

A Water-Soluble Pybox Derivative and Its Highly Luminescent Lanthanide Ion Complexes

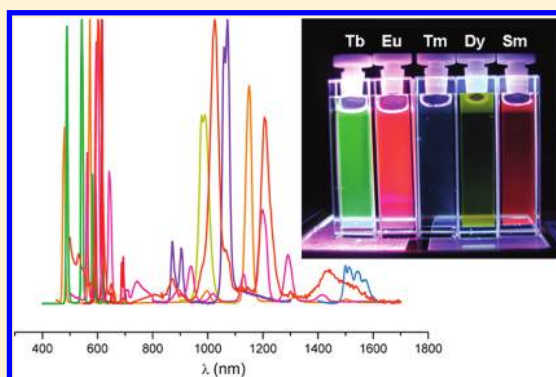
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S Supporting Information

ABSTRACT: A new water-soluble Pybox ligand, **1**, has been synthesized and found to crystallize in the monoclinic $P2_1/n$ space group with unit cell parameters $a = 6.0936(1)$ Å, $b = 20.5265(4)$ Å, $c = 12.0548(2)$ Å, and $\beta = 90.614(1)^\circ$. In the crystal, a water molecule is bound through hydrogen-bonding interactions to the nitrogen atoms of the oxazoline rings. This ligand was used to complex a variety of lanthanide ions, opening up new avenues for luminescence and catalysis in aqueous environment. These complexes are highly luminescent in aqueous solutions, in acetonitrile, and in the solid state. Aqueous quantum yields are high at 30.4% for Eu(III), 26.4% for Tb(III), 0.32% for Yb(III), and 0.11% for Nd(III). Er(III) did not luminesce in water, but an emission efficiency of 0.20% could be measured in D_2O . Aqueous emission lifetimes were also determined for the visible emitting lanthanide ions and are 1.61 ms for Eu(III) and 1.78 ms for Tb(III).

Comparing emission lifetimes in deuterated and nondeuterated water indicates that no water molecules are coordinated to the metal ion. Speciation studies show that three species form successively in solution and the log β values are 5.3, 9.6, and 13.8 for Eu(III) and 5.3, 9.2, and 12.7 for Tb(III) for 1:1, 2:1, and 3:1 ligand to metal ratios, respectively.



INTRODUCTION

The luminescence of lanthanide (Ln(III)) ions, of interest for applications such as lighting and bioimaging, is usually sensitized by coordinated ligands.^{1–4} Sensitization was first reported by Weissman with β -diketonate and salicylate ligands.⁵ In addition to β -diketonates,^{6–9} a large variety of additional ligands has since been screened, from simple chelating ligands such as dipicolinates^{10–13} and oligopyridines^{14,15} to macrocycles such as cyclen^{16,17} and crown ether^{18,19} derivatives and porphyrins,^{20,21} as well as cryptands²² and calixarenes.^{23–25} Water solubility is an important property of the complexes in applications such as bioimaging and anion sensing.²⁶ Luminescent and water-soluble complexes of Eu(III) and Tb(III) have been reported as binding tags for studying protein interactions,^{27,28} for bacterial spore²⁹ or singlet oxygen³⁰ detection, for signaling of carbonate chelation,³¹ as labels for prolactin human serum,³² and as luminescent tags on magnetic nanoparticles for cell imaging applications,³³ among others. Our group recently reported the use of pyridine-bis(oxazoline) as a sensitizer in highly luminescent lanthanide ion complexes in organic solvents.^{34–36} We showed that in para-derivatized Pybox ligands, when the oxazoline rings are unsubstituted, the ligands completely saturate the coordination sphere of the Ln(III) ion in solution and in the solid state, when the complex is prepared in a 3:1 ligand-to-metal ratio.^{34,35} The coordination of luminescence quenching solvent molecules containing O–H oscillators, such as water, is therefore avoided and radiative decay is promoted. Subsequently, the circular

dichroism spectrum of chiral assemblies of quinone-hydroquinone systems with a Sc(III)-Pybox complex³⁷ and circularly polarized luminescence of Ln(III) complexes of a chiral Pybox complex were reported.³⁸ While its use as a sensitizer of Ln(III) ion luminescence remains scarce, since Pybox was first reported by Nishiyama in 1989, it has been extensively utilized in catalysis.^{39–41} Nishiyama et al. showed that Pybox can be synthesized with substituted oxazoline rings and used as a ligand in a Ru(III) catalyst for the asymmetric hydrosilylation of ketones.⁴² Recent reports of enantioselective catalysis using transition-metal complexes with oxazoline-derivatized Pybox ligands include cross-coupling reactions on racemic halides with aryl zinc reagents,^{43–45} Nazarov cyclizations,⁴⁶ asymmetric [3 + 2] cycloadditions of racemic cyclopropanes and aldehydes⁴⁷ or alkynes with *N*-tosylaziridines,⁴⁸ carbonyl-ene reactions,⁴⁹ aminations,^{50,51} Negishi cross-coupling,^{52,53} Mukaiyama-aldol reactions,⁵⁴ allylic substitutions with N or O nucleophiles,⁵⁵ and copper-catalyzed reduction of secondary amines.⁵⁶ Pybox complexes of transition metals have also successfully been immobilized on solid supports to be used in catalytic processes.^{57–59} Pybox complexes of the rare earths have been used in Friedel–Crafts alkylations,⁶⁰ Mukaiyama-aldol reactions,^{61,62} and silylcyanation of aldehydes.⁶³ The lanthanide-Pybox-based systems studied thus far displayed luminescence only in organic solvents, including methanol, and were not

Received: October 11, 2011

Published: April 13, 2012

water-soluble. To date, only two types of water-soluble Pybox derivatives have been reported; the first has hydroxymethyl groups^{64,65} and the second carboxylate methyl ester at the oxazoline rings.⁶⁶ The synthesis of the simplest representative of the first type occurs via two unstable intermediates, and it has been characterized only by NMR of a derivative, as this water-soluble compound is hard to purify.^{64,65} However, it was used in cyclopropanation reactions,⁶⁷ in cycloaddition reactions of nitrones and activated alkenes,⁶⁸ and in Mukaiyama-aldol reactions.⁵⁴ The carboxylate derivative was initially isolated as an intermediate and only recently reported to catalyze catalytic H/D exchange in water.⁶⁹ Water solubility is a criterion that is also highly desirable for greener manufacturing procedures, such as in catalysis, as there is an increasing drive for more environmentally benign processes, which use water as a preferred, nontoxic solvent.^{70,71} Here we present a new, stable, and easily synthesized water-soluble Pybox ligand with an ethylene glycol ethyl ether at the para position of the pyridine ring and its highly luminescent complexes of lanthanide ions. Although not demonstrated here, the synthetic steps for isolation of this Pybox derivative can be easily followed to develop new, chiral, and water-soluble Pybox ligands for aqueous organic transformations.

EXPERIMENTAL SECTION

All commercially obtained reagents were of analytical grade and were used as received. Solvents were dried by standard methods. Lanthanide salts were dried under reduced pressure and heating and kept in a glovebox under a controlled atmosphere ($O_2 < 0.2$ ppm, $H_2O < 2$ ppm). Unless otherwise indicated, all data were collected at a constant temperature of 25.0 ± 0.1 °C. NMR spectra were recorded on Varian 400 and 500 MHz spectrometers with chemical shifts reported (δ , ppm) against tetramethylsilane (TMS) or sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS). Electrospray ionization mass spectra (ESI-MS) were collected in positive ion mode on a Waters Micromass ZQ quadrupole mass spectrometer. The samples were prepared by diluting solutions to a concentration of ~ 1 mg/mL with acetonitrile. All samples were filtered through a $0.2 \mu m$ syringe filter before injecting into the mass spectrometer.

The metal ion concentration of all stock solutions was determined by titration with standardized ethylenediaminetetraacetic acid (EDTA; 0.01 M) with hexamine buffer and using xylenol orange as indicator.⁷²

All reported photophysical data are the average of at least three independent measurements.

Ligand Synthesis. The ligand was synthesized according to modified literature procedures.^{42,73}

4-Chloro-*N*,*N'*-bis(2-chloroethyl)pyridine-2,6-dicarboxamide (a). A 5.00 g portion (27 mmol) of chelidamic acid and 20 μL of DMF were refluxed in 20 mL of $SOCl_2$ for 24 h. The excess thionyl chloride was removed to give 4-chloropyridine-2,6-dicarbonyl dichloride, which was used without further purification. A solution of the acid chloride in 100 mL of chloroform was added dropwise to the vigorously stirred solution of 6.95 g (60 mmol) of 2-chloroethylamine hydrochloride and 6.40 g (114 mmol) of KOH in minimal H_2O at 0 °C. The resulting mixture was stirred for another 2 h. The organic phase was diluted with 100 mL of $CHCl_3$, separated, washed with water (2×100 mL) and saturated $NaHCO_3$ (2×100 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure to give a bright white solid. Yield: 6.70 g (76.4%, from chelidamic acid). 1H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 2H), 3.86 (t, $J = 6$ Hz, 4H), 3.75 (t, $J = 6$ Hz, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$, TMS): δ 162.47, 149.84, 148.00, 125.62, 43.69, 41.30 ppm.

2,2'-(4-(2-Ethoxyethoxy)pyridine-2,6-diyl)bis(4,5-dihydrooxazole) (1). A 2.00 g portion (5 mmol) of 4-chloro-*N*,*N'*-bis(2-chloroethyl)pyridine-2,6-dicarboxamide and 1.46 g (26 mmol) of KOH were heated at 75 °C in 150 mL of 2-ethoxyethanol for 2 days. The solvent was then removed, and the crude material was purified by flash column

chromatography (2% NH_4OH in MeCN, silica) to give 0.7412 g of pure material. Yield: 48.6%. 1H NMR (400 MHz, CD_3CN , TMS): δ 7.63 (s, 2H), 4.48 (t, $J = 9.0$ Hz, 4H), 4.28 (m, 2H), 4.03 (t, $J = 9.0$ Hz, 4H), 3.77 (m, 2H), 3.56 (q, $J = 8.0$ Hz, 2H), 1.17 (t, $J = 8.0$ Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN , TMS): δ 166.06, 163.27, 148.62, 111.96, 68.60, 68.32, 68.26, 66.38, 54.97, 14.66. 1H NMR (400 MHz, D_2O , DSS): δ 7.54 (s, 2H), 4.59 (t, $J = 9.8$ Hz, 4H), 4.30 (m, 2H), 4.07 (t, $J = 9.8$ Hz, 4H), 3.91 (m, 2H), 3.68 (q, $J = 7.1$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, D_2O , DSS): δ 168.79, 166.34, 149.72, 115.19, 71.70, 70.63, 70.57, 69.60, 56.41, 16.81. ESI-MS: experimental $[M + H]^+ m/z$ 306.1454, calculated 306.145.

Synthesis of Metal Complexes. All metal complexes were prepared in a similar manner in air by mixing stoichiometric amounts of ligand and $Ln(NO_3)_3$ or $Ln(CF_3SO_3)_3$ ($Ln = Eu, Tb, Tm, Dy, Pr, Sm, Yb, Nd, Er$) in acetonitrile. After the mixture was heated for several hours, the solvent was removed under reduced pressure and the resulting material was dried in a vacuum oven overnight to give the metal complexes. Complexes were dissolved in an appropriate solvent prior to quantum yield and lifetime measurements. Since quantitative data were collected only on the complexes of Eu, Tb, Nd, Er, and Yb, characterization by ESI-MS and elemental analysis was carried out only for these complexes. Attempts to isolate X-ray-quality crystals of the metal complexes are ongoing.

[Eu(1)₃](NO₃)₃. ESI-MS: $[Eu(1)_3]^{3+}$ m/z found (calculated) 356.1117 (356.111). Anal. Calcd (found) for $[Eu(1)](NO_3)_3 \cdot 3H_2O$: C, 41.32 (41.14); H, 4.85 (4.84); N, 12.85 (12.74).

[Tb(1)₃](NO₃)₃. ESI-MS $[Tb(1)_3]^{3+}$ m/z found (calculated) 358.1111 (358.113). Anal. Calcd (found) for $[Tb(1)](NO_3)_3 \cdot 3H_2O$: C, 41.10 (40.37); H, 4.83 (4.75); N, 12.78 (12.52).

[Nd(1)₃](NO₃)₃. ESI-MS $[Nd(1)_3]^{3+}$ m/z found (calculated) 353.1104 (353.115). Anal. Calcd (found) for $[Nd(1)](NO_3)_3 \cdot 3H_2O$: C, 41.57 (41.53); H, 4.88 (4.80); N, 13.03 (12.92).

[Yb(1)₃](NO₃)₃. ESI-MS $[Yb(1)_3]^{3+}$ m/z found (calculated) 363.1159 (363.123). Anal. Calcd (found) for $[Yb(1)](NO_3)_3 \cdot 3H_2O$: C, 40.67 (39.93); H, 4.77 (4.73); N, 12.48 (12.61).

[Er(1)₃](NO₃)₃. ESI-MS $[Er(1)_3]^{3+}$ m/z found (calculated) 361.1115 (361.122). Anal. Calcd (found) for $[Er(1)](NO_3)_3 \cdot 3H_2O$: C, 40.84 (39.84); H, 4.80 (4.56); N, 12.70 (12.49).

Photophysical Characterization. Solutions for spectroscopic studies were prepared by dissolving the 3:1 metal to ligand complex in acetonitrile, in D_2O or in 0.1 M Tris-HCl buffer (pH 7.4). The solutions were diluted to a final concentration of 1×10^{-4} M. Absorption spectra were measured on a Perkin-Elmer Lambda 35 spectrometer and emission/excitation spectra on a Perkin-Elmer LS-55 fluorescence spectrometer or a Horiba Jobin Yvon Fluoro-3 spectrofluorometer. Slit widths for emission and excitation measurements were 5–10 nm, and the scan rate was 250 nm/s. On the Perkin-Elmer fluorimeter the data were collected in phosphorescence mode with a delay of 0 ms, a cycle time of 16 ms, and a gate time of 0.05 ms. The near-IR measurements and all lifetimes were recorded on a Horiba Jobin Yvon Fluoro-3 spectrofluorometer equipped with a Hamamatsu PMT NIR detector. Solutions were allowed to equilibrate for 1–2 h before photophysical measurements. For quantum yield measurements, both the absorption and emission/excitation spectra were measured using 0.2 cm path length cells, and while measuring the spectra the emitted light was at a right angle and along the long path length (1 cm). Quantum yields were measured for concentrations in the range 1×10^{-5} – 5×10^{-4} M. All measurements, except the triplet-state measurements, were performed at 25.0 ± 0.1 °C. The triplet-state measurements were performed at 77 K, as proposed by Crosby.⁷⁴ Singlet and triplet state energies are indicated as the 0–0 transitions, after deconvolution of the fluorescence and phosphorescence spectra into their Franck–Condon progressions.

Quantum yields were calculated using the equation

$$\Phi_x = \frac{n_x^2 A_{ref} I_{ref} E_x}{n_{ref}^2 A_x I_x E_{ref}} \Phi_{ref}$$

where Φ is the quantum yield of sample x and reference ref, n is the refractive index (1.343 in acetonitrile, 1.332 87 in water), A is the

absorbance at the excitation wavelength, I is the intensity of the corrected excitation spectrum at the excitation wavelength, and E is the integrated corrected emission spectrum. The spectra are always corrected for instrumental functions. Quantum yields for the reported solutions were measured against $\text{Cs}_3[\text{Eu}(\text{dipic})_3]$ ($\Phi_{\text{ref}} = 24.0\%$, $A_{279} \approx 0.15$, $7.5 \times 10^{-5} \text{ M}$) and $\text{Cs}_3[\text{Tb}(\text{dipic})_3]$ ($\Phi_{\text{ref}} = 22.0\%$, $A_{279} \approx 0.15$, $6.5 \times 10^{-5} \text{ M}$) in Tris buffer (0.1 M) as reference standards^{75,76} for the visible emitting species and $[\text{Yb}(\text{TTA})_3(\text{H}_2\text{O})_2]$ ($\Phi_{\text{ref}} = 0.35\%$, $1 \times 10^{-4} \text{ M}$, anhydrous toluene)⁷⁷ for the near-IR emitting complexes. The excitation wavelengths of the samples were chosen to ensure that there is a linear relationship between the intensity of emitted light and the concentration of the absorbing/emitting species ($A \leq 0.05$).

The intrinsic luminescence efficiency $\Phi_{\text{Ln}}^{\text{Ln}}$ is given by

$$\Phi_{\text{Ln}}^{\text{Ln}} = \frac{\tau_{\text{obs}}}{\tau_{\text{R}}}$$

where τ_{obs} is the experimentally determined emission lifetime and τ_{R} the radiative lifetime. τ_{R} can be obtained from the integrated emission spectrum, E_{TOT} , and the integrated emission band of a magnetic dipole transition, E_{MD} , if A_{MD} , the spontaneous emission probability of the magnetic dipole transition (e.g., $^5\text{D}_0 \rightarrow ^7\text{F}_1$ in Eu^{3+}), is known, by utilizing the equation⁷⁸

$$\frac{1}{\tau_{\text{R}}} = A_{\text{MD}} n^3 (E_{\text{TOT}}/E_{\text{MD}})$$

In this equation n is the refractive index of the solution. Klink et al. have calculated and confirmed experimentally that A_{MD} is 14.65 s^{-1} for $\text{Eu}(\text{III})$.⁷⁸ The efficiency of sensitization Φ_{sens} for the $\text{Eu}(\text{III})$ complexes can then be estimated, as

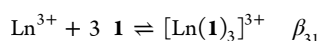
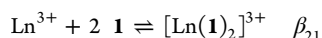
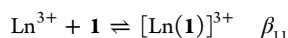
$$\Phi = \Phi_{\text{Eu}} = \Phi_{\text{sens}} \times \Phi_{\text{Eu}}^{\text{Eu}}$$

The number of coordinated water molecules q was determined through comparison of the emission lifetimes of $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ in water and deuterated water, using the equation below, proposed by Horrocks et al.⁷⁹

$$q = A(\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1})$$

where $A = 1.05$ for Eu and 4.2 for Tb.

Determination of Stability Constants. All the solutions were prepared in air in Nanopure (18.2 M Ω) water at constant ionic strength ($I = 0.1 \text{ M}$) using Et_4NCl and 0.1 M Tris-HCl buffer (pH 7.4). Stock solutions of lanthanide ions at 0.005 M were prepared by dissolving appropriate quantities of $\text{Ln}(\text{CF}_3\text{SO}_3)_3$ ($\text{Ln} = \text{Eu}, \text{Tb}$) in Nanopure water (18.2 M Ω). A stock solution of the ligand was also prepared at 0.01 M concentration in Nanopure water (18.2 M Ω) and was diluted as needed. In a typical experiment 50 mL of $1 \times 10^{-4} \text{ M}$ ligand was titrated against metal triflate solution. After each metal ion addition and a delay of 5 min, the emission spectrum was measured. Each titration run had at least 30 data points so that there was a good fit. A wide range of ligand to metal ion stoichiometric ratios was considered. At least three repeat titrations were performed for each system to account for experimental error. Stability constants, $\log \beta$, were refined using the HYPERQUAD2006 software package,⁸⁰ and speciation diagrams were drawn with the program HySS,⁸¹ assuming the three equilibria



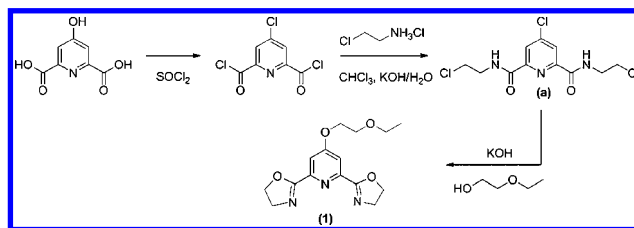
X-ray Crystallographic Characterization. Crystal data, data collection, and refinement details for $\mathbf{1} \cdot \text{H}_2\text{O}$ are given in Table S1 (Supporting Information). A suitable crystal was mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were measured using a

strategy that combines ω and ψ scans of 0.3° per frame and an acquisition time of 10 s per frame. Multiscan absorption corrections were applied. Cell parameters were retrieved using SMART⁸² software and refined using SAINTPlus⁸³ on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus⁸³ software. Absorption corrections were applied using SADABS.⁸⁴ The structure was solved by direct methods and refined by least-squares methods on F^2 using the SHELXTL⁸⁵ program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on the difference map and their parameters constrained to the parent site. The X-ray crystallographic information file can either be found on the same Web site or can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; e-mail @ccdc.cam.ac.uk). CCDC 868880 contains the supplementary crystallographic data for $\mathbf{1} \cdot \text{H}_2\text{O}$.

RESULTS AND DISCUSSION

PyboxO(CH_2)₂OEt (**1**) was synthesized following a procedure analogous to other para-derivatized Pybox ligands reported by our group³⁵ with an overall yield of 37% from chelidamic acid (Scheme 1). It was characterized by NMR spectroscopy and high-resolution ESI-MS.

Scheme 1. Synthetic Scheme for PyboxO(CH_2)₂OEt



X-ray-quality single crystals of $\mathbf{1} \cdot \text{H}_2\text{O}$ were obtained after a few weeks from a saturated solution of acetonitrile. The structure of this molecule is shown in Figure 1. **1** displays a

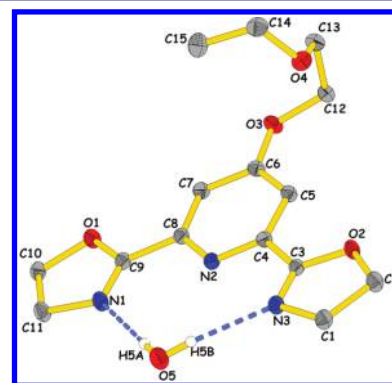


Figure 1. Thermal ellipsoid plot of $\mathbf{1} \cdot \text{H}_2\text{O}$ with atom labeling. Ellipsoids are shown at the 50% probability level. Hydrogen atoms on **1** are omitted for clarity.

pyridine ring with two oxazoline substituents on the 2- and 6-positions as well as an $\text{O}(\text{CH}_2)_2\text{OCH}_2\text{CH}_3$ chain at the para position. The two oxazoline rings are almost planar with the pyridine ring, with torsion angles $\text{N1}-\text{C9}-\text{C8}-\text{N2} = 3.2(1)^\circ$ and $\text{N2}-\text{C4}-\text{C3}-\text{N3} = -7.3(1)^\circ$. The nitrogen atoms of the oxazoline rings, which usually point in the opposite direction of the pyridine nitrogen atom due to stabilizing hydrogen-bonding interactions between these atoms and the aromatic C-H,⁸⁶ point in **1** toward the center of the cavity formed by the three

rings. This position is favored due to the presence of a solvent water molecule in the cavity, which hydrogen bonds with the nitrogen atoms of the oxazoline rings. The hydrogen-bonding distances and angles are $\text{N1}\cdots\text{H5A}-\text{O5} = 2.157(17) \text{ \AA}$, $174.9(2)^\circ$ and $\text{N3}\cdots\text{H5B}-\text{O5} = 2.170(17) \text{ \AA}$, $174.5(2)^\circ$. This water molecule further interacts with neighboring molecules of **1**, through weak hydrogen bonding to C–H groups of the oxazoline rings and the glycol moiety, as shown in Figure S1 in the Supporting Information.

In addition to common organic solvents such as dichloromethane, chloroform, and acetonitrile, **1** is also soluble in water. In aqueous solution the compound displays absorption maxima at 210 and 236 nm, with a shoulder at 295 nm, as shown in Figure 2. Excitation in the 236–300 nm range yields a broad emission with a maximum at 351 nm.

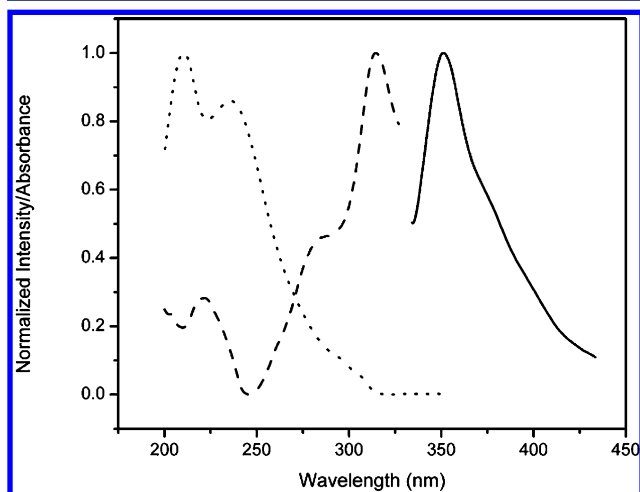


Figure 2. Absorption (dotted), excitation (dashed), and emission (solid) spectra of **1** in water.

Stirring the ligand with $\text{Ln}(\text{NO}_3)_3$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Tb}, \text{Nd}, \text{Yb}, \text{Er}$) in a 3:1 ligand to metal ratio in acetonitrile yielded the corresponding complexes $[\text{Ln}(\text{PyboxO}(\text{CH}_2)_2\text{OEt})_3](\text{NO}_3)_3$, which were characterized by high-resolution ESI-MS (Table S1 and Figures S3–S13, Supporting Information) and ^1H NMR of a complex with the diamagnetic $\text{La}(\text{III})$ (Figure S14, Supporting Information). The formation and characterization of these complexes confirm that the complexes with Pybox-type ligands are stable in a 3:1 ligand to metal ratio, as shown previously.^{34,35}

The $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ complexes are highly luminescent in solution, in solvents such as acetonitrile and water, and in the solid state, showing the characteristic metal-centered emission. The absorption spectra of the complexes, shown in Figure 3, are featureless in comparison with the free ligand, with a shoulder that can be discerned at 240 nm. Excitation maxima for the $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ complexes are at 290 nm, which corresponds to a second shoulder in the absorption spectra, consistent with ligand-centered sensitization. Excitation of the complexes at this wavelength yields the characteristic emission peaks for each $\text{Ln}(\text{III})$ ion, as shown in Figure 3. The emission spectrum of $\text{Tb}(\text{III})$ displays five distinct peaks at 489, 543, 582, 620, and 646 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4, 3, 2$) transitions. $\text{Eu}(\text{III})$ also displays five distinct peaks at 579, 592, 615, 649, and 693 nm corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transitions. The absence of splitting in the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of $\text{Eu}(\text{III})$, its symmetrical shape, and its

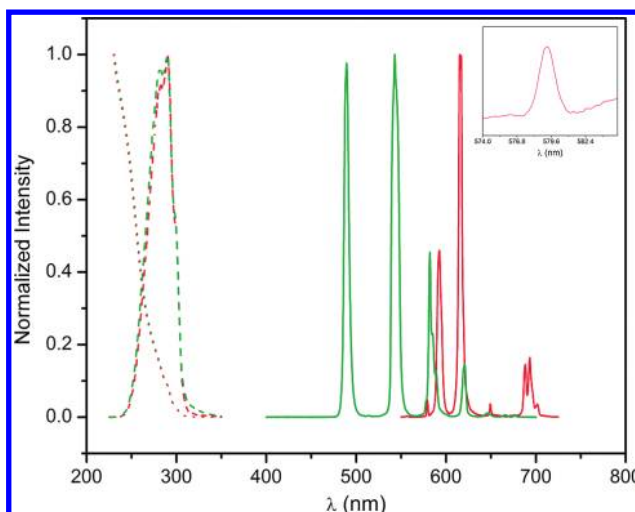


Figure 3. Absorption (dotted), excitation (dashed), and emission spectra (solid) of $[\text{Ln}(\text{1})_3]^{3+}$ ($\text{Ln} = \text{Tb}$ (green), Eu (red)) in H_2O . The inset shows the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of $\text{Eu}(\text{III})$ in more detail. $[\text{complex}] = 1 \times 10^{-4} \text{ M}$, $\lambda_{\text{exc}} = 290 \text{ nm}$.

narrow full width at half-maximum (fwhm) of 45 cm^{-1} , shown in detail in the inset of Figure 3, are indicative of the presence of only one species in solution. This value compares well with reported fwhm of $15\text{--}20 \text{ cm}^{-1}$ for single species measured at 12^{11} and 77 K .⁸⁷ The large intensity of the hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition with respect to the magnetic dipole allowed $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition indicates a low symmetry environment around the metal ion. The quantum yields of emission and excited state lifetimes were measured in different solvents and are summarized in Table 1. In acetonitrile, the emission efficiencies of $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ are 31.1 and 19.6%, respectively. Other para-derivatized Pybox sensitizers, previously reported by our group, display emission efficiencies in the range 26–76% for $\text{Eu}(\text{III})$ and 23–59% for $\text{Tb}(\text{III})$, which compare well with the data presented here. Similar high efficiencies were obtained in water with $\text{PyboxO}(\text{CH}_2)_2\text{OEt}$ as the sensitizer, with values of 30.4 and 26.4% for $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$, respectively. These values compare favorably with emission efficiencies of 16–24% reported for $\text{Eu}(\text{III})$ and 22–40% for $\text{Tb}(\text{III})$ in aqueous solution.^{11,88,89} These data, along with data collected in degassed solutions and Tris-HCl buffered aqueous solutions, show that different solvents do not influence the emission process appreciably, as the lanthanide ion's coordination sphere is adequately shielded by the three coordinated ligands.

The dependence of the emission efficiencies on solution concentrations was also investigated. It was observed that, in aqueous solution, within the concentration range 1×10^{-5} – $5 \times 10^{-4} \text{ M}$, the efficiencies, within experimental error, do not change appreciably (Figure S2, Supporting Information). This signifies that the complexes are stable within the concentration range studied.⁹⁰

While the shielding is important, the location of the ligand's singlet and triplet states plays an important role in determining the efficiencies of intersystem crossing and energy transfer from ligand to lanthanide ion. Their energies were therefore determined using the $\text{Gd}(\text{III})$ complex⁹¹ of **1** and are summarized in Table 1. The triplet state energy is $26\,200 \text{ cm}^{-1}$ in acetonitrile and slightly higher, at $26\,720 \text{ cm}^{-1}$, in water, consistent with a small degree of solvatochromism, likely

Table 1. Quantum Yields of Luminescence (Φ) and Singlet (1S) and Triplet (3T) States of $[\text{Ln}(\mathbf{1})_3]^{3+}$ in Different Solvents^a

	Φ_{Eu} (%)	Φ_{Tb} (%)	Φ_{Yb} (%)	Φ_{Nd} (%)	Φ_{Er} (%)
MeCN			1S 33 000 \pm 160 cm^{-1} ^b 3T 26 200 \pm 40 cm^{-1} ^b		
	31.1 \pm 2.3 $\Phi_{\text{sens}} = 59.9 \pm 6.8$ $\Phi_{\text{Eu}}^{\text{Eu}} = 51.7 \pm 4.4$	19.6 \pm 1.3	0.24 \pm 0.02	0.23 \pm 0.07	0.19 \pm 0.03
H ₂ O			1S 33 900 \pm 120 cm^{-1} ^{b,c} 3T 26 720 \pm 220 cm^{-1} ^{b,c}		
	30.4 \pm 5.9 $\Phi_{\text{sens}} = 70.6 \pm 14.0$ $\Phi_{\text{Eu}}^{\text{Eu}} = 43.0 \pm 2.2$	26.4 \pm 7.1	0.32 \pm 0.16	0.11 \pm 0.03	no emission
H ₂ O w/0.1 Tris-HCl	28.6 \pm 6.5	25.9 \pm 4.9			
H ₂ O w/0.1 Tris-HCl (degassed)	29.1 \pm 5.6	25.0 \pm 1.5			
D ₂ O			0.30 \pm 0.06	0.15 \pm 0.04	0.20 \pm 0.04

^aData are reported with standard deviations. All complexes as the nitrate salts with a concentration of 1×10^{-4} M. ^bReported as the 0–0 transition from Gd(III) complexes. ^cComplexes were dissolved in a 50:50 mixture of ethylene glycol and water.

due to variable hydrogen-bonding interactions between the oligo(ethylene) ligand moiety and the two different solvents.^{92,93} The singlet state shows a similar solvent-dependent behavior and is located approximately 7000 cm^{-1} higher than the triplet state, a gap conducive to good intersystem crossing.²⁵ The triplet state-lanthanide emissive states gaps are approximately 9000 cm^{-1} for Eu(III) and 6000 cm^{-1} for Tb(III), slightly larger than the suggested ranges for optimum energy transfer.^{94,95} The intrinsic quantum yield of emission of Eu(III) $\Phi_{\text{Eu}}^{\text{Eu}}$ ⁷⁸ can be determined to be 51.7 in acetonitrile and 43.0% in water (Table 1), with the latter value being slightly lower most likely due to luminescence quenching through the diffusion of outer-sphere water molecules.⁹⁶ Since the overall emission efficiency is a product of the sensitization efficiency, Φ_{sens} , and of $\Phi_{\text{Eu}}^{\text{Eu}}$, Φ_{sens} is 59.9% in acetonitrile and 70.6% in water. These values show that exclusion of solvent molecules from the first coordination sphere of the lanthanide ions and an overall combination of efficient intersystem crossing process with a good energy transfer between triplet state and excited state for the lanthanide ion are responsible for the high quantum yields of emission observed.

Other Ln(III) ions, which emit in the visible region of the spectrum, were also sensitized in aqueous solution. The emission spectra of the complexes of Dy(III), Pr(III), and Sm(III) with **1** are shown in Figure 4, while the spectrum of Tm(III) with **1** is shown in Figure 5. Absorption and excitation spectra and emission peak assignments are shown in Figures S15–S18 (Supporting Information). In the case of Dy(III) and Sm(III) no residual ligand emission is seen at the onset of the emission spectra of the metal ions, indicating efficient energy transfer. For Tm and Pr, with their emissive states 1G_4 situated at approximately 21 300 cm^{-1} and 3P_0 at approximately 21 390 cm^{-1} ,⁹⁷ respectively, significant residual ligand emission is seen, as a result of either inefficient ligand to metal energy transfer or due to back-transfer from the emissive state to the ligand.

Sensitization of the near-infrared-emitting Ln(III) ions Yb(III), Nd(III), and Er(III) was also achieved and is shown in Figure 6. Emission spectra with peak assignments along with absorption and excitation spectra for these three ions are shown in Figures S19–S21 (Supporting Information). Exciting the Yb(III) complexes at 290 nm resulted in its characteristic emission at 991 nm, corresponding to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition. Similarly, the Nd(III) complex displayed emission

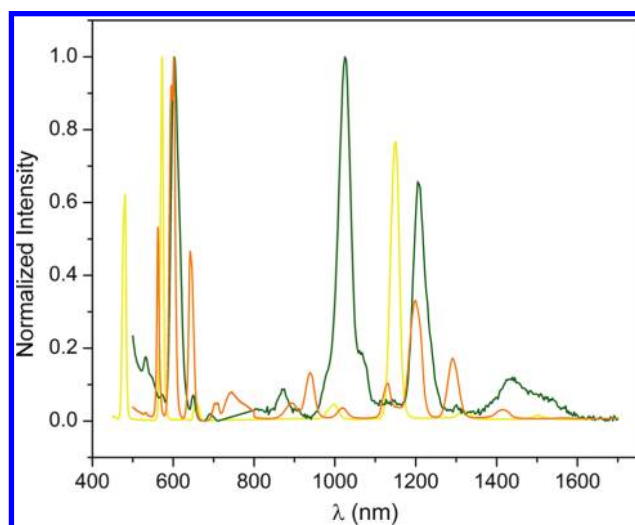


Figure 4. Emission spectra of the complexes $[\text{Ln}(\mathbf{1})_3]^{3+}$ (Ln = Dy (yellow), Pr (green), Sm (orange)). [complex] = 1×10^{-4} M, λ_{exc} 290 nm.

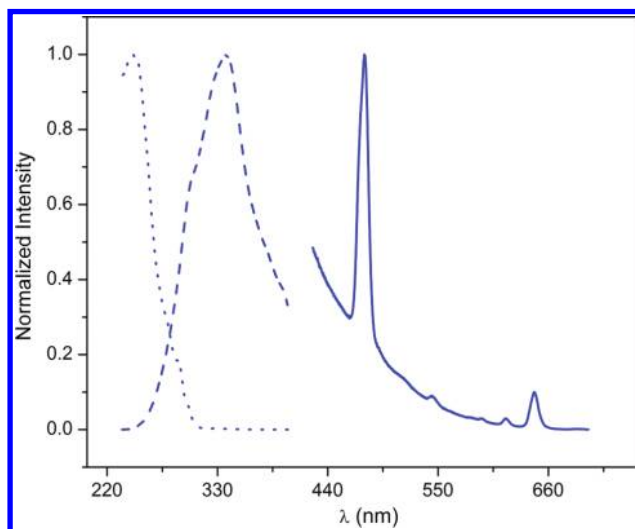


Figure 5. Absorption (dotted), excitation (dashed), and emission spectra (solid) of $[\text{Tm}(\mathbf{1})_3]^{3+}$. [complex] = 1×10^{-4} M, λ_{exc} 290 nm.

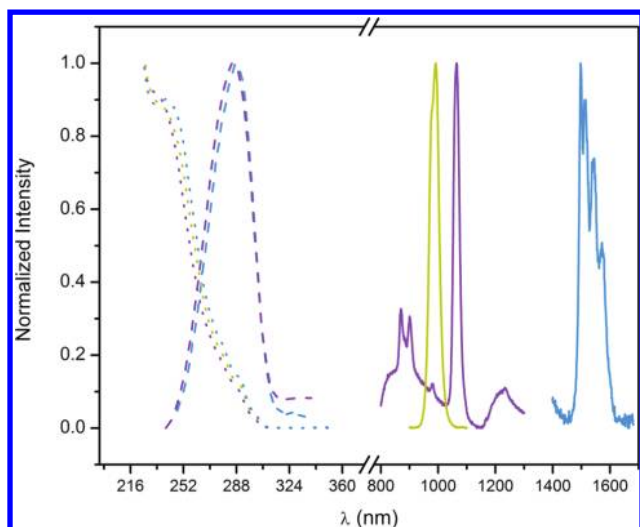


Figure 6. Absorption (dotted), excitation (dashed), and emission spectra (solid) of $[\text{Ln}(\mathbf{1})_3]^{3+}$ ($\text{Ln} = \text{Yb}$ (gold), Nd (purple), Er (blue)) in D_2O . $[\text{complex}] = 1 \times 10^{-4} \text{ M}$, $\lambda_{\text{exc}} = 290 \text{ nm}$.

bands at 876, 909, 1060, and 1336 nm, which correspond to the $^4\text{F}_{3/2} \rightarrow ^4\text{F}_j$ ($j = ^9/2, ^{11}/2, ^{13}/2$) transitions.

For the $\text{Er}(\text{III})$ complex the emission maximum is located at 1497 nm, corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. Emission was observed for all solvents with all near-IR-emitting ions, except for $\text{Er}(\text{III})$, whose emission is not observed in water but is in D_2O . This is due to the fact that water has strong absorption bands located in the 1500 nm region of the spectrum, while the absorption bands of D_2O are at 1900 nm.⁹⁸ The quantum yields of emission for the near-IR-emitting $\text{Ln}(\text{III})$ ions are summarized in Table 1 and are high in comparison with literature values, which are in the range 0.02–0.18% and 0.1–0.45% for $\text{Yb}(\text{III})$ and 0.004–0.02% and 0.02–0.038 for $\text{Nd}(\text{III})$ in H_2O and D_2O , respectively.^{98–100} The quantum yields for $\text{Er}(\text{III})$ are up to 10 times greater than the literature values of 0.004–0.019% in D_2O .^{98,99} The emission efficiencies for these ions are also fairly independent of the concentration chosen (Figure S2, Supporting Information).

The excited-state lifetimes for $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ were determined in water and deuterium oxide, confirming the absence of inner-sphere water molecules (q),⁷⁹ as summarized in Table 2, along with lifetimes in acetonitrile. The emission intensity decay curves could be fit to a single exponential, indicating that only one emissive species exists in solution.

Table 2. Excited State Lifetimes with Standard Deviations for the 3:1 Ligand to Metal Species in MeCN, H_2O , and D_2O Solutions and the Corresponding Number of Inner-Sphere Water Molecules

$\text{Ln}(\text{III})$	τ_{MeCN} (ms)	$\tau_{\text{H}_2\text{O}}$ (ms)	$\tau_{\text{D}_2\text{O}}$ (ms)	q
$\text{Eu}(\text{III})$	2.87 ± 0.15	1.61 ± 0.10	2.72 ± 0.02	0.24 ± 0.04
$\text{Tb}(\text{III})$	2.03 ± 0.05	1.78 ± 0.10	2.10 ± 0.08	0.30 ± 0.18

Both $\text{Eu}(\text{III})$ and $\text{Tb}(\text{III})$ display long emission lifetimes in acetonitrile at 2.87 and 2.03 ms, respectively. These are longer than lifetimes for similar complexes with thiophen-3-yl-derivatized and methoxy-derivatized Pybox reported by our group.^{34,35} The data in acetonitrile are mirrored by exceptionally long emission lifetimes in water and deuterated water, which are again consistent with an inner coordination sphere

from which water molecules are excluded. This is similar to what was previously observed for other Pybox derivatives, where it was shown that moderate amounts of water present in organic solvents did not influence the emission behavior.³⁵

Since previous studies on other para-derivatized Pybox-containing systems showed the selective formation of three species with 1:1, 2:1 and 3:1 ligand to metal ion stoichiometry in solution and in the solid state depending on the stoichiometry of the reagents used, we also performed speciation studies by emission spectroscopy on this new ligand and its complexes. Example titrations can be seen in Figures S22 and S23 (Supporting Information).

Table 3. Speciation Data of $\text{Ln}(\text{CF}_3\text{SO}_3)_3$ with $\text{PyboxO}(\text{CH}_2)_2\text{OEt}$ in Aqueous Solution with 0.1 M Tris Buffer Obtained by Emission Titrations ($I = 0.1 \text{ M Et}_4\text{NCl}$)

$\text{Ln}(\text{III})$	$\log \beta_{11}$	$\log \beta_{21}$	$\log \beta_{31}$
$\text{Eu}(\text{III})$	5.3 ± 0.5	9.6 ± 0.3	13.8 ± 0.4
$\text{Tb}(\text{III})$	5.3 ± 0.3	9.2 ± 0.1	12.7 ± 0.3

The stability constants $\log \beta$, summarized in Table 3, are consistent with the stepwise formation of 1:1, 2:1, and 3:1 ligand to metal complexes and as shown in the speciation diagrams shown in Figure 7 for the titration of **1** with $\text{Tb}(\text{III})$ and Figure S24 (Supporting Information) for the titration of **1** with $\text{Eu}(\text{III})$. The stability constants are higher than those for previously reported Pybox complexes with either hydrogen or a methoxy group at the para position of the pyridine ring. For those complexes stability constants were in the range $\log \beta_{31}$ 12.0–12.8 for $\text{Eu}(\text{III})$ and 11.7–12.2 for $\text{Tb}(\text{III})$. They are, however, not as high as for complexes with bromo- and thiophen-3-yl-derivatized Pybox, which showed stability constants in the range $\log \beta_{31}$ 14.9–15.5 for $\text{Eu}(\text{III})$ and 12.7–15.4 for $\text{Tb}(\text{III})$. Nonetheless, the complexes' stability prevents the coordination of water molecules in the first coordination sphere and resulting concentration quenching, leading to very efficient luminescence in aqueous solution.

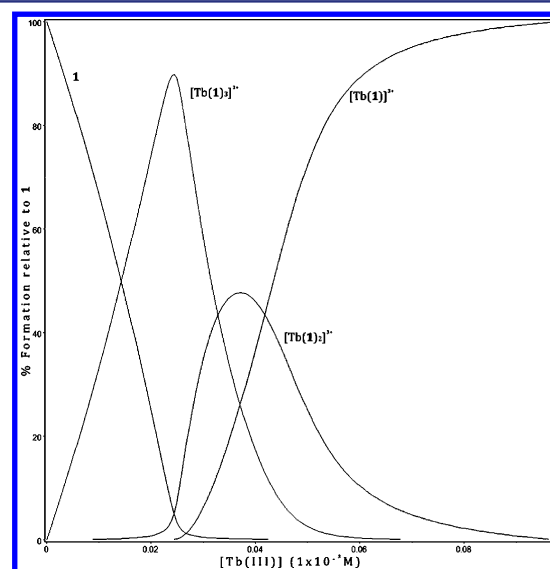


Figure 7. Speciation diagram of the titration of **1** with $\text{Tb}(\text{III})$ at constant 0.1 M ionic strength and pH 7.4.

■ CONCLUSIONS

In summary, we have successfully synthesized a water-soluble Pybox ligand that efficiently sensitizes emission of several Ln(III), in both the visible and near-IR regions, in organic solvents and also in aqueous solution. We have shown that the ligand successfully shields the coordination environment of the lanthanide ions from water molecules. Along with appropriately located singlet and triplet energy levels, high emission efficiencies could be measured in the visible and near-infrared regions of the spectrum, which are fairly independent of the solvent and complex concentration. These complexes are promising for luminescence applications in aqueous environments, and the new water-soluble ligand opens up new possibilities for aqueous catalysis.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and the CIF file giving ESI mass spectra, NMR spectra, and additional emission, absorption, and excitation spectra and crystal data for $1 \cdot \text{H}_2\text{O}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Science Foundation (Grant Nos. NSF-CHE0733458 and NSF-CHE1058805) and the University of Nevada, Reno, for supporting this work financially.

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