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Structural and Photophysical Studies of Highly Stable Lanthanide Complexes of Tripodal 8-Hydroxyquinolinate Ligands Based on 1,4,7-Triazacyclononane

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The tripodal H_3thqtcn ligand allows the synthesis of well-defined neutral monomeric *syn*-tris(hydroxyquinolinate) complexes of lanthanides. Pure [Ln(thqtcn)] complexes (Ln = Nd, **1**; Er, **2**; Yb, **3**) of the triply deprotonated ligand thqtcn^{3-} were prepared. Crystallographic characterization was carried out for complexes **1** and **3**, showing that the ligand is flexible enough to wrap around Ln^{III} of different size with a tricapped trigonal-prism coordination geometry. The partially protonated $H_{1.5}$thqtcn$^{1.5-}$ ligand also binds strongly to Ln^{III} ions in methanol and water (at pH ∼5). The X-ray diffraction study shows that protonated complexes crystallize as chiral dimers of formula $[Ln(H_{1.5}thqtcn)]_2(OTf)_3 \cdot 3MeOH$ (Ln = Nd, **4**; Yb, **5**) in which two equivalent monomeric complexes of the partially protonated $H_{1.5}$thqtcn$^{1.5-}$ are bridged by very strong hydrogen bonds between the phenol oxygen atoms. The ligand thqtcn^{3-} sensitizes efficiently the near-infrared emission of Er, Nd (0.10% Qy), and Yb (0.60% Qy). For the first time, the effect of ligand protonation on the efficiency of the solid-state luminescence emission of lanthanides complexes is demonstrated by the decrease of the luminescence quantum yield observed for $[Yb(H_{1.5}thqtcn)]_2(OTf)_3$ (0.26%) with respect to [Yb(thqtcn)] (0.60%). The water-soluble H_3thqtcn-SO_3 analogue of H_3thqtcn and its lanthanide complexes has been prepared. The solution quantum yields of the thqtcn-$SO_3{}^{3-}$ complexes were measured in water at pH 7.4 (0.016% for Nd^{III} and 0.14% for Yb^{III}) and in deuterated water (Nd, 0.047%; Yb, 0.55%), and they are among the highest reported in the literature for Yb^{III} in aqueous solutions. The high thermodynamic and kinetic stability in water at physiological pH of the gadolinium complex of thqtcn-$SO_3{}^{3-}$ indicate that the lanthanide complexes of thqtcn^{3-} and thqtcn-$SO_3{}^{3-}$ are highly resistant to hydrolysis and therefore are well suited for the development of luminescent devices and for application as probes in biomedical imaging.

Introduction

Recently, there is considerable interest in the complexes of lanthanide ions such as Nd^{III}, Yb^{III}, or Er^{III} that show efficient luminescence in the near-infrared (NIR) region[1] because of their potential application in lasers, in optical amplifiers, in light-emitting diodes,[2−8] and in “in vivo” imaging and biochemical analysis.[9−12]

One particularly promising class of NIR-emitting lanthanide complexes is based on the 8-hydroxyquinolate chelating motif. Notably hydroxyquinolinate complexes of Nd^{III}, Yb^{III}, and Er^{III} have recently been developed for their use in the fabrication of NIR-emitting organic light-emitting

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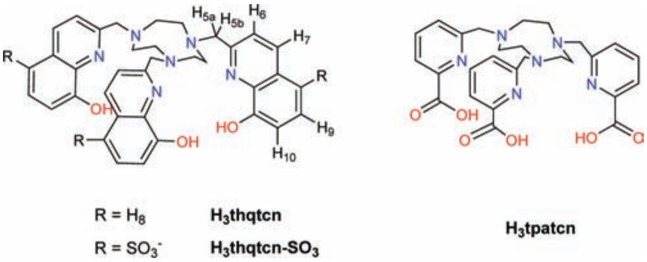
diodes (OLEDs).[4,6,13,14] Furthermore, recent studies indicate the possibility of using such OLEDs in silicon-based optoelectronics.[15,16] It should be noted that 8-hydroxyquinoline forms luminescent complexes with a large variety of metal ions, which has resulted in their extensive application in OLED and display technology. In particular, the tris(8-hydroxyquinoline)aluminum complex has played a major role in the development of OLEDs.[17,18] Although the ability of 8-hydroxyquinoline to bind strongly to the lanthanide ions has been known for a long time,[19] only very recently has the structural elucidation of these complexes been performed.[20−24] While it had been commonly assumed that tris(8-hydroxyquinolinate) complexes were formed like for the aluminum ion, these recent coordination chemistry studies show that different species are obtained depending on the reaction conditions, leading to different structures displaying different stoichiometries with 4:1, 6:2, 8:3, 9:3, and 8:2 ligand-to-metal ratios.[20−24] Furthermore, the formation of mononuclear anhydrous tris(8-hydroxyquinolinate) complexes seems not to occur, and in some of the isolated structures, the presence of water molecules coordinated to the metal center is observed, which is particularly unfavorable to the design of efficient NIR-emitting complexes. Conversely, the synthesis in anhydrous conditions leads to only trinuclear species.[22,23] These results suggests that most of the compounds usually used as components in device preparation might be, in reality, a mixture of species, making it difficult to quantitatively relate structural properties to luminescence properties and devices' efficiency and stability. Moreover, the lanthanide complexes of 8-hydroxyquinoline are sensitive to moisture, which leads to ligand dissociation, reducing the devices' stability and efficiency. The expansion of the coordination sphere of 8-hydroxyquinoline by attachment of amide or benzimidazole substituents has been proposed to achieve a more controllable coordination behavior,[25−27] but the stability of these systems with respect to ligand dissociation in the presence of moisture remains limited. A particularly efficient strategy to control the coordination chemistry of the hydroxyquinolinate derivatives and to obtain high stability and exclusion of the water molecules consists of the use of predisposed or preorganized multidentate ligands.[28] The use of 8-hydroxyquinoline-based hexadentate ligands has allowed the preparation of water-stable aluminum chelate with improved electrochemical stability.[29] Recently, Imbert and co-workers have been using this strategy for the design of water-stable 8-hydroxyquinolinate-based lanthanide complexes, which display efficient NIR emission in water and which are good candidates for biomedical applications.[30−32] Rather flexible tripodal and tetrapodal ligands were prepared in which 8-hydroxyquinoline binding units were connected through an amide function to the tris(ethylamine) or *N*,*N*′-bis(ethylenediamine) anchors. Potentiometric and luminescence solution studies indicated the presence in solution of 1:1 species in which coordination of all of the ligand arms to the metal center prevents water binding. However, the presence of multiple species with different degrees of protonation and their flexibility render difficult the investigation of their molecular structure. We have previously shown that the direct assembly of bidentate units into nonadentate tripodal ligands[33,34] such as H_3tpatcn (1,4,7-tris[(6-carboxypyridin-2-yl)methyl]-1,4,7-triazacyclononane) or decadentate tetrapodal[35] ligands using respectively a triazacyclononane or an ethylenediamine anchor provides a very good lanthanide−ligand complementarity and leads to well-defined, highly rigid, water-stable mononuclear complexes in which the metal is efficiently shielded from water molecules.



We have now applied this strategy to the preparation of well-defined 8-hydroxyquinolinate-based lanthanide chelates. The synthesis of the tripodal ligand H_3thqtcn (1,4,7-tris-[2-(8-hydroxyquinolinyl)methyl]-1,4,7-triazacyclononane) was previously reported by Cross and Sammes.[36] Here we describe the synthesis, the solid-state structural investigation, and the photophysical properties of mononuclear lanthanide complexes of the ligand H_3thqtcn and the photophysical solution properties of the water-soluble and highly water-stable lanthanides complexes of the new ligand H_3thqtcn-SO_3 (1,4,7-tris[2-(5-sulfo-8-hydroxyquinolinyl)methyl]-1,4,7-triazacyclononane).

Experimental Section

General Details. Solvents and starting materials were obtained from Aldrich, Fluka, Acros, and Alfa and used without further

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Table 1. Crystallographic Data for the Four Structures (OTf = $CF_3SO_3^-$)[a]

	[Nd(thqtcn)] (**1**)	[Yb(thqtcn)] (**3**)	$\{[Nd(H_{3/2}thqtcn)]^{3/2+}\}_2 \cdot 3OTf^- \cdot 3MeOH$ (**4**)	$\{[Yb(H_{3/2}thqtcn)]^{3/2+}\}_2 \cdot 3OTf^- \cdot 3MeOH$ (**5**)
formula	$C_{36}H_{33}N_6NdO_3$	$C_{36}H_{33}N_6YbO_3$	$C_{78}H_{78}F_9N_{12}Nd_2O_{18}S_3$	$C_{78}H_{78}F_9N_{12}O_{18}S_3Yb_2$
M_w	741.92	770.73	2035.25	2087.81
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$
a/Å	11.701(2)	11.5050(4)	12.9868(19)	12.886(4)
b/Å	33.114(6)	32.7650(14)	13.748(2)	13.706(4)
c/Å	8.1031(17)	8.0582(3)	23.950(4)	23.811(8)
α/deg	90	90	89.995(3)	88.664(5)
β/deg	108.902(7)	108.992(4)	74.878(2)	75.218(6)
γ/deg	90	90	77.080(3)	76.223(5)
V/Å^3, Z	2970.4(10), 4	2872.27(19),4	4016.0(10), 2	3946(2), 2
λ/Å	0.710 73	0.710 73	0.710 73	0.710 73
D_c/g cm^{-3}	1.659	1.782	1.683	1.757
μ(Mo Kα)/mm^{-1}	1.798	3.307	1.456	2.535
T/K	223(2)	100(2)	223(2)	223(2)
R1, wR2 [$I > 2\sigma(I)$]	0.0408, 0.0717	0.0545, 0.0723	0.0290, 0.0711	0.0408, 0.1080

[a] Structures were refined on F_0^2 using all data: $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

purification unless otherwise stated. Solvents were dried over the appropriate drying agents when required. Water and H_2O refer to high-purity water with a resistivity value of 18 MΩ·cm, obtained from the Millipore/Milli-Q purification system.

^1H and ^{13}C NMR spectra were recorded on Varian Mercury and Varian Unity 400 MHz spectrometers. Chemical shifts are reported in ppm with a solvent as the internal reference. The pD values are corrected for the deuterium isotopic effect.[37]

X-ray Crystallography. Crystals suitable for X-ray diffraction were obtained for **1** and **3**−**5**, while suitable crystals of **2** were not obtained. Diffraction data for **1**, **4**, and **5** were taken using a Bruker SMART CCD area detector three-circle diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). Diffraction data for **3** were taken using an Oxford Xcalibur diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). To prevent evaporation of cocrystallized solvent molecules, the crystals were coated with light hydrocarbon oil, and the data were collected at 223 K for **1**, **4**, and **5** and at 100 K for **3**. The cell parameters were obtained with intensities detected on three batches of 15 frames with a 30 s exposure time for complex **1**, 5 s for **4**, and 120 s for **5**. The crystal-to-detector distance was 5 cm. For three settings of Φ, 1271 narrow data were collected for 0.3° increments in ω with a 10 s exposure time for **4**, 30 s for **1**, and 120 s for **5**. At the end of data collection, the first 50 frames were re-collected to establish that crystal decay had not taken place during the collection. Unique intensities with $I > 10\sigma(I)$ detected on all frames using the Bruker *SMART* program were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the Bruker *SADABS* program. The cell parameters for complex **3** were obtained with intensities detected on three batches of five frames with 1.6−6.4 s exposure times. The crystal-to-detector distance was 5.5 cm. For three settings of Φ and θ, 196 narrow data were collected for 1° increments in ω with a 25 s exposure time for **3**. Unique intensities detected on all frames using the Oxford diffraction *Red* program were used to refine the values of the cell parameters. The substantial redundancy (×2.5) in data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the Oxford diffraction *ABSPACK* program. Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure (Table 1). The structures were solved by direct methods using the *SHELXTL*6.14 package, and for all structures, all atoms, including hydrogen atoms, were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F. Hydrogen atoms were refined isotropically except for H37 and H38 in complex **3**, which have been constrained.

Spectroscopic and Analytical Measurements. Mass spectra were recorded on a Bruker Daltonics Esquire 3000 plus mass spectrometer equipped with an electrospray source. Elemental analyses of the ligands were performed by the Service Central d'Analyses (Vernaison, France), whereas analyses of the Ln^{III} complexes were performed by the analytical laboratories of Prof. H. Malissa and G. Reuter (Lindlar, Germany) under a controlled atmosphere of argon. Absorption spectra were recorded on a Cary 50 Probe UV/vis spectrometer with Perkin-Elmer luminescence cells with a path length of 2 mm.

Potentiometric Titrations. Ligand protonation constants of H_3thqtcn-SO_3 were determined by potentiometric titrations. Solutions of 20 mL of H_3thqtcn-SO_3 (4.0×10^{-4} M) acidified to pH ~2.5 were titrated in a thermostatted cell (25.0 ± 0.1 °C) under a stream of argon with a 0.1 M KOH solution added by means of a 5 mL piston buret (Metrohm). The ionic strength was fixed with KCl (μ = 0.1 M). Titrations were carried out with a Metrohm 751 GPD Titrino potentiometer equipped with a combined pH−glass electrode (Metrohm). Calibration of the electrode system was performed prior to each measurement. The electromotive force is given by $E = E° + s\mathrm{pH}^+$ and both $E°$ and s were determined by titrating a known amount of HCl by 0.1 M KOH at μ = 0.1 M

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(KCl), using the acid range of the titration. The value used for the ion product of water is log $K_w = 13.77$.[38] More than 58 data points were collected for each experiment.

The data were mathematically treated by the program *HYPERQUAD2000*.[39,40] All values and errors represent the average of at least three independent experiments.

Luminescence Measurements. Low-resolution luminescence measurements (spectra and lifetimes) were recorded on a Fluorolog FL 3-22 spectrometer from Spex−Jobin−Yvon−Horiba with double-grating emission and excitation monochromators and a R928P photomultiplier. For measurements in the NIR spectral range, the spectrometer was fitted with a second measuring channel equipped with a FL-1004 single-grating monochromator and the light intensity was measured by two Jobin−Yvon solid-state InGaAs detectors: (i) DSS-IGA020L, cooled to 77 K (range 800−1600 nm), and (ii) DSS-IGA020A (range 800−1700 nm) working at room temperature and inserted into a LN2 housing including an elliptical mirror (90° beam path) and coupled to a Jobin−Yvon SpectrAcq2 data acquisition system. The equipment and experimental procedures for luminescence measurements in the visible and NIR range have been published previously by Comby et al.[41] All spectra were corrected for instrumental functions. Lifetimes were measured in the time-resolved mode and are averages of three independent measurements, which were made by monitoring the decay at the maxima of the emission spectra. The monoexponential decays were analyzed with Origin 7.0. Quantum yields of the complexes in solution at pH 7.4 and in the solid state were determined using an absolute method with a home-modified integrating sphere from Oriel and the previously described procedure.[42] The spectra were corrected for the instrumental function with an absolute method with an integration sphere.

Synthesis of the Ligands H_3thqtcn and H_3thqtcn-SO_3. The ligand H_3thqtcn has been synthesized in four steps from commercially available 8-hydroxy-2-methylquinoline. 1,4,7-Tris[2-(8-(2,2-dimethylpropanoyloxy)quinolinyl)methyl]-1,4,7-triazacyclononane was prepared according to the published procedure from Cross and Sammes.[36] Modification of the last step of the published procedure leads to an increased yield (11% vs 4%).

1,4,7-Tris[2-(8-hydroxyquinolinyl)methyl]-1,4,7-triazacyclononane (H_3thqtcn). A solution of the ester 1,4,7-tris[2-(8-(2,2-dimethylpropanoyloxy)quinolinyl)methyl]-1,4,7-triazacyclononane (1.171 g, 1.37 mmol) in degassed tetrahydrofuran (30 mL) was added to a degassed KOH solution in Milli-Q water (10 mL, 12.35 mmol). The reaction mixture was stirred at room temperature for 6 days and then neutralized (pH 7) by adding an aqueous solution of 1 M HCl (~6 mL). The crude product was extracted with ethyl acetate (75 mL) and the organic layer washed with a saturated aqueous solution of $NaHCO_3$ (5 × 15 mL) and then with a saturated aqueous solution of NaCl (5 × 15 mL) and finally dried with anhydrous Na_2SO_4. After evaporation of the solvent, the residue was triturated into ether to yield the trisprotonated form of the ligand H_3thqtcn as a pale-yellow solid (0.608 g, 74%).

^{1}H NMR (D_2O, 400 MHz, 298 K, pD 8.3): δ 3.55 (s, 12H, $N(CH_2)_2N$), 4.60 (s, 6H, $H_{5a/b}$), 6.81 (d, $J = 8.0$ Hz, 3H, H_{10}), 7.18 (d, $J = 8.0$ Hz, 3H, H_8), 7.25 (t, $J = 8.0$ Hz, 3H, H_9), 7.44 (d, $J = 8.8$ Hz, 3H, H_6), 8.15 (d, $J = 8.8$ Hz, 3H, H_7). ES-MS: *m*/*z* (%) 601.3 (100) $[M + H]^+$, 623.3 (7) $[M + Na]^+$. Anal. Calcd for H_3thqtcn·$0.5H_2O$·0.2KCl, $C_{36}H_{37}N_6O_{3.5}K_{0.2}Cl_{0.2}$ (624.64): C, 69.22; H, 5.97; N, 13.45. Found: C, 69.29; H, 6.01; N, 13.22.

1,4,7-Tris[2-(5-sulfo-8-hydroxyquinolinyl)methyl]-1,4,7-triazacyclononane (H_3thqtcn-SO_3). The ligand H_3thqtcn (0.104 g, 0.17 mmol) was covered by the minimum amount of oleum (H_2SO_4/SO_3, 20%, 1.5 mL). The mixture was stirred overnight at room temperature and poured onto ice. The solution was evaporated to dryness and dissolved in ethanol. Slow evaporation of the solution at 4 °C formed a yellow precipitate, which was purified by column chromatography on RP18 silica (Merck) with a gradient of solvents from 99.925:0.075 H_2O/trifluoroacetic acid to 90:10:0.1 H_2O/CH_3CN/trifluoroacetic acid, to afford the ligand [H_3thqtcn-SO_3]·$6H_2O$·$0.3H_2SO_4$ in 33% yield.

^{1}H NMR (D_2O, 400 MHz, 298 K, pD 8.3): δ 2.95 (s, 12H, $N(CH_2)_2N$), 3.85 (s, 6H, $H_{5a/b}$), 6.66 (d, $J = 7.6$ Hz, 3H, H_{10}), 7.60 (d, $J = 7.6$ Hz, 3H, H_9), 7.72 (t, $J = 7.6$ Hz, 3H, H_7), 8.75 (d, $J = 7.6$ Hz, 3H, H_6). ES-MS: *m*/*z* (%) 641.2 (100) $[M + H]^+$. Anal. Calcd for H_3thqtcn-SO_3·$6H_2O$·$0.3H_2SO_4$; $C_{36}H_{48.6}N_6O_{13.2}S_{3.3}$ (978.40): C, 44.23; H, 4.95; N, 8.60. Found: C, 44.07; H, 4.99; N, 8.63.

Synthesis of the Lanthanide Complexes of H_3thqtcn. [Ln(thqtcn)] (Ln = Nd, 1; Er, 2; Yb, 3). A solution of $Ln(OTf)_3$ (Ln = Nd, Er, Yb; 0.09 mmol) in methanol (4 mL) was added to a solution of H_3thqtcn (0.09 mmol) in methanol (4 mL). The addition of 0.85 equiv of a 1 M aqueous solution of KOH afforded a limpid yellow solution, which was refrigerated at 4 °C overnight. KOTf was eliminated by filtration. The addition of a KOH solution (an additional 3.3 equiv) to the resulting solution led, after cooling at 4 °C, to the formation of a yellow microcrystalline solid, which was separated by filtration, washed with methanol and Milli-Q water, and dried under a secondary vacuum for 2 days to yield [Ln(thqtcn)] (48−79%).

Anal. Calcd for [Nd(thqtcn)], $C_{36}H_{33}N_6O_3Nd$: C, 58.28; H, 4.48; N, 11.33. Found: C, 58.45; H, 4.35; N, 11.20.

Monocrystals of **1** suitable for X-ray diffraction were obtained by slow diffusion of a 1 mM methanol solution of KOH into a 4 mM 1:1:0.85 Nd/H_3thqtcn/KOH solution at 4 °C. Monocrystals of **3** were obtained by extraction of the isolated complex in hot acetonitrile followed by slow evaporation of the solvent.

Anal. Calcd for [Er(thqtcn)], $C_{36}H_{33}N_6O_3Er$: C, 56.53; H, 4.35; N, 10.99. Found: C, 56.98; H, 4.22; N, 10.73. Anal. Calcd for [Yb(thqtcn)], $C_{36}H_{33}N_6O_3Yb$: C, 56.10; H, 4.32; N, 10.90. Found: C, 55.81; H, 4.06; N, 10.65.

$[Ln(H_n thqtcn)]^{n+}$ (Ln = Nd, 4; Yb, 5). The partially protonated species were prepared in situ by mixing equimolar amounts of the ligand and the appropriate $Ln(OTf_3)$ salt in deuterated methanol (MeOD). Aliquots of a 1 M KOD solution in D_2O were successively added, and the complex formation was followed by ^{1}H NMR. The addition of 0.85 equiv is required for full complexation of the ligand. However, beyond 0.85 equiv, precipitation of a yellow powder occurred.

$[Nd(H_n thqtcn)]^{n+}$. ^{1}H NMR (CD_3OD, 400 MHz, 25 °C): δ −1.50 (s, 3H, H_{5a}/H_{5b}), −0.12 (s, 3H, $N(CH_2)_2N$), 5.09 (s, 3H, H_{5a}/H_{5b}), 6.68 (s, 3H, H_9), 6.83 (s, 3H, $N(CH_2)_2N$), 6.83 (s, 3H, H_{10}), 7.47 (d, $J = 8.0$ Hz, 3H, H_8), 8.40 (d, $J = 8.0$ Hz, 3H, H_6), 8.62 (d, $J = 8.0$ Hz, 3H, H_7), 9.10 (s, 3H, $N(CH_2)_2N$), 9.91 (s, 3H, $N(CH_2)_2N$). ^{1}H NMR (CD_3OD, 400 MHz, 40 °C): δ −1.08 (s, 3H, H_{5a}/H_{5b}), −0.01 (s, 3H, $N(CH_2)_2N$), 5.03 (s, 3H, H_{5a}/H_{5b}), 6.53 (s,

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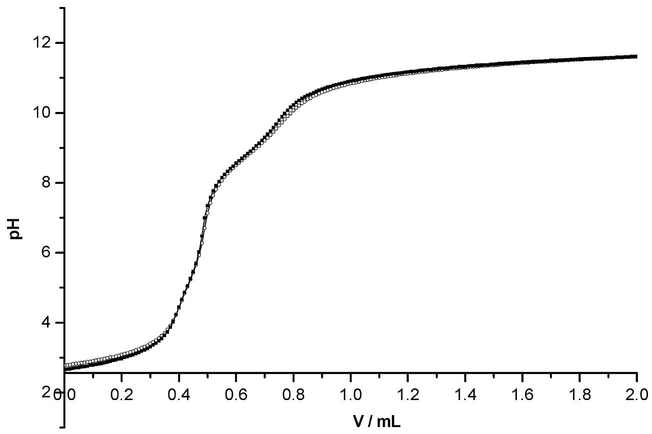

Figure 1. Potentiometric titration curves for H_3thqtcn-SO_3 (0.4 mM): (○) 1 mM NaOH added; (■) 1 mM HCl added. $T = 25$ °C, $I = 0.1$ M (KCl).

3H, H_9), 6.73 (s, 3H, H_{10}), 6.84 (s, 3H, $N(CH_2)_2N$), 7.50 (d, $J =$ 8.0 Hz, 3H, H_8), 8.41 (d, $J = 8.0$ Hz, 3H, H_6), 8.67 (d, $J = 8.0$ Hz, 3H, H_7), 8.72 (s, 3H, $N(CH_2)_2N$), 8.43 (s, 3H, $N(CH_2)_2N$).

[Yb($H_n$thqtcn)]$^{n+}$. ^{1}H NMR (CD_3OD, 400 MHz, 25 °C): δ −12.11 (s, 3H, ($N(CH_2)_2N$), −4.88 (s, 3H, $N(CH_2)_2N$), −3.70 (s, 3H, H_{5a}/H_{5b}), 2.77 (s, 3H, $N(CH_2)_2N$), 4.59 (s,3H, H_{5a}/H_{5b}), 4.59 (s, 3H, H_{10}), 7.87 (s, 3H, H_9), 8.25 (d, $J = 8.0$ Hz, 3H, H_8), 9.23 (s, 3H, H_6), 9.95 (s, 3H, H_7), 15.16 (s, 3H, $N(CH_2)_2N$). ^{1}H NMR (CD_3OD, 400 MHz, 15 °C): δ −13.16 (s, 3H, $N(CH_2)_2N$), −5.41 (s, 3H, $N(CH_2)_2N$), −4.18 (s, 3H, H_{5a}/H_{5b}), 3.60 (s, 3H, $N(CH_2)_2N$), 4.47 (s,3H, H_{10}), 5.55 (s, 3H, H_{5a}/H_{5b}), 7.89 (s, 3H, H_9), 8.27 (d, $J = 8.0$ Hz, 3H, H_8), 9.25 (d, $J = 8.0$ Hz, 3H, H_6), 9.99 (d, $J =$ 8.0 Hz, 3H, H_7), 15.80 (s, 3H, $N(CH_2)_2N$). Slow diffusion of isopropyl ether into the above solutions yielded yellow crystals suitable for X-ray diffraction (Ln = Nd, **4**; Yb **5**).

Synthesis of the Lanthanide Complexes of H_3thqtcn-SO_3. [Ln(thqtcn-SO_3)] (Ln = Nd, 6; Er, 7; Yb, 8). Complexes for ^{1}H NMR and luminescence measurements were prepared in situ by mixing stoichiometric amounts of the ligand H_3thqtcn-SO_3 and the appropriate Ln(OTf)$_3$. ^{1}H NMR was performed in D_2O after adjustment of the pD value with a KOD solution. Solutions (1 mM) of the [Ln(thqtcn-SO_3)] complexes in 0.1 M Tris-buffered saline (pH 7.4) were used for luminescence studies.

[Nd(thqtcn-SO_3)]. ^{1}H NMR (D_2O, 400 MHz, 25 °C, pD 7.7): δ 0.46 (s, 3H, $N(CH_2)_2N$), 0.78 (s, 3H, $N(CH_2)_2N$), 1.68 (s, 3H, $N(CH_2)_2N$), 4.82 (s, 3H, $N(CH_2)_2N$), 5.46 (s, 3H, H_{5a}/H_{5b}), 5.97 (s, 3H, H_{5a}/H_{5b}), 6.87 (d, $J = 7.0$ Hz, 3H, H_{10}), 8.89 (d, $J = 7.0$ Hz, 3H, H_9), 9.83 (d, $J = 8.0$ Hz, 3H, H_6), 10.32 (d, $J = 8.0$ Hz, 3H, H_7). ^{1}H NMR (D_2O, 400 MHz, 70 °C, pD 7.7): δ 0.62 (s, 3H, $N(CH_2)_2N$), 1.30 (s, 3H, $N(CH_2)_2N$), 1.75 (s, 3H, $N(CH_2)_2N$), 4.50 (s, 3H, $N(CH_2)_2N$), 5.16 (s, 3H, H_{5a}/H_{5b}), 5.54 (s, 3H, H_{5a}/H_{5b}), 6.81 (d, $J = 7.0$ Hz, 3H, H_{10}), 8.75 (d, $J = 7.0$ Hz, 3H, H_9), 9.46 (d, $J = 8.0$ Hz, 3H, H_6), 10.52 (d, $J = 8.0$ Hz, 3H, H_7).

Results and Discussion

Characterization of the Ligands H_3thqtcn and H_3thqtcn-SO_3. The ^{1}H NMR spectrum of the ligand H_3thqtcn in D_2O at pD 8.3 and 25 °C displays seven resonances in agreement with a C_{3v} symmetry of the ligand in solution with one single signal for the 12 protons of the 1,4,7-triazacyclononane core, one signal assigned to the three methylene groups of the pendant arms, and five signals for the hydroxyquinoline rings. Similarly to H_3thqtcn, the sulfonated analogue adopts a C_{3v} symmetry in solution as suggested by the ^{1}H NMR in D_2O at pD 8.3, which displays six resonances: one signal for the protons of the triazacyclononane ring, one for the methylene pendant arms, and four signals for the aromatic protons of the hydroxyquinoline moiety.

The high solubility of the ligand H_3thqtcn-SO_3 allowed the determination of its deprotonation constants by potentiometric titration of the protonated form ([H_8thqtcn-SO_3]$^{5+}$) of the ligand acidified to pH 2.5, with a 0.1 M solution of KOH in 0.1 M KCl at 298 K. The fully protonated [H_{12}thqtcn-SO_3]$^{9+}$ ligand has 12 deprotonation sites, three pyridinium groups, three tertiary nitrogen atoms, three hydroxyl oxygen atoms, and three sulfonic groups. The three sulfonates are completely deprotonated under the experimental conditions used. The deprotonation constants of [H_8thqtcn-SO_3]$^{5+}$ are defined in eqs 1 and 2.

$$(H_{8-i}L)^{(2-i)+} \leftrightarrow (H_{7-i}L)^{(1-i)+} + iH^+ \qquad (1)$$

$$K_{ai} = [(H_{7-i}L)^{(1-i)+}][H^+]^i/[(H_{8-i}L)^{(2-i)+}] \quad (i = 1-8) \qquad (2)$$

Analysis of the potentiometric curves (Figure 1) over the pH range 2.5−12.26 allowed the precise determination of four deprotonation constants [pK_{a3} = 8.01(8), pK_{a4} = 8.78(1), pK_{a5} = 8.98(4), pK_{a6} = 10.25(2)], while it was possible to obtain only the sum of pK_{a1} + pK_{a2} [8.51(1)] and of pK_{a7} + pK_{a8} [22.51(3)].

The two lowest pK_a values are assigned to the deprotonation of the pyridinium nitrogen, and they are in agreement with the values reported for the tripodal ligand based on sulfonated 2-carboxy-8-hydroxyquinoline [3.7(1) and 4.62(7)][32] and with the value of 3.92 published for 5-sulfo-8-hydroxyquinoline.[38] The pK_a of the third pyridinium proton is too low to be determined in the conditions used. pK_{a3}−pK_{a5} are assigned to the deprotonation of the hydroxyl groups of the three quinolinate groups and are similar to the values reported for 5-sulfo-8-hydroxyquinoline (average pK_a value of 8.42). The three highest pK_a values are assigned to deprotonation of the three tertiary nitrogen atoms of the triazacyclononane cycle, and their values are consistent with the high pK_a values found in a tripodal ligand containing three 3-hydroxy-2-pyridylmethyl groups (12.09, 10.86, and 9.73). A significantly lower pK_a (∼5.5) value is found for one of the triazacyclononane nitrogen atoms in poly(aminocarboxylate) derivatives including the H_3tpatcn (1,4,7-tris[(6-carboxypyridin-2-yl)methyl]-1,4,7-triazacyclononane) ligand probably because of the lower electron-withdrawing character of the hydroxyquinolinate group compared to the picolinate one.[43]

Synthesis and Molecular Structure of [Ln(thqtcn)] Complexes. The lanthanide complexes [Ln(thqtcn)] (Ln = Nd, **1**; Er, **2**; Yb, **3**) of the triply deprotonated ligand thqtcn^{3-} were prepared by mixing equimolar amounts of the Ln^{III} triflate salt and of the ligand H_3thqtcn in methanol followed by slow diffusion of a 1 M KOH solution (4.15 equiv) at 4 °C. Elemental analyses of all complexes are consistent with

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(43) Mazzanti, M.; Gateau, C.; Nonat, A. Unpublished results.

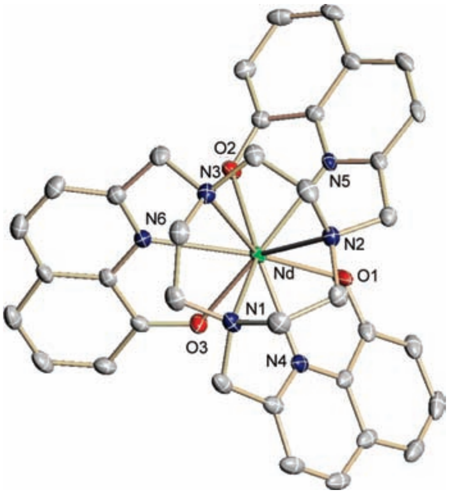

Figure 2. Ellipsoid plot of **1**, top view (30% probability).

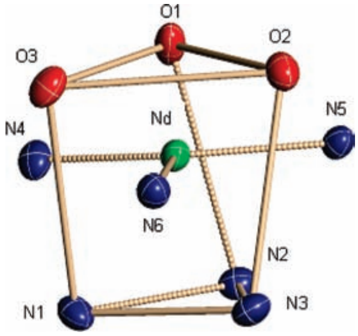

Figure 3. Coordination polyhedron of Nd in [Nd(thqtcn)].

the presence of analytically pure [Ln(thqtcn)] species. The complexes are insoluble in all solvents commonly used in the laboratory. The complexes **1** and **3** are isostructural, and accordingly only the ORTEP diagram of **1** is shown in Figure 2, and the corresponding coordination polyhedron is presented in Figure 3. Selected distances and angles are presented for both complexes in Tables 2 and 3.

In both complexes, the metal ion is nine-coordinated by the nine donor atoms of the ligand: three nitrogen atoms from the 1,4,7-triazacyclononane ring, three nitrogen atoms from the 8-hydroxyquinolinate unit, and three oxygen atoms from the hydroxyquinoline units. The hydroxyquinoline pendant arms bind the metal in a helical fashion, and both enantiomers Λ and Δ are found in the crystallographic structure of **1** and **3**, leading to the centrosymmetric space group *P*2(1)/*c*. Similar coordination geometries have been previously found for the nonacoordinated complexes [Ln(tpatcn)] (Ln = Nd, Eu, Gd, Lu) complexes[33] and [Eu(pytztcn)] (H_3pytztcn = 1,4,7-tris[(6-(1*H*-tetrazol-5-yl)pyridin-2-yl)methyl]-1,4,7-triazacyclononane).[34]

The coordination polyhedron of **1** and **3** can be described as a slightly distorted tricapped trigonal prism with a pseudo-C_3 symmetry (Figure 3). In both complexes, one triangular face is formed by the three nitrogen atoms of the 1,4,7-triazacyclononane macrocycle and the second one by the three quinolinate oxygen atoms. The three nitrogen atoms of the hydroxyquinolinate groups occupy the capping positions. The triangular oxygen faces are slightly twisted around the 3-fold axis with respect to the nitrogen faces. The average values of the torsion angles formed by the atoms of the rectangular faces are 22(2)° for Nd and 17(1)° for Yb; a slightly higher distortion from a regular trigonal-prismatic geometry was found for the [Nd(tpatcn)] [24.2(8)°] and [Lu(tpatcn)] [19.4(3)°] complexes. The planes defined by the two triangular faces are almost parallel in both complexes (angles between the planes are 2.0° for Nd and 2.24° for Yb). The distance between the baricenters of the triangular faces gives an estimate of the degree of helical wrapping of the ligand in the complex. This distance is larger in the [Nd(thqtcn)] complex (3.56 Å) than in the [Yb(thqtcn)] complex (3.49 Å), indicating a regular increase in helicity and increased compression of the trigonal prism. A similar trend was previously observed in the complexes of tpatcn, where the distance between the baricenters of the triangular faces evolves regularly from the [Nd(tpatcn)] complex (3.61 Å) to the [Lu(tpatcn)] complex (3.49 Å) with an intermediate distance found at [Eu(tpatcn)] (3.56 Å). In both series of complexes (tpatcn and thqtcn), the regular evolution of helicity is associated with a regular decrease of the metal−donor atoms distances, in agreement with the decrease in ionic radii along the lanthanide series.[44] Average Ln−$N_{\text{quinolinyl}}$ distances in the [Ln(thqtcn)] complex are close to the one reported for the [Ln(tpatcn)] complex and the decrease of 0.12 Å for thqtcn from Nd to Yb (a decrease of 0.11 Å was found from [Nd(tpatcn)] to [Lu(tpatcn)]). The same similarity is observed for Ln−O distances, with decreases of 0.071 and 0.122 Å from Nd to Yb. A slightly lower decrease (0.071 Å) is found for the average Ln−$N_{\text{macrocyclic}}$ distances from Nd to Yb, which can be compared to the decrease of 0.10 Å found for the tpatcn^{3-} complexes from Nd to Lu. These results indicate that the ligand thqtcn^{3-} is flexible enough to encapsulate lanthanide ions of different size. Moreover, its flexibility is similar to that found for tpatcn^{3-} in spite of the increased rigidity of the 8-hydroxyquinolinate group compared to the picolinate one. The assembly of 8-hydroxyquinolinate units into a nonadentate tripodal ligand allows the synthesis of well-defined neutral monomeric tris(hydroxyquinolinate) complexes of lanthanides that are isostructural along the series. Moreover, while tridentate 2-carboxamide-8-hydroxyquinoline has recently led to the isolation of lanthanide complexes in different isomeric forms (syn, three ligands arranged “up, up, up”; anti, three ligands arranged “up, up, down”), the use of a tripodal anchor to arrange the bidentate hydroxyquinolinate units leads to the formation of pure *syn*-tris(hydroxyquinolinate) complexes. This should be particularly convenient for relating the luminescent properties of tris(hydroxyquinolinate) complexes of lanthanides to their structure.

Molecular Structure of the $\{[Ln(H_{1.5}thqtcn)]^{3/2+}\}_2$ Complexes. The formation of lanthanide complexes of thqtcn^{3-} has also been investigated in solution by ^{1}H NMR spectroscopy. ^{1}H NMR titration of a 1:1 Ln/thqtcn (Ln = Nd, Yb) aqueous solution with increasing amounts of KOD (or Et_3N) shows the progressive disappearance of the signals assigned to the free ligand accompanied by the appearance

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[44] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

Table 2. Selected Bond Distances (Å) and Angles (deg) in Complexes [Nd(thqtcn)] and [Yb(thqtcn)]

	[Nd(thqtcn)]	[Yb(thqtcn)]		[Nd(thqtcn)]	[Yb(thqtcn)]
M−O1	2.393(3)	2.268(3)	M−N3mcy	2.789(3)	2.731(4)
M−O2	2.409(3)	2.290(4)	M−N4py	2.609(4)	2.496(5)
M−O3	2.406(3)	2.292(4)	M−N5py	2.621(4)	2.500(4)
M−N1mcy	2.788(4)	2.708(4)	M−N6py	2.608(4)	2.512(4)
M−N2mcy	2.796(4)	2.712(4)			
O1−M−O3	89.59(11)	88.52(13)	N4−M−N1	60.44(12)	61.27(15)
O1−M−O2	92.16(11)	87.23(13)	N5−M−N1	121.61(13)	80.66(14)
O3−M−O2	93.42(11)	90.20(12)	N6−M−N1	80.74(12)	122.92(14)
O1−M−N4	64.16(11)	66.88(15)	O1−M−N2	91.51(12)	148.90(13)
O3−M−N4	69.33(12)	147.02(14)	O3−M−N2	147.47(11)	88.30(13)
O2−M−N4	149.81(11)	67.94(13)	O2−M−N2	119.00(11)	123.70(13)
O1−M−N5	73.10(10)	143.87(12)	N4−M−N2	82.01(12)	124.17(15)
O3−M−N5	149.63(12)	68.72(14)	N5−M−N2	59.90(12)	61.22(13)
O2−M−N5	63.34(13)	66.04(14)	N6−M−N2	122.23(11)	79.93(13)
N4−M−N5	121.02(12)	119.03(16)	N1−M−N2	63.25(12)	64.33(15)
O1−M−N6	146.18(12)	70.56(13)	O1−M−N3	150.68(11)	91.99(13)
O3−M−N6	63.70(11)	65.94(14)	O3−M−N3	119.72(11)	122.99(14)
O2−M−N6	70.57(11)	147.05(13)	O2−M−N3	87.24(11)	146.78(14)
N4−M−N6	118.53(12)	120.66(13)	N4−M−N3	122.68(12)	81.25(14)
N5−M−N6	119.69(12)	119.85(15)	N5−M−N3	80.55(11)	123.77(13)
O1−M−N1	121.16(12)	124.99(14)	N6−M−N3	60.00(12)	60.81(14)
O3−M−N1	88.64(12)	146.43(13)	N1−M−N3	63.29(11)	63.91(14)
O2−M−N1	146.65(11)	89.63(14)	N2−M−N3	63.70(12)	64.37(13)

Table 3. Selected Bond Distances and Angles for the $\{[Ln(H_{3/2}thqtcn)]^{3/2+}\}_2$ (Ln = Nd, Yb) Complexes

	$\{[Nd(H_{3/2}thqtcn)]^{3/2+}\}_2$	$\{[Yb(H_{3/2}thqtcn)]^{3/2+}\}_2$
M1−O3	2.4845(18)	2.367(4)
M1−O2	2.5044(18)	2.399(4)
M1−O1	2.5145(18)	2.405(4)
M1−N6	2.686(2)	2.615(5)
M1−N5	2.693(2)	2.614(6)
M1−N4	2.672(2)	2.579(6)
M1−N3	2.569(2)	2.466(5)
M1−N2	2.591(2)	2.489(5)
Nd1−N1	2.577(2)	2.473(5)
M2−O43	2.4929(18)	2.385(4)
M2−O41	2.4645(18)	2.351(4)
M2−O42	2.4700(18)	2.356(4)
M2−N44	2.703(2)	2.642(5)
M2−N46	2.702(2)	2.626(6)
M2−N45	2.707(2)	2.623(6)
M2−N42	2.598(2)	2.478(6)
M2−N41	2.598(2)	2.480(5)
M2−N43	2.586(2)	2.486(5)
O1−M1−N4	122.41(6)	126.18(16)
O2−M1−N5	122.12(6)	125.65(16)
O3−M1−N6	123.81(7)	127.36(17)
O41−M2−N44	122.46(6)	126.38(16)
O42−M2−N45	121.59(6)	125.46(17)
O43−M2−N46	121.20(6)	125.23(16)

of a new set of 11 paramagnetically shifted signals. At pH ~5, only one set of 11 paramagnetically shifted signals is observed in agreement with the presence in solution of C_3-symmetric lanthanide complexes. At pH >5, precipitation of [Ln(thqtcn)] complexes occurs. These results suggest that lanthanide complexes of partially protonated forms of the $thqtcn^{3-}$ ligand are formed at pH <5. A similar experiment was also performed in methanol: after the addition of 0.85 equiv of KOD to a 1:1 Ln/H_3thqtcn mixture (Ln = Nd, Yb) in a MeOD solution, the ^{1}H NMR signals assigned to the free ligand disappear, in agreement with the complete formation of complexed forms of the ligand. The addition of larger amounts of KOD leads to the precipitation of [Ln(thqtcn)] complexes as yellow solids. The ^{1}H NMR spectrum of 1:1:0.85 Ln/thqtcn/KOH mixtures (Ln = Nd, Yb, Er) in a MeOD solution at 25 °C displays a single set of 11 signals, in agreement with an average C_3 symmetry in solution. Moreover, the pattern remains unchanged between 15 and 70 °C, indicating the absence of dynamic processes. An high conformational rigidity had also been observed for the [Ln(tpatcn)] complexes.[33] The spectra of the Nd^{III} (**4**) and Yb^{III} (**5**) complexes (Figure 4) were completely assigned by a 2D-COSY experiment combined with a $^1H-^1H$ NOESY experiment at different temperatures. Four resonances are assigned to the 12 methylenic protons of the 1,4,7-triazacyclononane core, two to the methylenic protons of the pendant arms, and five to the aromatic protons. For the Er^{III} complex, the assignement is more difficult because of the presence of overlapping peaks.

The formation of partially protonated species is in agreement with the high values of the pK_a values associated with the phenol protonation in the 8-hydroxyquinoline derivatives[45] and in the analogous sulfonated ligand [H_3thqtcn-SO_3] (see above). One example of structural characterization of the lanthanide complexes coordinated by a protonated pentadentate 8-hydroxyquinoline derivative has been previously reported.[25] These species are particularly interesting because often 8-hydroxyquinolinate complexes used in optical devices are prepared without adding a base and are therefore likely to involve protonated complexes.

The Ortep view of complex **4** is presented in Figure 5, and selected bond distances and angles for **4** and **5** are given in Table 3. In **4** and **5**, two equivalent monomeric complexes of the partially protonated $H_{1.5}thqtcn^{1.5+}$ are bridged by hydrogen bonds between the oxygen atoms of the deprotonated phenol group and the OH of the protonated ones (Table

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(45) Irving, H.; Ewart, J. A. D.; Wilson, J. T. *J. Am. Chem. Soc.* **1949**, 2672–2674.

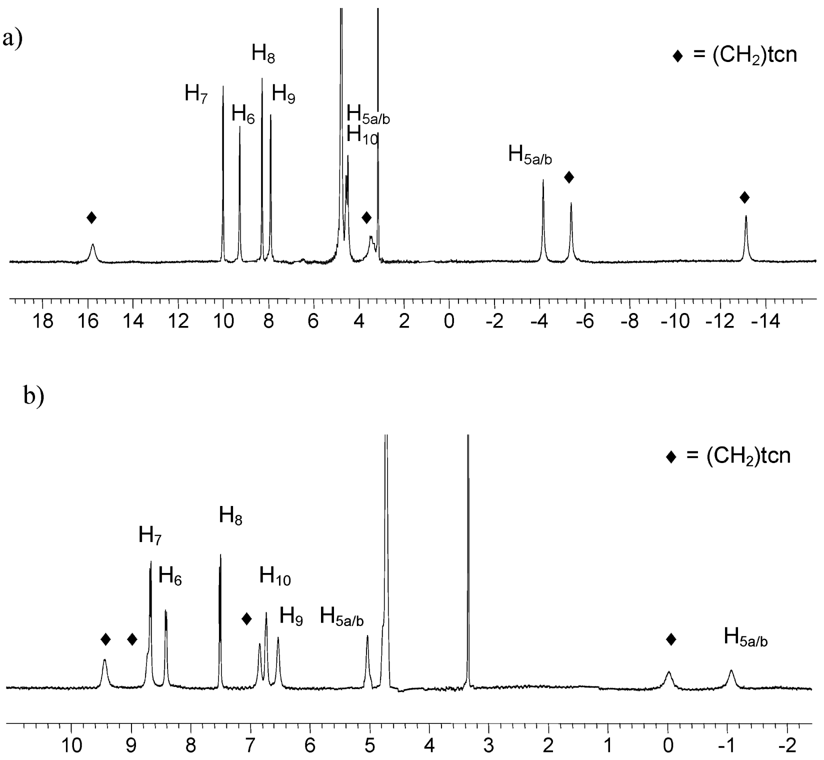

Figure 4. ^{1}H NMR spectra in MeOD at 400 MHz of (a) a 1:1:0.85 Yb/thqtcn/KOH solution, 15 °C, and (b) a 1:1:0.85 Nd/thqtcn/KOH solution, 40 °C.

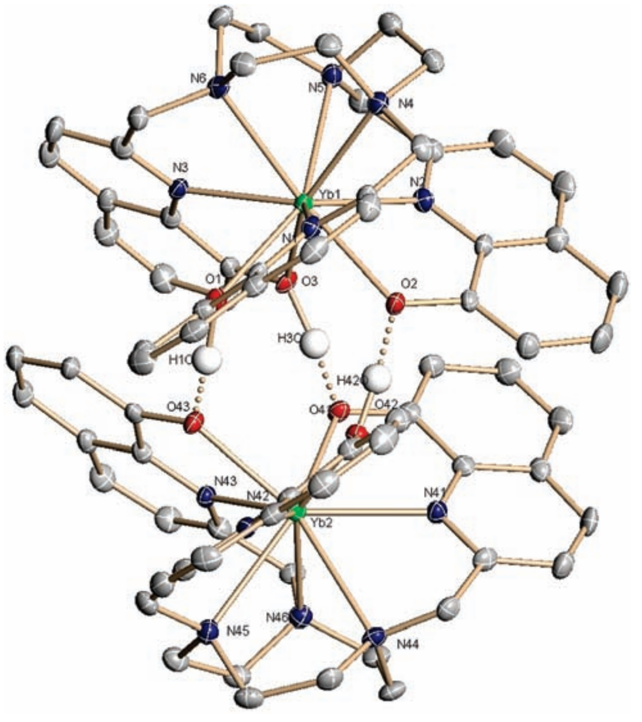

Figure 5. ORTEP diagram of $[Yb_2H_3L_2]^{3+}$ in **4** with 30% thermal contours for all atoms.

Table 4. Hydrogen Bond Distances in $\{[Ln(H_{3/2}thqtcn)]^{3/2+}\}_2$ (Ln = Nd, Yb)

$[Nd_2H_3(thqtcn)_2](OTf)_3$			$[Yb_2H_3(thqtcn)_2](OTf)_3$		
D	d(D−H)/Å	d(H···A)/Å	D	d(D−H)/Å	d(H···A)/Å
O1	1.12(4)	1.32(4)	O1	1.15(11)	1.31(11)
O2	1.16(5)	1.27(5)	O2	1.05(10)	1.39(10)
O3	1.19(5)	1.24(5)	O3	1.17(11)	1.26(11)

4). Hydrogen bonds are very strong[46] with average O−O distances of 2.433(6) Å for Nd and 2.43(2) Å for Yb. Moreover, the three hydrogen bonds are rather symmetric in the Nd complex, with the proton located halfway between two phenolate oxygen atoms at distances ranging from 1.12(4) to 1.32(4) Å. In the Yb complex, two hydrogen bonds show a similar symmetry, while one of the hydrogen bonds is less symmetric, with the proton located closer to one of the quinolinate oxygen atoms [1.05(10) and 1.39(10) Å]. The high symmetry of the hydrogen bonds suggests the presence of the same $+^3/_2$ charge for each complex in each dimer. A comparison of the structural parameters of the two dimeric structures shows that smaller metal−ligand bond lengths are observed for the Yb dimer [average Yb−O = 2.38(1) Å, $Yb-N_{quinolinyl}$ = 2.48(1) Å, and $Yb-N_{macrocycle}$ = 2.62(2) Å] compared to the Nd dimer, although the differences (0.07 and 0.1 Å) are a little smaller than the difference of the ionic radii (0.12). These results indicate that the partially protonated ligand has a similar complementarity for differently sized metals. In both dimers, each metal has a coordination sphere similar to the monomeric [Ln(thqtcn)] complexes in which the nine donor atoms are connected to the metal center. Similar distortions of the coordination geometry from a regular trigonal prism are observed in the $\{H_3[Ln(thqtcn)]_2\}^{3+}$ dimer and in the [Ln(thqtcn)] complexes. The two planes defined by the trigonal faces are parallel as found in the monomers, but the distances between the baricenters are significantly longer (3.67 Å for Nd and 3.60 Å for Yb) than those found for the monomeric complexes (3.56 Å for Nd and 3.49 Å for Yb) as a result of dimer formation. The

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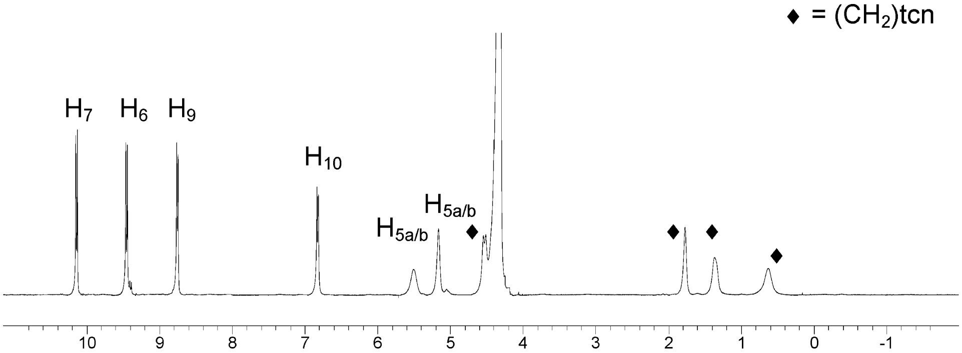

Figure 6. ^{1}H NMR spectrum of a 1:1 Nd/thqtcn-SO_3 solution in D_2O, pD 7.7, 70 °C, 400 MHz.

average M−$N_{quinolinyl}$ distances in the monomeric and dimeric structures are the same [2.61(2) and 2.58(1) Å, respectively, for Nd]. A longer mean M−O distance is observed [2.40(1) Å in the monomer and 2.48(3) Å in the Nd^{III} dimer] probably because of the lower basicity of the protonated hydroxyquinoline oxygen and the dimer formation. The dimer formation also results in shorter distances between the metal and macrocyclic nitrogen atoms with respect to the monomer. These results suggest that the arrangement of the quinolinate groups in the H_3thqtcn ligand can afford strong metal−ligand interactions even when the ligand remains partially protonated, which is in agreement with the high stability of these species in aqueous solution.

Lanthanide Complexes of thqtcn-SO_3^{3-}. In order to assess quantitatively the stability of lanthanide complexes of triazacyclononane-based tris(hydroxyquinolinate)-based tripodal ligands, the water-soluble H_3thqtcn-SO_3 analogue of H_3thqtcn has been prepared. The sulfonyl moiety is known to help the solubilization in water of hydrophobic entities through the formation of negatively charged species.[30] The solubility in water and the thermodynamic and kinetic stabilities in water at physiological pH are crucial properties for the application of lanthanide complexes as luminescent tags in biological systems. H_3thqtcn-SO_3 leads to water-soluble Ln^{III} complexes at physiological pH. The spectrum of a 1:1 Nd/thqtcn-SO_3 solution in D_2O at 70 °C and pD 7.7 shows the presence of four signals assigned to the 12 protons of the 1,4,7-triazacyclononane macrocycle (δ 0.62, 1.30, 1.75, and 4.50), two signals for the six methylene protons of the ligand arms (δ 5.16 and 5.54), and four corresponding to the four aromatic protons of hydroxyquinoline (δ 6.81, 8.75, 9.46, and 10.52) (Figure 6).

The nature and stability of the species formed between the Gd^{III} ion and the ligand H_3thqtcn-SO_3 have first been probed at variable pH and in equimolar solutions of ligand and metal ion by potentiometric titration (pH range 2.4−12.15). The Gd^{III} ion was chosen as a representative example because it lies in the middle part of the Ln^{III} series, and a large amount of stability data with different ligands have been reported for this ion.

The potentiometric titration curve of a 1:1 solution of the Gd^{III} ion and the ligand shows a pH variation, indicating the release of protons upon coordination. This titration did not enable us to determine the global stability constants defined by eqs 3 and 4 in spite of several models tested to refine the titration data probably because of the high kinetic stability of the complexes in solution.

$$\mathrm{Ln_{aq}}^{3+} + \mathrm{L}^{6-} + n\mathrm{H}^+ \leftrightarrow [\mathrm{Ln(H}_n\mathrm{L)}]^{(n-3)+} \qquad (3)$$

$$\beta_{11n} = [\mathrm{Ln(H}_n\mathrm{L)}]^{(n-3)+}]/[\mathrm{Ln_{aq}}]^{3+} + [\mathrm{L}]^{6-} + [\mathrm{H}^+]^n \qquad (4)$$

In order to avoid any problems due to the slow kinetics of the complexation, a general procedure to determine the conditional stability constant at physiological pH via a spectrophotometric competition batch titration versus diethylenetriaminopentaacetic acid (H_5dtpa) at pH 7.4 and 4.5 has been used. The experimental protocols used have been previously described by Raymond and co-workers.[47,48] In our case, H_5dtpa is not able to displace the ligand H_3thqtcn-SO_3 when added in a 100:1 ratio to a solution of the [Gd(thqtcn-SO_3)] complex, indicating that the complex is kinetically inert. The protocol described by Raymond and co-workers has therefore been adapted, and aliquots of the H_5dtpa stock solution (final concentration 0.125 μM to 1.25 mM) were added to solutions containing a constant concentration of the Gd^{III} ion (12.5 μM) and Tris (pH 7.4) or acetate buffers (pH 4.5). After stirring for 5 h at room temperature to ensure formation of the Gd-dtpa complex, a stock solution of H_3thqtcn-SO_3 (final concentration 12.5 μM) was added, and the mixture was stirred for 4 days at room temperature to reach thermodynamic equilibrium. Then, the concentration of free and complexed thqtcn-SO_3^{3-} ligand in each batch of solution was determined by spectrophotometry. The double log plot of the measured concentrations and the refinement by a linear fit is presented Figure 7.

This method allows a precise measurement of the pGd (pGd = −log $[M]_{free}$ at pH 7.4, $[M]_{total} = 1$ μM and [thqtcn-$SO_3]_{total} = 10$ μM) for the ligand thqtcn-SO_3^{3-}: 12.3 ($pGd^{dtpa} - 0.7$) at pH 4.5 and 19.8 ($pGd^{dtpa} + 0.2$) at pH 7.4. They are similar to the value reported for the gadolinium complex of $dtpa^{5-}$ (diethylenetriaminopentaacetic acid; pGd = 19.6 at pH 7.4 and 13.0 at pH 4.5), which is widely used as a contrast agent for clinical MRI examination. The high stability at physiological pH and the high kinetic stability of the gadolinium complex of thqtcn-SO_3^{3-} indicate that the

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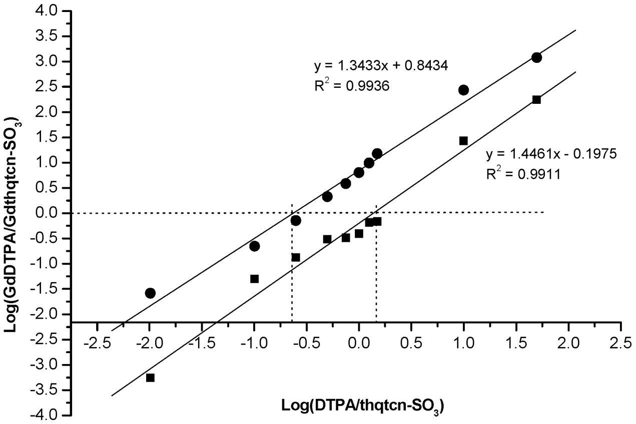

Figure 7. Competition batch titration of H_3thqtcn-SO_3 vs H_5dtpa. The x intercept indicates the difference in pGd between the two ligands: (■) pH 7.4; (●) pH 4.5.

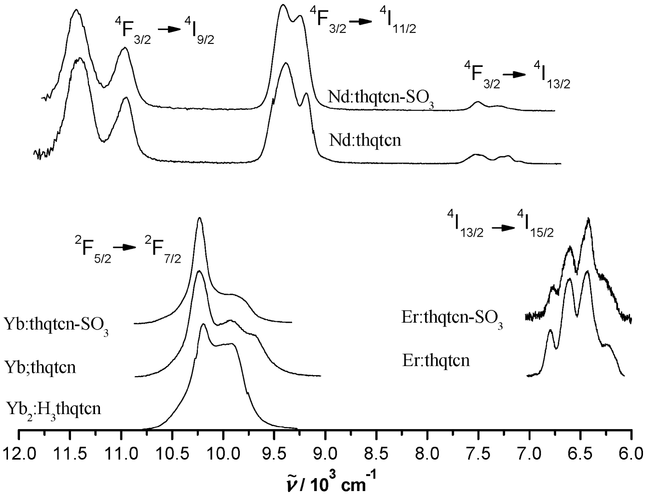

Figure 8. Emission spectra in the NIR region ($\tilde{\nu}_{ex} = 26\,950-27\,550$ cm^{-1}) of the chelates of Er^{III}, Nd^{III}, and Yb^{III} at room temperature. The Ln/thqtcn and Yb_2H_3-thqtcn complexes are in the solid state, and the Ln/thqtcn-SO_3 complexes are in solution in water at pH 7.4.

lanthanide complexes of thqtcn-SO_3^{3-} are well suited for application as probes in biomedical imaging. Furthermore, these stability studies confirm that the inclusion of 8-hydroxyquinolinate binding groups into a nonadentate triazacyclononane-based ligand leads to lanthanide chelates highly resistant to hydrolysis, which should provide very useful tools in the development of luminescent devices.

Sensitization of Lanthanide-Centered NIR Emission by thqtcn^{3-} and thqtcn-SO_3^{3-}. The electronic features of 8-hydroxyquinolinate ligands are well suited to populate the NIR-emitting excited states of Nd^{III}, Er^{III}, and Yb^{III}.[49] Accordingly the complexes of thqtcn^{3-} with Nd^{III}, Er^{III}, and Yb^{III} and the partially protonated $[Yb(H_{1.5}thqtcn)]_2(OTf)_3$ complex display strong metal-centered NIR luminescence in the solid state. Furthermore, the water-soluble thqtcn-SO_3^{3-} complexes of Nd^{III}, Er^{III}, and Yb^{III} retain sizable luminescence in aqueous solutions at pH 7.4. Moreover, the ligand luminescence almost disappears, with only a faint emission from the singlet state (≈10% compared with the free ligand), which indicates an efficient energy-transfer process from the ligand levels to the acceptor levels of the metal ions. At room temperature and upon broad-band excitation through both ligand levels at 370 (solutions and solid state, 27 030 cm^{-1}), 415 (solutions, 24 100 cm^{-1}), or 450 nm (solid state, 22 220 cm^{-1}), the luminescence spectra are identical for all species and display peaks corresponding to the expected f−f NIR transitions. The Yb^{III} complexes emit in the 10 750−9250 cm^{-1} range, with a sharp band at 10 230 cm^{-1} assigned to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and a broader vibronic component at longer wavelength. The Nd^{III} complexes display three bands in the 11 670−6870 cm^{-1} range, with the main band occurring between 9810 and 8750 cm^{-1} ($^4F_{3/2} \rightarrow {}^4I_{11/2}$), with a maximum at 9416 cm^{-1}; two other bands are visible between 11 670 and 10 540 cm^{-1} ($^4F_{3/2} \rightarrow {}^4I_{9/2}$) and between 7810 and 6870 cm^{-1} ($^4F_{3/2} \rightarrow {}^4I_{13/2}$). Finally, the luminescence spectrum of the Er^{III} complex of thqtcn-SO_3^{3-} in solution was recorded, displaying the typical $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition centered at 6433 cm^{-1}.

The shape of the luminescence spectra of the thqtcn-SO_3^{3-} complexes of Nd^{III}, Er^{III}, and Yb^{III} remains unchanged when water is replaced by deuterated water, as expected, but the overall intensity increases considerably. Furthermore, we have determined the lifetimes (Table 5) of the $Nd(^4F_{3/2})$, $Er(^4I_{13/2})$, and $Yb(^2F_{5/2})$ excited states upon excitation using the Nd:YAG line at 355 nm for these complexes in a water solution. The luminescence decays are all monoexponential, and the corresponding lifetimes amount, in water, to 0.16(3) and 2.47(1) μs for Nd^{III} and Yb^{III}, respectively, while they are appreciably longer in deuterated water [0.413(23) and 8.63(4) μs, respectively]. For Er^{III}, the lifetime signal is too small to adjust the data. The Nd^{III} and Yb^{III} lifetimes in deuterated water are in line with those published for poly(aminocarboxylate) complexes derived from dtpa (H_5dtpa = diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid)[50] (0.58 μs for Nd^{III} 1.46 μs for Er^{III}, and 10.4 s for Yb^{III}, respectively, and, more recently, for the ligand TsoxMe [0.61(1) and 14.6(1) μs, respectively, for Nd^{III} and Yb^{III}].[41] In the case of Nd^{III} and Yb^{III}, lifetime data can be used to determine the number of bound water molecules q by using either eq 5 for Nd^{III}, proposed by Faulkner et al.[51] and calibrated with poly(aminocarboxylate) complexes with q = 0−2, or eq 6 for Yb^{III}, proposed by Beeby et al.[52] on the basis of complexes in solution with $q \leq 1$.

$$q = A(\Delta k_{\mathrm{obs}}) - C \quad \text{for Nd}^{\mathrm{III}} \tag{5}$$

$$q = A(\Delta k_{\mathrm{obs}} - B) \quad \text{for Yb}^{\mathrm{III}} \tag{6}$$

where A = 130 ns (Nd^{III}) and 1 μs (Yb^{III}), C = 0.4, and $B = 0.2\ \mu s^{-1}$; $k_{obs} = 1/\tau_{obs}$ is expressed in μs^{-1} and ns^{-1} for

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Table 5. Metal-Ion-Centered Lifetimes (τ/μs) for Nd($^4F_{3/2}$), Yb($^2F_{5/2}$), and Er($^4I_{13/2}$) in the Podates (Ln = Nd, Er, Yb) at pH 7.4 (HBS Buffer) in a Water/D_2O Solution and in the Solid State, Number of Water Molecules Bound in the Inner-Coordination Sphere, and Absolute Quantum Yields (%)

compound	λ_{ex}:λ_{an}/nm	τ/μs	Q^L_{Ln}/%	τ/μs	Q^L_{Ln}/%	q^a	η_{sens}
			Solid State				
[Yb(thqtcn)]	370:976	7.13(2)	0.60(2)				>1
[Yb_2H_3(thqtcn)$_2$]·(OTf)$_3$	370:978	4.05(2)	0.26(1)				>1
[Nd(thqtcn)]	363:1063	0.494(20	0.10(1)				0.85
[Er(thqtcn)]	371:1509	1.17(2)	$4.32 \cdot 10^{-3}(10^{-4})$				0.024
			Solution				
		H_2O	H_2O	D_2O	D_2O		
[Yb(thqtcn-SO_3)]		2.05(4)	0.14(1)	8.63(4)	0.55(5)	0.17	>1
[Nd(thqtcn-SO_3)]	370:1065	0.16(3)	0.016(1)	0.413(23)	0.047(7)	0.1	0.42
[Er(thqtcn-SO_3)]	370:1509		$<2 \times 10^{-3}$	0.642(35)	5.7×10^{-3}		

^{a} From eqs 1 and 2.

Yb^{III} and Nd^{III}, respectively. and $\Delta k_{obs} = k_{obs}(H_2O) - k_{obs}(D_2O)$. In this way, we obtain $q = 0.1$ and 0.17 for Nd^{III} and Yb^{III}, respectively. These values, which are close to 0, suggest that the thqtcn-SO_3^{3-} complexes adopt in a water solution a nonacoordinated structure in which there are no water molecules coordinated to the metal ion. This would suggest a structure analogous to that of the thqtcn^{3-} complexes in the solid state. Indeed, given the uncertainty on q (±0.1−0.3), most likely the residual values do not reflect the presence of solution equilibria involving hydrated species but rather they arise from second-sphere effects not taken into account by parameters B and C.

To quantify the ability of the chromophoric subunits of the thqtcn^{3-} and thqtcn-SO_3^{3-} ligands to sensitize the NIR-emitting lanthanides, the absolute quantum yields of the Ln^{III} podates have been determined upon ligand excitation in the solid state (for thqtcn^{3-} and Ln = Nd, Er, and Yb and for [Yb($H_{1.5}$thqtcn)]$_2$(OTf)$_3$) and in H_2O and D_2O solutions at pH 7.4 (for thqtcn-SO_3^{3-} and Ln = Nd, Er, and Yb). All data are summarized in Table 5.

The solid-state quantum yields and lifetimes of the Ln^{III} podates of thqtcn^{3-} are sizable and comparable with those reported very recently for the tris-chelate complexes of a tridentate 2-carboxamide-8-hydroxyquinolinate ligand with Nd [$Q^L_{Ln}/\% = 0.14(2)$ and $\tau = 0.39$ μs], Yb [$Q^L_{Ln}/\% = 0.56(2)$ and $\tau = 11.1(1)$ μs], and Er [$Q^L_{Ln}/\% = 0.012(1)$ and $\tau = 1.15(2)$ μs].[26]

Furthermore, a comparison of the solid-state quantum yields of [Yb(thqtcn)] and of [Yb($H_{1.5}$thqtcn]$_2$(OTf)$_3$, showing a significant decrease for the partially protonated complex [0.26(1) vs 0.60(2)], which presents coordinated hydroxo groups, allows for the first time a quantitative evaluation of the deactivation of luminescence emission by the presence of coordinated hydroxyl groups. This is particularly relevant because the synthetic conditions for the tris-8-hydroxyquinolinate chelates of lanthanide complexes used in the preparation of OLED devices[13] do not involve base addition, and they are therefore likely to yield partially protonated species.

The solution quantum yields of the thqtcn-SO_3^{3-} complexes in water at pH 7.4 amount to 0.016 and 0.14% for Nd^{III} and Yb^{III}, respectively, and they increase by a factor of 3 or 4 in deuterated water (Nd, 0.047%; Yb, 0.55%), consistent with the trend observed for the lifetimes. Er^{III} luminescence in water is too weak for a quantum yield to be determined, but the corresponding value could be measured in D_2O. These quantum yields are the same order of magnitude as those reported for TsoxMe[31] and among the highest reported in the literature for Yb^{III} in aqueous solutions.[32,53] This is quite remarkable because the sensitization of the Yb ion is particularly difficult in the presence of proximate OH vibrations in the coordination sphere because they induce a large quenching effect for the ions that have a small energy gap between excited levels.

The overall sensitization process of lanthanide-centered luminescence is given by

$$Q^L_{Ln} = \eta_{sens} Q^{Ln}_{Ln} = \eta_{isc}\eta_{et} Q^{Ln}_{Ln} = \eta_{isc}\eta_{et}\frac{\tau_{obs}}{\tau_{rad}} \qquad (7)$$

where Q^L_{Ln} is the quantum yield upon ligand excitation, η_{sens} the efficiency of the overall ligand-to-metal energy transfer, η_{isc} the efficiency of the intersystem crossing, η_{et} the efficiency of the $^3\pi\pi^*$-to-Ln energy transfer, and Q^{Ln}_{Ln} the intrinsic quantum yield, i.e., the quantum yield obtained upon direct Ln^{III} excitation. In order to calculate the efficiency of the sensitizing process with eq 7, the radiative lifetime values, which are difficult to determine experimentally, are needed. Literature data for τ_{rad} measured for Nd^{III}, Er^{III}, and Yb^{III} ions vary widely depending on the solvent and the physical state of the sample;[51,54−57] with the data reported for Er^{III} ranging from 0.66 (aqua ion) to 14 ms (in dimethyl sulfoxide). Taking into account the aqua ion values (0.42 ms for Nd^{III} and 0.66 ms for Er^{III}) proposed by Carnall[55] and the value of 2 ms commonly assumed for Yb,[57] the aqueous solution data point to $\eta_{sens} \approx 0.5-0.9$ for Nd^{III} and <0.01 for Er^{III}, while a value of >1 is obtained for Yb^{III}, indicating that the actual radiative lifetime is larger than 2 ms in our system. Accordingly, the observed modest overall quantum yields are essentially due to deactivation processes involving vibrational oscillators located outside the first coordination sphere.

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The photophysical studies of the lanthanide complexes of the ligand thqtcn^{3-} have been carried out in the solid state because of their insolubility in aqueous solution at pH 7.4. The results are reported in Table 5. All of the emission spectra obtained by ligand excitation display the electronic sharp transition, as described previously, arising both from ligand-field split sublevels and from vibronic components. The emission from solutions of thqtcn-SO$_3^{3-}$ complexes and that from the solid-state samples with thqtcn^{3-} complexes are almost identical. The luminescence decays of the solid-state samples were also measured under ligand excitation and fit perfectly to single-exponential functions. Indeed, these studies demonstrate that at the concentration and pH used the thqtcn-SO$_3^{3-}$ complexes do not dissociate in water, do not contain coordinated water molecules, and present a rather well-defined and rigid inner-coordination sphere.

Conclusion

The nonadentate ligand thqtcn^{3-} allows the reproducible preparation of pure mononuclear lanthanide complexes in which three hydroxyquinolinate groups are arranged in a *syn* fashion around the metal center. These complexes are resistant to hydrolysis and, even in conditions where the ligand is partially protonated, ligand dissociation does not occur. The ligand thqtcn^{3-} sensitizes efficiently the NIR luminescent emission of Er, Nd (0.10% Qy), and Yb (0.60% Qy). Dimeric complexes of the partially protonated thqtcn ligand were also isolated. For the first time, the effect of ligand protonation on the efficiency of the solid-state luminescence emission of lanthanide complexes is demonstrated by the decrease of the luminescence quantum yield observed for [Yb(H$_{1.5}$thqtcn)]$_2$(OTf)$_3$ (0.26%) with respect to [Yb(thqtcn)] (0.60%). The complexes of thqtcn^{3-} appear particularly well suited for OLED applications and should provide a better understanding of the structure−property relationship in hydroxyquinolinate chelates of lanthanides. Future work will be directed at tuning the ligand properties in order to increase the luminescent efficiency and to develop OLED devices. Furthermore, the new ligand thqtcn-SO$_3^{3-}$ allows the reproducible preparation of mononuclear water-soluble lanthanide complexes, which display sizable NIR luminescence in a water solution (0.016% for Nd^{III} and 0.14% for Yb^{III}, which is among the highest reported in the literature for Yb^{III}) and very high stability at physiological pH anticipating their potential application in biomedical analysis.

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Supporting Information Available: Complete tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for compounds **1** and **3**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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