# Luminescent Lanthanide Coordination Polymers

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One-dimensional lanthanide coordination polymers with the formula Ln(isonicotinate)$_3$(H$_2$O)$_2$ (Ln = Ce, Pr, Nd, Sm, Eu, Tb; **1a**−**f**) were synthesized by treating nitrate or perchlorate salts of Ln(III) with 4-pyridinecarboxaldehyde under hydro(solvo)thermal conditions. Single-crystal and powder X-ray diffraction studies indicate that these lanthanide coordination polymers adopt two different structures. While Ce(III), Pr(III), and Nd(III) complexes adopt a chain structure with alternating Ln−(carboxylate)$_2$−Ln and Ln−(carboxylate)$_4$−Ln linkages, Sm(III), Eu(III), and Tb(III) complexes have a doubly carboxylate-bridged infinite-chain structure with one chelating carboxylate group on each metal center. In both structures, the lanthanide centers also bind to two water molecules to yield an eight-coordinate, square antiprismatic geometry. The pyridine nitrogen atoms of the isonicotinate groups do not coordinate to the metal centers in these lanthanide(III) complexes; instead, they direct the formation of Ln(III) coordination polymers via hydrogen bonding with coordinated water molecules. Photoluminescence measurements show that Tb(isonicotinate)$_3$(H$_2$O)$_2$ is highly emissive at room temperature with a quantum yield of ∼90%. These results indicate that highly luminescent lanthanide coordination polymers can be assembled using a combination of coordination and hydrogen bonds. Crystal data for **1a**: monoclinic space group $P2_1/c$, $a$ = 9.712(2) Å, $b$ = 19.833(4) Å, $c$ = 11.616(2) Å, $\beta$ = 111.89(3)°, $Z$ = 4. Crystal data for **1f**: monoclinic space group $C2/c$, $a$ = 20.253(4) Å, $b$ = 11.584(2) Å, $c$ = 9.839(2) Å, $\beta$ = 115.64(3)°, $Z$ = 8.

## Introduction

Self-assembly processes directed by either hydrogen bonds[1−3] or metal−ligand ligation[4−9] have been extensively utilized to construct supramolecular systems with novel topologies and potentially interesting functions. Our group recently became interested in the supramolecular engineering of optically active coordination networks, in particular, the crystal engineering of acentric and chiral coordination polymers for second-order nonlinear optical applications.[10,11] Our work focuses on the construction of neutral coordination polymers using anionic bifunctional linking groups such as pyridinecarboxylates with the aim of delineating the relationship between bridging ligands and resulting coordination polymers and eventual rational synthesis of functional solids based on molecular building blocks.[10−13] Although the synthesis of coordination polymers based on transition metals has become widespread over the past decade,[4−13] there are few reports on lanthanide coordination polymers despite their potential utility as luminescent and sensory materials.[14] Herein we wish to report the synthesis and characterization of highly luminescent lanthanide coordination polymers resulting from self-assembly processes directed by both metal−ligand ligation and hydrogen-bonding interactions.

## Experimental Section

**Materials and Methods.** All chemicals were purchased from Aldrich and used without further purification. The IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. X-ray powder diffraction data (XRPD) were recorded on a Rigaku RU300 diffractometer at 60 kV and 300 mA for Cu Kα radiation ($\lambda$ = 1.5406 Å), with a scan speed of 2°/min and a step size of 0.02° in 2$\theta$. Elemental and thermogravimetric analyses were done at the Microanalytical Laboratory of the University of Illinois at Urbana-Champaign. TGA experiments were carried out on a Shimadzu TGA 150 instrument at a heating rate of 15 °C/min.

**Synthesis of Ce(isonicotinate)$_3$(H$_2$O)$_2$, 1a.** A mixture of 40% Ce-(ClO$_4$)$_3$ solution in water (0.365 mL, 0.5 mmol) and 4-pyridinecarboxaldehyde (2 mmol) was thoroughly mixed with ethanol (0.2 mL) in a heavy-walled Pyrex tube. The Pyrex tube was sealed under vacuum (while frozen with liquid nitrogen) and heated in an oven at 120 °C. Crystalline products were obtained after 3 days of heating. Yield: 52%. Anal. Calcd for C$_{18}$H$_{16}$N$_3$O$_8$Ce: C, 39.9; H, 2.97; N, 7.75. Found: C, 39.8; H, 2.96; N, 7.83. IR (cm$^{-1}$): 3423 (ms), 3030 (ms), 1590 (s), 1548 (s), 1497 (ms), 1413 (s), 1226 (m), 1062 (m), 1005 (m), 862 (ms), 772 (ms), 714 (ms), 687 (ms), 676 (ms), 549 (w).

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**Synthesis of Pr(isonicotinate)₃(H₂O)₂, 1b.** Pr(NO₃)₃·6H₂O (0.218 g, 0.5 mmol) and 4-pyridinecarboxaldehyde (0.214 g, 2 mmol) were mixed with ethanol (0.2 mL) and H₂O (0.1 mL) in a heavy-walled Pyrex tube. The Pyrex tube was sealed under vacuum (while frozen with liquid nitrogen) and heated in an oven at 120 °C. Crystalline products were obtained after 5 days of heating. Yield: 93%. Anal. Calcd for C₁₈H₁₆N₃O₈Pr: C, 39.8; H, 2.97; N, 7.73. Found: C, 39.0; H, 2.90; N, 8.09. IR (cm⁻¹): 3421 (ms), 3032 (ms), 1589 (s), 1548 (s), 1497 (ms), 1414 (s), 1226 (m), 1062 (m), 1005 (m), 863 (ms), 772 (ms), 715 (ms), 687 (ms), 674 (ms), 550 (w).

The syntheses of **1c–f** were carried out similarly to that of **1b**.

**Nd(isonicotinate)₃(H₂O)₂, 1c.** Yield: 51%. Anal. Calcd for C₁₈H₁₆N₃O₈Nd: C, 39.5; H, 2.95; N, 7.69. Found: C, 39.5; H, 2.84; N, 7.58. IR (cm⁻¹): 3400 (ms), 3070 (ms), 1590 (s), 1549 (s), 1497 (ms), 1414 (s), 1226 (m), 1062 (m), 1005 (m), 863 (ms), 772 (ms), 715 (ms), 685 (ms), 675 (ms), 552 (w).

**Sm(isonicotinate)₃(H₂O)₂, 1d.** Yield: 36%. Anal. Calcd for C₁₈H₁₆N₃O₈Sm: C, 39.1; H, 2.92; N, 7.60. Found: C, 38.7; H, 2.78; N, 7.19. IR(cm⁻¹): 3386 (ms), 3042 (ms), 1588 (s), 1544 (s), 1495 (ms), 1414 (s), 1225 (m), 1060 (m), 1001 (m), 864 (ms), 774 (ms), 713 (ms), 692 (ms), 681 (ms), 557 (w).

**Eu(isonicotinate)₃(H₂O)₂, 1e.** Yield: 61%. Anal. Calcd for C₁₈H₁₆N₃O₈Eu: C, 39.0; H, 2.91; N, 7.58. Found: C, 38.4; H, 2.83; N, 7.57. IR (cm⁻¹): 3406 (ms), 3044 (ms), 1591 (s), 1549 (s), 1496 (ms), 1414 (s), 1226 (m), 1061 (m), 1003 (m), 865 (ms), 774 (ms), 714 (ms), 694 (ms), 682 (ms), 553 (w).

**Tb(isonicotinate)₃(H₂O)₂, 1f.** Yield: 51%. Anal. Calcd for C₁₈H₁₆N₃O₈Tb: C, 38.5; H, 2.87; N, 7.49. Found: C, 38.1; H, 2.87; N, 7.39. IR (cm⁻¹): 3384 (ms), 3042 (ms), 1591 (s), 1544 (s), 1495 (ms), 1416 (s), 1225 (m), 1060 (m), 1002 (m), 865 (ms), 774 (ms), 714 (ms), 694 (ms), 680 (ms), 560 (w).

**X-ray Data Collections and Structure Determinations.** Data collections for both **1a** and **1f** were carried out with an Enraf-Nonius CAD4-Turbo diffractometer equipped with Mo Kα radiation. Data were collected using the Nonius EXPRESS program.[15] Of the 6292 (2099) reflections measured, 4184 (1637) reflections with $I > 2\sigma(I)$ were used in structure solution and refinement for **1a** (**1f**). The structures were solved by direct methods[16] and refined[17] on $F^2$ by full-matrix least-squares calculations using anisotropic displacement parameters for all non-hydrogen atoms. For **1a**, two of the isonicotinate groups were disordered and were modeled with two different orientations. The hydrogen atoms on coordinated water molecules (H1, H1A, H2, H2A) were located in a difference electron density map and refined isotropically. All the other hydrogen atoms were located by geometric placement. Refinement converged at R1 = 0.026, wR2 = 0.063 [$I > 2\sigma(I)$], R1 = 0.051, wR2 = 0.071 (all data), and GOF = 1.04. The largest difference peak and hole are 1.04 and −0.77 e/Å³, respectively. For **1f**, the hydrogen atoms of the coordinated water molecules could not be located. All the other hydrogen atoms were located by geometric placement. Refinement converged at R1 = 0.043, wR2 = 0.103 [$I > 2\sigma(I)$], R1 = 0.069, wR2 = 0.112 (all data), and GOF = 1.06. The largest difference peak and hole are 1.48 and −0.66 e/Å³, respectively. Experimental details for X-ray data collections of **1a** and **1f** are given in Table 1. Selected bond distances and angles for **1a** and **1f** are listed in Table 2.

**Photoluminescence Measurements.** The photoluminescence measurements were carried out on powder samples inside capillary tubes. The spectra were taken with a 366 nm excitation source using an integrating sphere. The CCD detector was first calibrated with a standard sample. For the photoluminescence efficiency measurements, a sample was placed in the path of the excitation source. The excitation light intensity was first estimated by using a photodiode that is sensitive to wavelengths < 400 nm. The difference between the light intensity (<400 nm) without a sample and with a sample was assumed to be the absorbed photon energy ($I_0$). The emitted light intensity was

estimated by using a photodiode that is sensitive to wavelengths > 400 nm. To eliminate the background emission, the photon energy with wavelengths > 400 nm without a sample inside the integrating sphere was also measured. The difference between the light intensity (>400 nm) with a sample and without a sample was assumed to be the emitted photon energy ($I$). The value of $I/I_0$ is defined as the external quantum efficiency.

## Results and Discussion

**Synthesis.** One-dimensional lanthanide coordination polymers with a general formula of Ln(isonicotinate)₃(H₂O)₂ (Ln = Ce, Pr, Nd, Sm, Eu, Tb; **1a–f**) were synthesized from the reactions between nitrate or perchlorate salts of Ln(III) and 4-pyridin-

**Table 1.** Crystallographic Data for **1a** and **1f**

| | **1a** | **1f** |
|---|---|---|
| empirical formula | CeC₁₈H₁₆N₃O₈ | TbC₁₈H₁₆N₃O₈ |
| a, Å | 9.712(2) | 20.253(4) |
| b, Å | 19.833(4) | 11.584(2) |
| c, Å | 11.616(2) | 9.839(2) |
| β, deg | 111.89(3) | 115.64(3) |
| V, Å³ | 2076.2(7) | 2081.1(7) |
| Z | 4 | 8 |
| fw | 542.46 | 561.26 |
| space group | P2₁/c (No. 14) | C2/c (No. 15) |
| T, °C | 293(2) | 293(2) |
| λ(Mo Kα), Å | 0.710 73 | 0.710 73 |
| $\rho_{calc}$, g/cm³ | 1.735 | 1.791 |
| $\mu$(Mo Kα), cm⁻¹ | 22.4 | 34.5 |
| min and max residual density, e/Å³ | −0.77, 1.04 | −0.66, 1.48 |
| R1:[a] $I > 2\sigma(I)$ (all) | 0.026 (0.051) | 0.043 (0.069) |
| wR2:[a] $I > 2\sigma(I)$ (all) | 0.063 (0.071) | 0.103 (0.112) |
| goodness of fit[a] | 1.04 | 1.06 |

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $\{\sum[w(F_o - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$; GOF = $\{\sum[w(F_o{}^2 - F_c{}^2)^2]/(\text{no. of reflns} - \text{no. of params})\}^{1/2}$.

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg) for **1a** and **1f**

| Complex **1a** | | | |
|---|---|---|---|
| Ce1−O1 | 2.546(2) | Ce1−O5 | 2.473(2) |
| Ce1−O2 | 2.566(3) | Ce1−O6 | 2.494(2) |
| Ce1−O3 | 2.510(2) | Ce1−O7 | 2.470(2) |
| Ce1−O4 | 2.454(2) | Ce1−O8 | 2.449(2) |
| O1−Ce1−O2 | 122.27(8) | O3−Ce1−O5 | 78.62(7) |
| O1−Ce1−O3 | 141.85(8) | O3−Ce1−O6 | 79.09(7) |
| O1−Ce1−O4 | 77.42(7) | O3−Ce1−O7 | 140.23(7) |
| O1−Ce1−O5 | 138.48(7) | O3−Ce1−O8 | 79.68(7) |
| O1−Ce1−O6 | 70.68(7) | O4−Ce1−O5 | 70.28(6) |
| O1−Ce1−O7 | 69.20(8) | O4−Ce1−O6 | 80.43(6) |
| O1−Ce1−O8 | 72.13(8) | O4−Ce1−O7 | 84.11(7) |
| O2−Ce1−O3 | 70.38(8) | O4−Ce1−O8 | 147.31(7) |
| O2−Ce1−O4 | 136.09(7) | O5−Ce1−O6 | 126.34(7) |
| O2−Ce1−O5 | 71.08(8) | O5−Ce1−O7 | 81.95(7) |
| O2−Ce1−O6 | 141.00(7) | O5−Ce1−O8 | 142.22(7) |
| O2−Ce1−O7 | 70.58(7) | O6−Ce1−O7 | 139.22(7) |
| O2−Ce1−O8 | 72.66(8) | O6−Ce1−O8 | 78.59(7) |
| O3−Ce1−O4 | 120.35(7) | O7−Ce1−O8 | 95.77(7) |

| Complex **1f** | | | |
|---|---|---|---|
| Tb1−O1 | 2.380(6) | Tb1−O3 | 2.450(5) |
| Tb1−O2B | 2.282(6) | Tb1−O4 | 2.403(5) |
| O1−Tb1−O3 | 73.5(2) | O2B−Tb1−O3 | 127.2(2) |
| O1−Tb1−O4 | 141.9(2) | O2B−Tb1−O4 | 84.7(2) |
| O1−Tb1−O1A | 143.2(2) | O2C−Tb1−O3A | 127.2(2) |
| O1−Tb1−O3A | 73.6(2) | O2C−Tb1−O3 | 75.4(2) |
| O1−Tb1−O4A | 74.0(2) | O2C−Tb1 −O4 | 77.0(2) |
| O1−Tb1−O2B | 103.8(2) | O3−Tb1−O4 | 130.3(2) |
| O1−Tb1−O2C | 83.5(2) | O3−Tb1−O3A | 52.6(2) |
| O2B−Tb1−O3A | 75.4(2) | O3−Tb1−O4A | 143.4(2) |
| O2B−Tb1−O2C | 157.3(2) | O4−Tb1−O4A | 72.0(2) |

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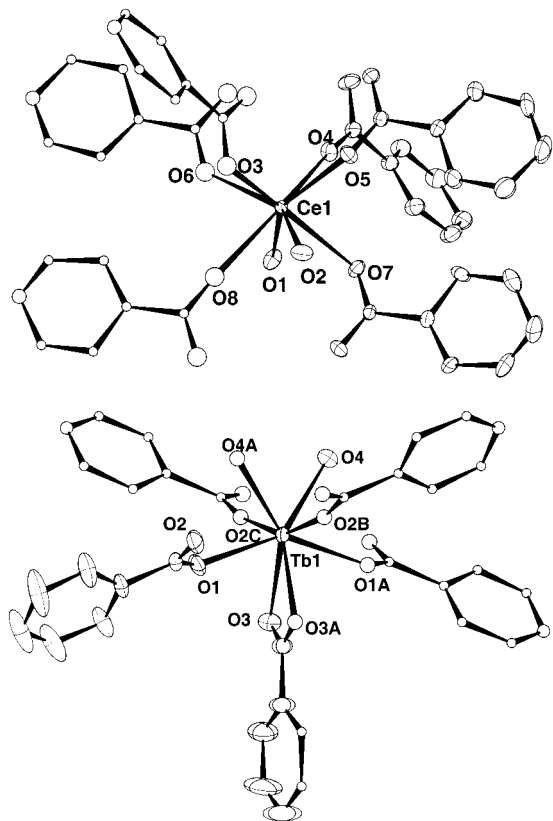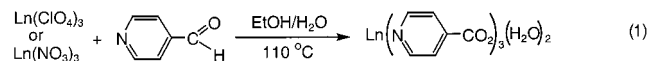
**Figure 1.** Coordination geometry of (top) the Ce1 center in **1a** and (bottom) the Tb1 center in **1f**. The asymmetric unit is represented with thermal ellipsoids at 50% probability.

ecarboxaldehyde in a mixture of ethanol and water at 110 °C (eq 1). The formulations of **1a**–**f** were supported by elemental



analyses and thermogravimetric analyses (TGA). The presence of strong IR peaks at ~1549 and ~1414 cm$^{-1}$ indicated the formation of isonicotinate groups from 4-pyridinecarboxalde-hyde during the hydro(solvo)thermal reactions.[18] 4-Pyridinecar-boxaldehyde has presumably been oxidized by nitrate or perchlorate groups to result in the isonicotinate ligand under hydro(solvo)thermal conditions. In situ generation of desired ligands (via oxidation or hydrolysis) was recently successfully used in our group to synthesize extended coordination networks with bifunctional bridging ligands.[10–13] Such reaction conditions favor the formation of less soluble neutral coordination polymers owing to the presence of excess amounts of metal cations.

**X-ray Structures.** X-ray single-crystal diffraction studies reveal the 1-D polymeric nature of both **1a** and **1f**. However, **1a** and **1f** have entirely different coordination environments. **1a** crystallizes in the monoclinic space group $P2_1/c$, with all the atoms lying on general positions. The Ce1 center in **1a** coordinates to six carboxylate oxygen atoms of bridging isonicotinate groups and to two water molecules (Figure 1). The coordination geometry around the Ce1 center can be described as a distorted square antiprism with O–Ce1–O bond angles ranging from 70.3 to 147.3°. The Ce center is alternately bridged by two and four carboxylate groups to adjacent Ce centers to result in an infinite 1-D chain (Figure 2). All the carboxylate
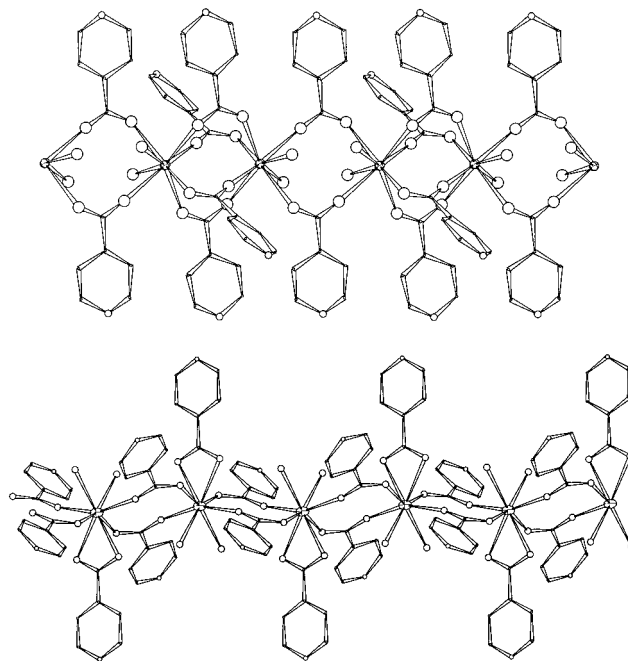
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**Figure 2.** Illustration of 1-D chains in (top) **1a** and (bottom) **1f**. The ellipsoids represent the Ln centers, while the circles with increasing sizes represent C, N, and O, respectively.
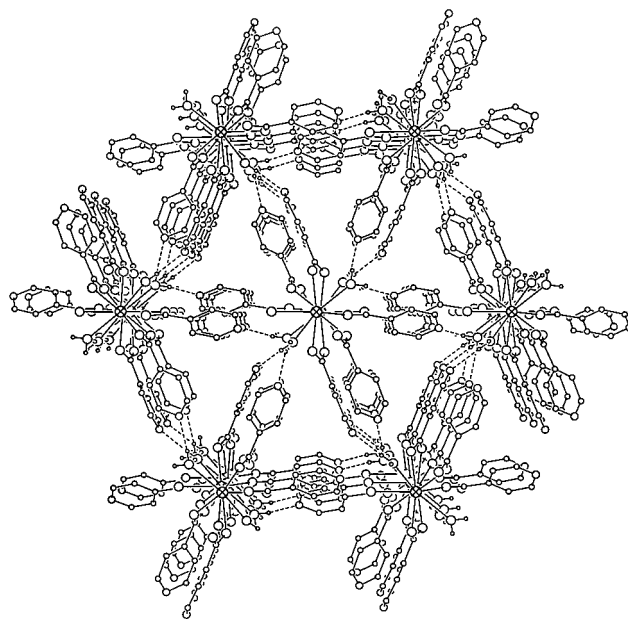


**Figure 3.** Perspective view of **1a** down the *a* axis showing the 3-D network resulting from hydrogen bonding between pyridyl nitrogen atoms and coordinated water molecules. O(1)–H(1)···N(2): 2.774(4) Å, 168(4)°. O(1)–H(1A)···N(1): 2.788(3) Å, 169(4)°. O(2)–H(2A)···N(3): 2.835(5) Å, 174(2)°.

bridges adopt a syn-anti conformation to exhibit a Ce–Ce distance of 5.379 Å. The carboxylate-bridged 1-D chains are linked to each other via hydrogen bonds between pyridyl nitrogen atoms and coordinated water molecules to form a 3-D network (Figure 3).

Compound **1f** crystallizes in the monoclinic space group *C*2/*c*. The Tb1 center lies on a crystallographic 2-fold axis. In contrast to the Ce1 center in **1a**, the Tb1 center in **1f** coordinates to four carboxylate oxygen atoms of bridging isonicotinate groups, two carboxylate oxygen atoms of the chelating isoni-cotinate group, and two water molecules (Figure 1). The Tb1
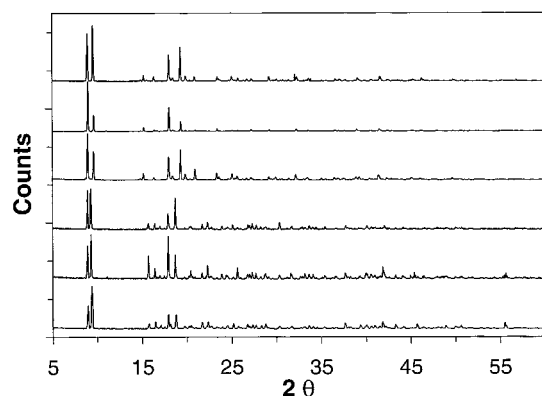
**Figure 4.** X-ray powder diffraction patterns for **1a−f**. The patterns from the bottom to the top represent Ce, Pr, Nd, Sm, Eu, and Tb compounds, respectively.

**Table 3.** TGA Results for Compounds **1a−f**

| compd | obsd wt loss, % | wt loss expected for two water molecules, % | temp range, °C | onset dec temp, °C |
|---|---|---|---|---|
| **1a** | 6.61 | 6.64 | 164−193 | 439 |
| **1b** | 6.37 | 6.63 | 134−188 | 443 |
| **1c** | 6.48 | 6.59 | 178−211 | 462 |
| **1d** | 6.22 | 6.52 | 126−159 | 448 |
| **1e** | 6.45 | 6.50 | 115−145 | 439 |
| **1f** | 6.43 | 6.42 | 125−155 | 459 |

center also has a distorted square antiprism coordination geometry with O−Tb1−O bond angles ranging from 52.9 to 157.4°. The Tb centers in **1f** are doubly bridged by carboxylate groups of isonicotinate ligands to form an infinite 1-D chain (Figure 2). The carboxylate bridges also adopt a syn-anti conformation to exhibit a Tb−Tb distance of 4.928 Å. The shorter Tb−Tb distance in **1f** is a result of the smaller Tb radius (vs Ce). Although we have not been able to locate the hydrogen atoms on coordinated water molecules, the presence of interchain hydrogen bonds in **1f** can be inferred from the short distances between pyridyl nitrogen atoms and coordinated water oxygen atoms (N1−O4 distance 2.799 Å; N2−O4 distance 2.955 Å). The assembly of bulk **1a−f** thus appears to be steered by the interchain hydrogen bonds formed between pyridine nitrogen atoms of isonicotinate bridging groups and coordinated water molecules. The directing role of hydrogen bonds in the formation of **1a−f** is further supported by a control experiment with benzaldehyde in place of 4-pyridinecarboxaldehyde; no coordination polymer analogous to **1a−f** could be obtained under similar conditions.

Interestingly, X-ray powder diffraction studies indicate that Pr and Nd compounds adopt the same structure as **1a** while Sm and Eu compounds have the same structure as **1f** (Figure 4). The difference in coordination environments among **1a−f** is probably a result of the reduction in atomic radius from Ce to Tb (i.e., lanthanide contraction). The steric demand on a metal center is probably less when a carboxylate group adopts chelation rather than a bridging mode. Compounds **1a−f** represent one of the few known carboxylate-bridged lanthanide coordination polymers.[14,19,20]

**TGA and Photoluminescent Results.** The formulations of **1a−f** as Ln(isonicotinate)₃(H₂O)₂ were further supported by TGA results which all exhibited weight losses corresponding

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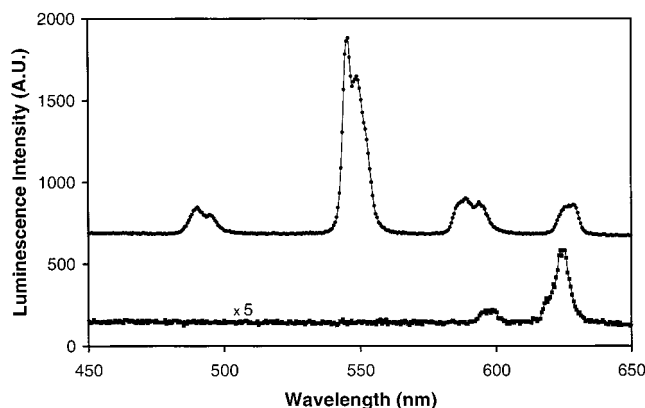


**Figure 5.** Photoluminescence spectra of **1e** (bottom) and **1f** (top) with a 366 nm excitation source.

to two water molecules per formula unit (Table 3). We have measured the photoluminescence spectra of powder samples of the europium compound **1e** and terbium compound **1f** at room temperature. When excited at a 366 nm source, **1e** and **1f** emit red and green light, respectively (Figure 5). The emission peaks of **1e** at 595 and 620 nm can be assigned to $^5D_0 \rightarrow ^7F_n$ ($n = 1$, 2) transitions, while the emission peaks of **1f** at 490, 545, 585, and 625 nm can be assigned to $^5D_4 \rightarrow ^7F_n$ ($n = 6, 5, 4, 3$) transitions, respectively. It is interesting to note that the $^5D_0 \rightarrow ^7F_2$ transition is much more intense than the $^5D_0 \rightarrow ^7F_1$ transition in **1e**. This is entirely consistent with the fact that the Eu centers in **1e** do not possess inversion symmetry.[21] The $^5D_0 \rightarrow ^7F_2$ transition is the preferred transition for europium-containing luminescent materials. The crystal-field splitting is also clearly present in all the transitions in **1f**, apparently as a result of the large $J$ values involved in these transitions. By using an integrating sphere, we also estimate that the photoluminescence efficiencies are 8.6% and 90.0% for compounds **1e** and **1f**, respectively.

## Summary

We have demonstrated the assembly of interesting lanthanide coordination polymers using a combination of coordination and hydrogen bonds. A combination of X-ray single-crystal and powder diffraction studies reveals a very interesting structural trend from **1a** to **1f** as a result of lanthanide contraction. Photoluminescence measurements indicate that the terbium compound **1f** is highly emissive with a quantum yield of ∼90%. Further work is being directed toward the synthesis of lanthanide coordination networks with both luminescence properties and tunable porosities for potential detection of volatile organics.

**Supporting Information Available:** Figures presenting an ORTEP drawing of **1a** and TGA curves of **1a−f** and X-ray crystallographic files, in CIF format, for the structure determinations of **1a** and **1f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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