quenching by proximate and distant O−H, N−H, and C−H oscillators.[1]

Excitation of the complexes with UV and visible light within ligand-centered absorption transitions results in the characteristic linelike luminescence of Nd^{III} at 850−1450 nm and Yb^{III} at 900−1100 nm (Figure 5 and Figures S45−S51, Supporting Information). The absolute quantum yield of lanthanide luminescence upon ligand excitation (Q_L^{Ln} in Table 3) is independent of the excitation wavelength (350 or 508−527 nm) within experimental error, which suggests that excitation and absorption spectra of the complexes match each other. The presence of an intense ligand-centered visible absorption band (ILCT) in these complexes allows for convenient excitation of the near-infrared lanthanide luminescence with visible light of wavelengths up to 600 nm (Figure 4 and Figures S29−S37, Supporting Information). The luminescence decay of the complexes (τ) is a single exponential function in every case, indicating the presence of only one emitting Ln^{III} center in the solid state (Table 3).

The photophysical data are in line with the formulation of the Nd^{III} and Yb^{III} complexes as [Nd(κ^3-ligand)$_3$] and [Yb(κ^3-ligand)$_2$·(κ^1-ligand)·H_2O] species, respectively, as ascertained by X-ray diffraction. For instance, the luminescence quantum yield and lifetime of the Nd^{III} complexes at room temperature are in the ranges 0.04−0.33% and 0.33−1.88 μs, respectively, and are typical of anhydrous Nd^{III} species (Table 3).[17] In the case of the Yb^{III} complex, the low values of $Q_L^{Yb} = 0.07\%$ and $\tau = 0.82$ μs indeed reflect that a water molecule is bound to the metal ion; for an anhydrous Yb^{III} complex, one would expect $Q_L^{Yb} > 0.5\%$ and $\tau > 5$ μs.[32]

Table 3. Luminescence Properties of Nd^{III} and Yb^{III} Complexes in the Solid State at Room Temperature

complex	$\tau/\mu s^a$	$Q_L^{Ln}/\%^b$ UV	$Q_L^{Ln}/\%^b$ VIS	$Q_{Ln}^{Ln}/\%^c$	$\eta_{sens}/\%^c$
$[Nd(L)_3]$	0.87(4)	0.15	0.15	0.32	47
$[Nd(LCl_2)_3]$	1.26(3)	0.31	0.33	0.47	71
$[Nd(LBr_2)_3]$	1.82(2)	0.33	0.29	0.67	43
$[Nd(LCl_2-F)_3]$	1.22(1)	0.16	0.13	0.45	29
$[Nd(LCl_2-Me)_3]$	1.88(1)	0.30	0.26	0.70	37
$[Nd(L-Cl)_3]$	0.47(1)	0.10	0.11	0.17	63
$[Nd(L-Br)_3]$	0.51(2)	0.09	0.10	0.19	53
$[Nd(L-Cl_2Me)_3]\cdot 2H_2O$	0.33(1)	0.03	0.04	0.12	33
$[Yb(LBr_2)_3\cdot H_2O]$	0.82(1)	0.09	0.07	0.07	100

[a] $\lambda_{exc} = 355$ nm for τ. [b] Q_L^{Ln} were measured at two excitation wavelengths: at 350 nm for Q_L^{Ln}(UV) and at the maximum of the visible absorption band (508−527 nm, Table 2) of the complex for Q_L^{Ln}(VIS). Estimated error on Q_L^{Ln} is ± 15%. [c] These values were calculated from the equations $Q_L^{Ln}(VIS) = \eta_{sens} \times Q_{Ln}^{Ln}$ and $Q_{Ln}^{Ln} = \tau/\tau_{rad}$ and assuming τ_{rad} (Nd) = 270 μs[33] and τ_{rad} (Yb) = 1.21 ms,[34] see text. The errors on Q_{Ln}^{Ln} and η_{sens} are comparable to the uncertainties on τ and Q_L^{Ln}.

The quantum yield of lanthanide luminescence upon ligand excitation can be expressed as $Q_L^{Ln} = \eta_{sens} \times Q_{Ln}^{Ln}$, where η_{sens} is the efficiency with which the ligand sensitizes the metal-centered luminescence and Q_{Ln}^{Ln} is the intrinsic quantum yield of the lanthanide ion. The latter can be estimated from the equation $Q_{Ln}^{Ln} = \tau/\tau_{rad}$ by taking the literature values of radiative lifetimes τ_{rad}(Nd) = 270 μs[33] and τ_{rad}(Yb) = 1.21 ms[34] (reported for Nd^{III}/Y_2O_3 and $[Yb(DTPA)]^{2-}$, respectively, where DTPA stands for diethylenetriaminepentaacetate). The calculated values of η_{sens} and Q_{Ln}^{Ln} listed in Table 3 rely on the assumption that τ_{rad} is constant and applicable for the entire set of complexes. However, τ_{rad} is known to depend on the identity of the compound,[1] and thus, these estimates should be viewed with caution, especially when it comes to absolute values. However, relative values can be discussed relatively safely because one does not expect τ_{rad} to vary much in the investigated Nd^{III} compounds since the composition of their inner coordination sphere is very similar.

The following trends are observed in the photophysical properties of Nd^{III} complexes (Table 3):

(i) Halogenation of the 8-hydroxyquinoline moiety in positions 5 and 7 results in a significant increase of the Nd^{III} luminescence because of the removal of two proximate quenching C−H bonds; compare complexes with HL, $HLCl_2$, and $HLBr_2$. Thus, complexes with 5,7-dihalogenated ligands demonstrate reduced nonradiative deactivation processes of the $^4F_{3/2}$ state of Nd^{III}, reflected in the longer luminescence lifetimes, and higher intrinsic quantum yields, Q_{Nd}^{Nd} (Table 3). In particular, comparison of $[Nd(L)_3]$ and $[Nd(LBr_2)_3]$ complexes assuming that the only difference in their nonradiative deactivation is the quenching contribution by two

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C−H bonds at positions 5 and 7 (i.e., assuming that C−Br oscillators do not quench) leads to an estimate of the quenching rate of Nd^{III} by these C−H bonds as being 6.0×10^5 s^{-1} per complex molecule (i.e., per six C−H bonds):

$$1/\tau = k^{\mathrm{rad}} + \sum k_{\mathrm{CH}}^{\mathrm{nr}} + \sum k_{\mathrm{other}}^{\mathrm{nr}} \qquad (1)$$

$$\Delta(1/\tau) = \{k_{\mathrm{CH(5)}}^{\mathrm{nr}} + k_{\mathrm{CH(7)}}^{\mathrm{nr}}\} \qquad (2)$$

It should be noted that a similar effect was previously reported for lanthanide complexes with 8-hydroxyquinolines.[14,16a]

(ii) A priori, it was expected that substitution or removal of the C−H bond(s) in the benzoxazole ring would improve Nd^{III} emission.[1,17] However, the replacement of hydrogen atoms with an electron-*withdrawing* halogen group (F, Cl, Br) results in a decrease in Nd^{III} luminescence. It is likely that an electron-withdrawing halogen group decreases the electron density at the coordinating N atom of the benzoxazole ring and thus weakens the metal−ligand bond, which, in turn, promotes nonradiative deactivation in the complex. In the case of substitution with a F group (cf. complexes with $HLCl_2$ and $HLCl_2$−F), this is reflected in the lower value of η_{sens}. In the case of a Cl or Br group (cf. complexes with HL, HL−Cl, and HL−Br), this is reflected in lower values of $Q_{\mathrm{Ln}}^{\mathrm{Ln}}$, τ, and $Q_{\mathrm{L}}^{\mathrm{Ln}}$, which points to an enhanced deactivation of the $^4F_{3/2}$ state of Nd^{III}. In line with the explanation provided above, the addition of an electron-*donating* methyl group to the benzoxazole ring has an overall beneficial effect on Nd^{III} luminescence, resulting in a longer excited-state lifetime and higher $Q_{\mathrm{Nd}}^{\mathrm{Nd}}$ (cf. complexes with $HLCl_2$ and $HLCl_2$−Me).

The photophysical properties of complex $[Nd(L\text{-}Cl_2Me)_3]\cdot 2H_2O$ can be rationalized by taking into account the detrimental effect of two electron-withdrawing Cl groups leading to a shorter lifetime, somewhat compensated by the beneficial effect of the electron-donating methyl group (see arguments above). However, the presence of two interstitial water molecules in this complex, which can potentially quench the Nd^{III} luminescence, even when present in second coordination sphere, may also play a role. For example, these water molecules may be engaged in hydrogen bonding with phenolate oxygens of the 8-hydroxyquinoline moiety[17] and in that way may be situated close enough to the Nd^{III} ion to quench its excited state.

The addition of Cl ("light" atom) or Br ("heavy" atom) to the benzoxazole ring or 8-hydroxyquinoline group results in a change of sensitization efficiency η_{sens} in the Nd^{III} complexes in the order HL−Cl > HL−Br ≈ HL and $HLCl_2$ > HL ≈ $HLBr_2$ (Table 3). Thus, there is no apparent "heavy atom" effect[14] operating in these complexes resulting from the grafting of the Br group; if this effect exists, it is likely to be counterbalanced by electronic effects consecutive to the ligand modification. On the other hand, the removal of two quenching C−H bonds in the 8-hydroxyquionoline group exerts a sizable effect on the overall luminescence quantum yield of lanthanide center $Q_{\mathrm{L}}^{\mathrm{Ln}}$, which almost doubles in the case of ligands $HLCl_2$ and $HLBr_2$ compared to ligand HL (Table 3), as was observed previously with various 8-quinolinate complexes of lanthanides.[14,16a]

It is of interest to note that Nd^{III} complexes with $HLCl_2$−Me and $HLBr_2$ have nearly identical photophysical parameters (Table 3), which demonstrates that similar results can be achieved by modification either in one or in both of the constituent chromophores of the ligand.

The calculated sensitization efficiency η_{sens} in Nd^{III} complexes with benzoxazole ligands is reasonable, although not optimum, 29−71%, while for the Yb^{III} complex, it appears to be quantitative (Table 3). This difference might be related to the fact that the excited state of Yb^{III} can be populated by a reversible electron-transfer from the ligand,[1,2a] which is not possible for the Nd^{III} ion.

Conclusions

Benzoxazole-substituted 8-hydroxyquinoline ligands form mononuclear nine-coordinate complexes with neodymium, $[Nd(\kappa^3\text{-ligand})_3]$, and an eight-coordinate complex with ytterbium, $[Yb(\kappa^3\text{-ligand})_2\cdot(\kappa^1\text{-ligand})\cdot H_2O]$, and sensitize their near-infrared luminescence upon excitation with UV or visible light with a reasonably good efficiency compared to other organic ligands.[1] Moreover, these tridentate ligands saturate the coordination sphere of the large Nd^{III} ion in the tris complexes and provide a wide variety of means to modulate the NIR luminescence of their lanthanide complexes; for example, enhanced lanthanide emission is achieved by halogenation of the 5,7- positions in 8-hydroxyquinoline or by the addition of electron-donating substituents to benzoxazole. The well-known affinity of 8-hydroxyquinolines toward various chemical elements[11,29,35] makes these ligands of interest in the design of functional complexes and materials incorporating "hard" and "soft" cations.

Experimental Section

General Methods, Equipment, and Chemicals Used. Elemental analyses were performed by Dr. E. Solari, Service for Elemental Analysis, Institute of Chemical and Chemical Engineering Sciences (EPFL). Absorption spectra were measured on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer; ^1H NMR spectra (presented as δ in ppm and J in Hz) were recorded on a Bruker Avance DRX 400 MHz spectrometer. Luminescence emission spectra were measured on a Fluorolog FL 3-22 spectrometer from Horiba-Jobin Yvon-Spex equipped for both visible and NIR measurements. Quantum yield data for solid samples were determined on the same instrument, through an absolute method[36] using a home-modified integrating sphere. The estimated error on values of quantum yields

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Table 4. Crystal Data and Structure Refinement

compound	$[Nd(L)_3]$	$[Nd(LCl_2)_3]$	$[Nd(LCl_2{-}Me)_3]$	$[Nd(LBr_2)_3]$	$[Yb(LBr_2)_3 \cdot H_2O]$
empirical formula	$C_{48}H_{27}N_6NdO_6$	$C_{51}H_{26}Cl_8N_7NdO_6$	$C_{51}H_{27}Cl_6N_6NdO_6$	$C_{48}H_{21}Br_6N_6NdO_6$	$C_{48}H_{23}Br_6N_6O_7Yb$
fw	928.00	1260.63	1176.73	1401.41	1448.22
temp [K]	100(2)	100(2)	100(2)	100(2)	140(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$	$C2/c$	$Fdd2$
unit cell dimensions	$a = 12.9950(15)$ Å $b = 17.385(3)$ Å $c = 21.426(4)$ Å $\alpha = 66.996(13)°$ $\beta = 75.498(12)°$ $\gamma = 71.783(12)°$	$a = 18.136(2)$ Å $b = 23.572(4)$ Å $c = 24.642(5)$ Å $\alpha = 90°$ $\beta = 103.471(12)°$ $\gamma = 90°$	$a = 27.779(9)$ Å $b = 24.452(7)$ Å $c = 18.562(8)$ Å $\alpha = 90°$ $\beta = 116.18(3)°$ $\gamma = 90°$	$a = 27.58(3)$ Å $b = 23.90(3)$ Å $c = 18.20(2)$ Å $\alpha = 90°$ $\beta = 115.59(17)°$ $\gamma = 90°$	$a = 28.8111(15)$ Å $b = 12.8615(6)$ Å $c = 27.6934(15)$ Å $\alpha = 90°$ $\beta = 90°$ $\gamma = 90°$
vol [Å]^3	4186.5(12)	10245(3)	11315(7)	10819(21)	10261.9(9)
Z	4	8	8	8	8
ρ (calcd) [Mg/m^3]	1.472	1.635	1.382	1.721	1.875
μ [mm^{-1}]	1.298	1.488	1.250	5.441	6.549
F(000)	1860	5000	4680	5352	5512
cryst size [mm^3]	0.34 × 0.20 × 0.10	0.64 × 0.17 × 0.10	0.53 × 0.08 × 0.07	0.51 × 0.19 × 0.06	0.30 × 0.20 × 0.15
θ range	3.32−26.37°	3.33−27.50°	3.33−23.32°	3.39−23.06°	2.75−26.37°
index ranges	$-16 \le h \le 16$ $-21 \le k \le 21$ $-26 \le l \le 26$	$-23 \le h \le 22$ $0 \le k \le 30$ $0 \le l \le 32$	$-30 \le h \le 30$ $-27 \le k \le 27$ $-20 \le l \le 20$	$-30 \le h \le 27$ $0 \le k \le 26$ $0 \le l \le 19$	$-35 \le h \le 35$ $-16 \le k \le 16$ $-34 \le l \le 33$
reflns collected	16807	23493	67125	7532	5177
independent reflns	16807 [R(int) = 0.0000]	23493 [R(int) = 0.0000]	8148 [R(int) = 0.1672]	7532 [R(int) = 0.0000]	5177 [R(int) = 0.0000]
completeness to θ	26.37° − 98.1%	27.50° − 99.8%	23.32° − 99.4%	23.06° − 99.2%	26.37° − 99.9%
max/min transm	1.0000/0.5553	1.0000/0.5498	1.0000/0.4767	1.0000/0.3427	1.00000/0.76586
data/restraints/params	16807/6/1101	23493/0/1315	8148/0/631	7532/288/604	5177/147/378
GOF on F^2	1.117	1.097	1.086	1.056	1.036
final R indices [$I > 2\sigma(I)$]	R1 = 0.0903 wR2 = 0.2027	R1 = 0.0914 wR2 = 0.2305	R1 = 0.0777 wR2 = 0.1594	R1 = 0.0963 wR2 = 0.2469	R1 = 0.0466 wR2 = 0.1084
R indices (all data)	R1 = 0.1146 wR2 = 0.2120	R1 = 0.1319 wR2 = 0.2568	R1 = 0.1364 wR2 = 0.1856	R1 = 0.1846 wR2 = 0.2875	R1 = 0.0583 wR2 = 0.1116
absolute structure param					0.026(18)
largest diff. peak/hole [e/Å^3]	3.587/−2.448	10.651/−2.008	1.060/−0.950	2.871/−1.906	1.894/−0.985

[a] Data in common: wavelength, 0.71073 Å; refinement method, full-matrix least-squares on F^2; abs correction, semiempirical from equivalents.

is ±15%. Luminescence lifetimes were measured with a previously described instrumental setup.[17] All luminescence spectra were corrected for the instrumental function.

Spectroscopic studies were conducted in solutions in CH_2Cl_2 (Fisher Scientific, analytical reagent grade) freshly prepared before each experiment or in the solid state using optical cells of 2-mm path length and quartz capillaries with an internal diameter of 2 mm. All spectroscopic measurements were conducted with the samples of Ln^{III} complexes obtained directly from the synthesis and used without further purification.

Absorption spectra were recorded at room temperature in the spectral range 250−800 nm. Estimated errors are ±1 nm for λ_{max} and ±5% for ε. The concentration of the samples was in the range $(1.59-3.09) \times 10^{-4}$ M for the ligands, $(3.85-5.67) \times 10^{-5}$ M for the Nd^{III} complexes, and 4.39×10^{-5} M for the Yb^{III} complex.

The chemical microanalyses by EDX were performed on an FEI XL30 SFEG SEM with an EDX detector from Oxford Instrument. It was equipped with a standard Everhart-Thornley secondary electron detector and a Schottky field emission gun. Samples were deposited and analyzed on an undoped silicon wafer cleaned with an ultrasonic bath of acetone, ethanol, and deionizer water. To avoid a charging effect, all samples were coated with 17 nm of carbon. These experiments were performed at the Interdisciplinary Centre for Electron Microscopy (CIME EPFL).

Chemicals obtained from commercial suppliers were used without further purification: $LnCl_3 \cdot 6H_2O$ (99.9%, Aldrich), 8-hydroxyquinoline-2-carboxaldehyde (Acros), DMF (absolute, puriss > 99.5%, over mol. sieve, Fluka), and DMSO (Acros, 99.7%, extra dry, over mol. sieve, water < 50 ppm). Chromatography was performed on a column with an internal diameter of 30 mm using silica gel 60 for preparative chromatography (Fluka, catalogue number 60752). The progress of reactions and elution of products was followed on a TLC plate (silica gel 60 F_{254} on aluminum sheets, Merck).

X-Ray Crystallography. In order to grow crystals for X-ray analysis, a small sample (1−2 mg) of the complex was recrystallized by slow evaporation (1−4 weeks) of a mixed CH_2Cl_2/CH_3CN solution under air in the dark. The complexes were difficult to crystallize, and multiple attempts were required in order to get suitable crystals. Acetonitrile when used as a cosolvent was found to be beneficial to the growth of good quality crystals.

The crystal data and structure refinement parameters are presented in Table 4. Data collections for the five crystal structures were performed at low temperatures using Mo Kα radiation. An Oxford Diffraction Sapphire/KM4 CCD was employed for $[Yb(LBr_2)_3 \cdot H_2O]$, while the remaining samples were measured on a Bruker APEX II CCD. Both diffractometers have a κ geometry goniometer. Data were reduced by means of CrysAlis PRO[37] for $[Yb(LBr_2)_3 \cdot H_2O]$ and EvalCCD[38] for the remaining samples and then corrected for absorption.[39] Solution and refinement for all crystal structures were performed using SHELXTL.[40] All structures were refined using full-matrix least-squares on F^2 with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. The

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(37) *CrysAlis PRO*; Oxford Diffraction Ltd.: Abingdon, Oxfordshire, U.K., 2008.

(38) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220.

(39) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

(40) *SHELXTL*, release 6.1.4; Bruker AXS Inc.: Madison, WI, 2003.

SQUEEZE[41] algorithm was used to take into account highly disordered solvent molecules, and it has been applied to all structures. A twinning problem was found in the case of [Nd(L)$_3$]. The twinning by reticular merohedry was analyzed using the TWINROTMAT routine of PLATON.[42] A HKLF5 file was then generated and used in the refinement of the structure, obtaining a final BASF parameter of 0.35(2).

Synthesis of the Ln^{III} Complexes (General Notes). Synthesis of the ligands is provided in the Supporting Information. Synthesis of Ln^{III} complexes was performed under air in THF/water solutions using a stoichiometric ratio of reagents. Neutral ligands may not be completely soluble in THF at room temperature but form clear solutions upon warming or upon deprotonation. Solutions of neutral ligands in THF were pale yellow but turned red upon deprotonation. The use of ethanol or aqueous ethanol as a solvent in these reactions is not recommended due to the low solubility of the ligands in ethanol, which may result in contamination of the complexes with unreacted ligands. Besides, as a word of caution, we would recommend using noncoordinating organic bases, such as (NEt$_4$)OH, instead of NaOH in these reactions, because a combination of NaOH with certain ligands and lanthanides may result in the formation of mixed metal complexes containing both sodium and lanthanide (instead of tris complexes) either as a major product or as an impurity. All complexes were soluble to some extent in CH$_2$Cl$_2$ and were insoluble in alkanes, arenes, ethers, alcohols, and acetonitrile.

Synthesis of Complex [Nd(L)$_3$]. The ligand HL (60 mg, 0.23 mmol) was dissolved in hot THF (70−80 °C, 3 mL), followed by the addition of NaOH (9.15 mg, 0.23 mmol) dissolved in water (0.75−1 mL, used as a stock solution with approximately 100 mg of NaOH per 10 mL of water) to give a red solution. A solution of NdCl$_3$·6H$_2$O (27.3 mg, 0.0762 mmol) in ethanol/water (0.5/1.5 mL) was added dropwise over 5 min. Upon addition, the color of the reaction mixture changed to deep red, and a precipitate formed. The suspension was stirred for 10 min at 70−80 °C, cooled to 40−50 °C, and filtered while warm. In order to remove unreacted ligand, the solid was first washed with THF (until filtrates were pale red), followed by washing with ethanol/water (1:1) and ether (until filtrates were colorless). The complex was dried under vacuum at room temperature. Dark violet red solid: 65 mg (0.07 mmol, 92%). Anal. calcd for $C_{48}H_{27}N_6NdO_6$ (MW 928.00): C, 62.12; H, 2.93; N, 9.06. Found: C, 61.68; H, 3.13; N, 8.46. The microanalysis by energy dispersive X-ray spectrometry indicated that this complex did not contain Na.

Synthesis of Nd^{III} and Yb^{III} Complexes (General Procedure). The ligand was dissolved in hot THF (70−80 °C; 5 mL for HLCl$_2$−F; 3 mL for other ligands) followed by the addition of (NEt$_4$)OH (20% w/w solution in water, Aldrich) dissolved in water (0.5 mL) to give a red solution. A solution of LnCl$_3$·6H$_2$O in ethanol/water (0.5/1.5 mL) was added dropwise over 5 min. Upon addition, the color of the reaction mixture changed to deep red, and a precipitate formed. The suspension was stirred for 10 min at 70−80 °C, cooled to 40−50 °C, and filtered while warm. In order to remove unreacted ligands, the solid was *first* washed either with THF or with THF/water, depending on the solubility of the precipitates. This was *always* followed by washing with ethanol/water (1:1) and ether (until filtrates were colorless). The complex was dried under a vacuum at room temperature. *Note*. NaOH could not be used as a base in most of these reactions because sodium salts of the ligands (apart from ligands HL, HL−Cl, and HL−Br) have very low solubility in common organic solvents or their mixtures with water and precipitate as red solids upon mixing of the reagents. Further details are provided below.

[Nd(L−Cl)$_3$]. The reaction was performed with HL−Cl (60 mg, 0.202 mmol), (NEt$_4$)OH (0.202 mmol), and NdCl$_3$·6H$_2$O (24.2 mg, 0.067 mmol). The complex was washed with THF/water (1:1). Dark violet-red solid: 42 mg (0.041 mmol, 61%). Anal. calcd for $C_{48}H_{24}Cl_3N_6NdO_6$ (MW 1031.34): C, 55.90; H, 2.35; N, 8.15. Found: C, 55.75; H, 2.74; N, 7.70.

[Nd(L−Br)$_3$]. The reaction was performed with HL−Br (60 mg, 0.176 mmol), (NEt$_4$)OH (0.176 mmol), and NdCl$_3$·6H$_2$O (21 mg, 0.0586 mmol). The complex was washed with THF/water (1:1). Dark violet-red solid: 47 mg (0.040 mmol, 69%). Anal. calcd for $C_{48}H_{24}Br_3N_6NdO_6$ (MW 1164.69): C, 49.50; H, 2.08; N, 7.22. Found: C, 49.65; H, 2.25; N, 6.86.

[Nd(L−Cl$_2$Me)$_3$]·2H$_2$O. The reaction was performed with HL−Cl$_2$Me (60 mg, 0.163 mmol), (NEt$_4$)OH (0.163 mmol), and NdCl$_3$·6H$_2$O (19.3 mg, 0.054 mmol). The complex was washed with a small amount of THF/water (3:1; <3 mL) and a large amount of THF/water (1:1, until filtrates were pale red). Dark brown solid: 46 mg (0.038 mmol, 70%). Anal. calcd for $C_{51}H_{27}Cl_6N_6NdO_6 \cdot 2H_2O$ (MW 1212.79): C, 50.51; H, 2.58; N, 6.93. Found: C, 50.74; H, 2.65; N, 6.42.

[Nd(LCl$_2$)$_3$]. The reaction was performed with HLCl$_2$ (60 mg, 0.165 mmol), (NEt$_4$)OH (0.165 mmol), and NdCl$_3$·6H$_2$O (19.7 mg, 0.055 mmol). The complex was washed with a large amount of THF (filtrates were initially red but quickly turned colorless) and THF/water (1:1). Dark purple-red solid: 61 mg (0.054 mmol, 98%). Anal. calcd for $C_{48}H_{21}Cl_6N_6NdO_6$ (MW 1134.67): C, 50.81; H, 1.87; N, 7.41. Found: C, 50.85; H, 1.65; N, 7.45.

[Nd(LCl$_2$−Me)$_3$]. The reaction was performed with HLCl$_2$−Me (60 mg, 0.153 mmol), (NEt$_4$)OH (0.153 mmol), and NdCl$_3$·6H$_2$O (18.3 mg, 0.051 mmol). The complex was washed with a large amount of THF/water (3:1, until filtrates were pale red). Dark purple-red solid: 53 mg (0.045 mmol, 88%). Anal. calcd for $C_{51}H_{27}Cl_6N_6NdO_6$ (MW 1176.75): C, 52.05; H, 2.31; N, 7.14. Found: C, 51.84; H, 2.05; N, 6.93.

[Nd(LCl$_2$−F)$_3$]. The reaction was performed with HLCl$_2$−F (60 mg, 0.152 mmol), (NEt$_4$)OH (0.152 mmol), and NdCl$_3$·6H$_2$O (17.9 mg, 0.050 mmol). The complex was washed with a small amount of THF and a large amount of THF/water (3:1, until filtrates were pale red). Reddish-purple solid: 55 mg (0.046 mmol, 93%). Anal. calcd for $C_{48}H_{18}Cl_6F_3N_6NdO_6$ (MW 1188.65): C, 48.50; H, 1.53; N, 7.07. Found: C, 47.35; H, 1.27; N, 6.73.

[Ln(LBr$_2$)$_3$·*n*H$_2$O] (Ln = Nd, *n* = 0; Ln = Yb, *n* = 1). The reaction was performed with HLBr$_2$ (50 mg, 0.113 mmol), (NEt$_4$)OH (0.113 mmol), and LnCl$_3$·6H$_2$O (0.0375 mmol). The complexes were washed with a small amount of THF (<3 mL, filtrates were red) and a large amount of THF/water (1:1, until filtrates were pale red or colorless). Nd^{III} and Yb^{III} complexes had distinctly different colors in the solid state. **[Nd(LBr$_2$)$_3$].** Dark purple-red solid: 42 mg (0.030 mmol, 80%). Anal. calcd for $C_{48}H_{21}Br_6N_6NdO_6$ (MW 1401.38): C, 41.14; H, 1.51; N, 6.00. Found: C, 40.72; H, 1.53; N, 5.76. **[Yb(LBr$_2$)$_3$·H$_2$O].** Bright red solid: 42 mg (0.029 mmol, 75%). Anal. calcd for $C_{48}H_{21}Br_6N_6O_6Yb \cdot H_2O$ (MW 1448.20): C, 39.81; H, 1.60; N, 5.80. Found: C, 40.35; H, 2.06; N, 5.29.

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Supporting Information Available: Synthesis of *o*-aminophenols, 5,7-dibromo-2-methyl-8-hydroxyquinoline, 2-methyl-8-benzyloxyquinolines, 2-carboxaldehyde-8-benzyloxyquinolines, benzyl-protected ligand precursors, and benzothiazole-/benzoxazole-substituted 8-hydroxyquinoline ligands; attempted synthesis of lanthanide complexes with ligands HLS, HLS−Cl, and HLS−CF_3; ^{1}H NMR spectra of precursors (Figures S1−S17) and ligands (Figures S18−S28); absorption spectra of ligands and complexes (Figures S29−S44); luminescence spectra of Nd^{III} complexes (Figures S45−S51) and CIF files of the crystal structures, CCDC 721487−721491. This material is available free of charge via the Internet at http://pubs.acs.org.

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