

Novel Lanthanide Coordination Polymers Prepared by Microwave Heating: [Ln(L)₃(H₂O)₂](H₂O)₃ (Ln = Eu, Tb, Gd; L = *trans*-(3-py)-CH=CH-COO)

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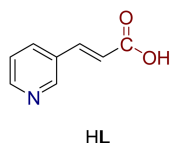
Three isostructural lanthanide coordination polymers, [Ln(L)₃(H₂O)₂](H₂O)₃ {Ln = Eu (**1**), Tb (**2**), Gd (**3**); L = *trans*-3-(3-pyridyl)acrylate, (3-py)-CH=CH-COO}, were prepared from HL, lanthanide nitrate, and NaOH in H₂O by microwave heating. In all coordination polymers, the metal is bonded to eight oxygen atoms, and all pyridyl nitrogen atoms do not coordinate to the metals. All polymers have a 1-D loop-connected chain structure. The hydrogen atoms in the aqua ligands and lattice water molecules all participate in the hydrogen bonds of the O-H...O or O-H...N type. The hydrogen bonds connect the 1-D chains to create a 2-D network. Polymer **1** exhibited red luminescence in the solid state at room temperature.

Key Words : Lanthanide coordination polymers, Crystal structure, Microwave heating, Luminescence

Introduction

Coordination polymers currently draw much attention due to their desirable properties applicable to various fields, including catalysis, magnetism, adsorption-desorption, photoluminescence, electrical conductivity, gas storage, and drug delivery.¹⁻⁵ Linking ligands possessing pyridyl-pyridyl, pyridyl-amine, multicarboxylate, or pyridyl-carboxylate terminals are commonly employed as organic spacers in constructing coordination polymers.⁶⁻²¹ In particular, the pyridyl-carboxylate-type ligands show intriguing coordination modes because they contain both an oxygen donor (carboxylate terminal) and a nitrogen donor (pyridyl terminal).⁶ Consistent with the well-established hard-soft acid-base (HSAB) concept, the harder oxygen atoms prefer to coordinate to *f*-block metals and the softer nitrogen atoms to *d*-block metals in *d-f* coordination polymers.¹³⁻¹⁸

trans-3-(3-Pyridyl)acrylic acid (HL), a pyridyl-carboxylate type ligand, has been used for the preparation of several coordination polymers of *d*-block metals.¹⁹⁻²³ In addition, two *f*-block coordination polymers were synthesized by employing this ligand: a 1-D Eu coordination polymer, [Eu(L)₃(H₂O)]₂,²⁴ and a 1-D Nd coordination polymer [Nd(L)₃(H₂O)].¹⁸ This ligand was also used to prepare a 3-D Cu-Nd (3*d*-4*f*) polymer [Cu₃Nd₂(L)₆(NO₃)₆].¹⁸



Coordination polymers are commonly synthesized by hydrothermal or solvothermal methods, which require a long reaction time at relatively high temperatures. Microwave-assisted syntheses are currently utilized to synthesize various

compounds because of its wonderful advantages of the short reaction time and high reproducibility. In particular, several coordination polymers were recently prepared by microwave heating.²⁵⁻³² In our ongoing study of coordination polymers, we decided to adopt the microwave-heating method to prepare *f*-block coordination polymers of the title ligand (L). We herein report the synthesis of three isostructural lanthanide coordination polymers, [Ln(L)₃(H₂O)₂](H₂O)₃ {Ln = Eu (**1**), Tb (**2**), Gd (**3**)}, together with their physical properties.

Experimental Section

Lanthanide nitrates were purified by recrystallization. *trans*-3-(3-Pyridyl)acrylic acid (HL) was purchased and used as received. Infrared (IR) samples were prepared as KBr pellets, and their spectra were obtained in the range of 400-4000 cm⁻¹ on a Nicolet 320 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA4000/SDT 2960 instrument at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University. Elemental analyses were carried out by the Analytical Laboratory at Kangneung-Wonju National University. Solid-state luminescent spectra were obtained with an Aminco-Bowman Series2 (Xenon lamp, 150 W).

Preparation of [Eu(L)₃(H₂O)₂](H₂O)₃ (1**).** All three polymers in the same way. [Eu(NO₃)₃·5H₂O] (100 mg, 0.234 mmol) was added to a mixture of HL (100 mg, 0.702 mmol), 0.7 mL of 1 M NaOH(aq) (0.7 mmol), and H₂O (4 mL) in a 25 mL Teflon-lined autoclave vessel. The mixture was heated in a microwave oven (700 W) for 1 min. The resulting solution was filtered and then air-cooled slowly. After 1 h, the resulting colorless crystals were filtered and washed with ethanol (5 mL × 3) and H₂O (5 mL × 3) to give polymer **1** (40 mg, 0.058 mmol).

Data for polymer **1** (24.8% yield): IR (KBr, cm^{-1}): 3557 (m), 3370 (m), 3298 (m), 2895 (m), 2376 (m), 2087 (m), 1735 (m), 1643 (s, $\nu_{\text{C}=\text{C}}$), 1551 (s), 1393 (s), 1300 (w), 1257 (s), 1173 (w), 1120 (w), 1036 (w), 984 (s), 886 (m), 853 (w), 814 (m), 760 (m), 700 (m), 640 (m), 600 (m), 545 (m), 479 (m). Anal. Calc. for $\text{C}_{24}\text{H}_{28}\text{EuN}_3\text{O}_{11}$ ($M_r = 686.45$): C, 41.99; H, 4.11; N, 6.12%. Found: C, 41.82; H, 3.87; N, 6.39%.

Data for polymer **2** (23.1% yield): IR (KBr, cm^{-1}): 3554 (w), 3176 (s), 2378 (w), 1644 (s, $\nu_{\text{C}=\text{C}}$), 1548 (s), 1400 (s), 1301 (w), 1259 (m), 1180 (w), 1122 (w), 1036 (w), 882 (m), 814 (m), 704 (m), 640 (w), 602 (w), 546 (w), 487 (w). Anal. Calc. for $\text{C}_{24}\text{H}_{28}\text{TbN}_3\text{O}_{11}$ ($M_r = 693.41$): C, 41.57; H, 4.07; N, 6.06%. Found: C, 41.67; H, 3.69; N, 6.29%.

Data for polymer **3** (25.0% yield): IR (KBr, cm^{-1}): 3558 (m), 2929 (s), 2377 (w), 1644 (s, $\nu_{\text{C}=\text{C}}$), 1553 (s), 1391 (s), 1301 (w), 1258 (s), 1177 (w), 1122 (m), 1036 (w), 985 (s), 883 (s), 815 (s), 756 (m), 705 (m), 639 (s), 598 (s), 543 (m), 488 (m). Anal. Calc. for $\text{C}_{24}\text{H}_{28}\text{GdN}_3\text{O}_{11}$ ($M_r = 691.74$): C, 41.67; H, 4.08; N, 6.07%. Found: C, 41.26; H, 3.87; N, 6.52%.

X-ray Structure Determination. All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube (CCRF). Absorption corrections were made by SADABS on the basis of the Laue symmetry of equivalent reflections.³³ All calculations were carried out with SHELXTL programs.³⁴ A colorless crystal of polymer

1 of approximate dimensions $0.30 \times 0.20 \times 0.18 \text{ mm}^3$, shaped as a block, was used for crystal and intensity data collection. A colorless crystal of polymer **2** (a block, $0.20 \times 0.16 \times 0.10 \text{ mm}^3$) and a colorless crystal of polymer **3** (a block, $0.30 \times 0.10 \times 0.06 \text{ mm}^3$) were used.

All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located and refined freely. Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 854763-854765 contain the supplementary crystallographic data for coordination polymers **1-3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Results and Discussion

Preparation. Three lanthanide coordination polymers, $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$ {Ln = Eu (**1**), Tb (**2**), Gd (**3**)}, were synthesized in H_2O by microwave heating (Scheme 1). Polymer **1** was prepared from *trans*-3-(3-pyridyl)acrylic acid (HL), NaOH(aq), and $[\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$. Polymers **2**

Table 1. X-ray data collection and structure refinement

	Polymer 1	Polymer 2	Polymer 3
Empirical formula	$\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_{11}\text{Eu}$	$\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_{11}\text{Tb}$	$\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_{11}\text{Gd}$
Formula weight	686.45	693.41	691.74
Temperature, K	296(2)	296(2)	296(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a , Å	9.5586(2)	9.5383(1)	9.5502(2)
b , Å	12.6152(2)	12.5674(2)	12.5828(2)
c , Å	22.9512(4)	22.9514(4)	22.9473(4)
β (°)	97.579(1)	97.627(1)	97.697(1)
V , Å ³	2743.36(9)	2726.88(7)	2732.69(9)
Z	4	4	4
D_{calc} , g cm ⁻³	1.662	1.689	1.681
μ , mm	2.349	2.656	2.490
$F(000)$	1376	1384	1380
θ range (°)	1.79–28.47	1.79–28.29	1.85–28.24
T_{max}	0.6772	0.7771	0.8650
T_{min}	0.5392	0.6186	0.5221
No. of reflections measured	46206	47186	38817
No. of reflections unique	6877	6747	6648
No. of reflections with $I > 2\sigma(I)$	5363	4220	4202
No. of parameters	464	464	464
Max., in $\Delta\rho$ (e Å ⁻³)	1.654	0.701	0.716
Min., in $\Delta\rho$ (e Å ⁻³)	−0.318	−0.579	−1.020
GOF on F^2	1.030	1.016	1.054
$R1^a$	0.0239	0.0302	0.0350
$wR2^b$	0.0515	0.0498	0.0508

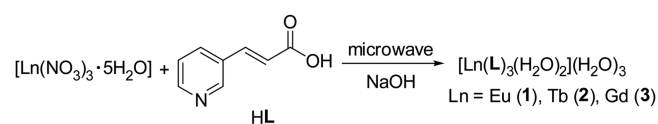
^a $R_1 = \sum ||F_o| - |F|| / \sum |F_o|$, ^b $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$

Table 2. Selected bond lengths (Å) and bond angles (°)

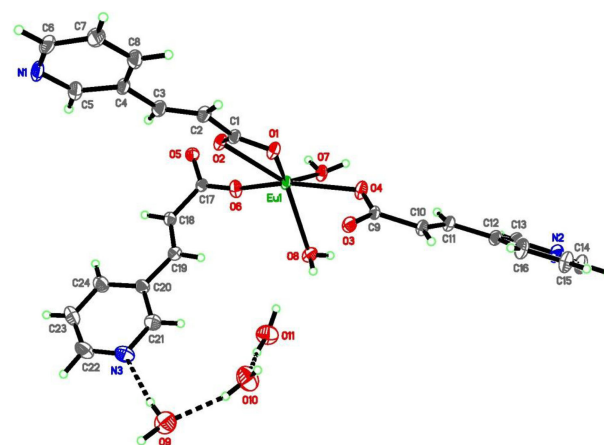
Polymer 1					
Eu1–O6	2.3118(2)	Eu1–O3#1	2.349(2)	Eu1–O4	2.382(2)
Eu1–O5#2	2.408(2)	Eu1–O7	2.422(2)	Eu1–O2	2.484(2)
Eu1–O8	2.499(2)	Eu1–O1	2.523(2)		
O6–Eu1–O3#1	89.37(6)	O6–Eu1–O4	148.26(6)	O3#1–Eu1–O4	103.59(6)
O3#1–Eu1–O7	139.80(6)	O4–Eu1–O7	78.31(6)	O6–Eu1–O2	74.57(6)
O7–Eu1–O8	73.13(6)	O2–Eu1–O8	142.02(6)	O4–Eu1–O1	85.76(6)
Polymer 2					
Tb1–O6	2.285(2)	Tb1–O3#1	2.311(2)	Tb1–O4	2.349(2)
Tb1–O5#2	2.380(2)	Tb1–O7	2.392(3)	Tb1–O2	2.455(2)
Tb1–O8	2.476(3)	Tb1–O1	2.497(2)		
O6–Tb1–O3#1	89.46(9)	O6–Tb1–O4	148.93(9)	O3#1–Tb1–O4	102.53(8)
O3#1–Tb1–O7	139.27(10)	O4–Tb1–O7	78.80(9)	O6–Tb1–O2	74.73(8)
O7–Tb1–O8	72.99(10)	O2–Tb1–O8	141.88(9)	O4–Tb1–O1	84.43(8)
Polymer 3					
Gd1–O6	2.297(3)	Gd1–O3#1	2.321(3)	Gd1–O4	2.368(3)
Gd1–O5#2	2.481(3)	Gd1–O7	2.409(3)	Gd1–O2	2.468(2)
Gd1–O8	89.47(10)	Gd1–O1	2.510(3)		
O6–Gd1–O3#1	139.54(10)	O6–Gd1–O4	148.68(9)	O3#1–Gd1–O4	103.08(9)
O3#1–Gd1–O7	73.04(11)	O4–Gd1–O7	78.98(11)	O6–Gd1–O2	74.73(9)
O7–Gd1–O8	2.297(3)	O2–Gd1–O8	142.02(10)	O4–Gd1–O1	84.89(9)

Symmetry transformations used to generate equivalent atoms: #1 = $-x + 1, -y + 1, -z$; #2 = $-x, -y + 1, -z$.

and **3** were prepared in the same way by using the corresponding metal nitrates. The NaOH(aq) solution was used to deprotonate the carboxylate group in HL. Although the reaction time is just 1 min due to high microwave power (700 W), the preparation is reproducible. All polymers were characterized by IR, elemental analysis, TGA, and X-ray single crystallography. The IR spectra of polymers **1–3** show a strong absorption band in the range of 1643–1644 cm^{-1} due to the C=C bond in the ligand backbone.

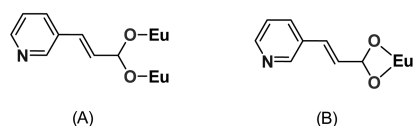
**Scheme 1**

Crystal Structures. Polymers **1–3** are isostructural, and therefore only the structure of polymer **1** will be discussed in detail. Figure 1 shows an asymmetric unit of polymer **1**, which consists of one Eu^{3+} ion, three **L** ligands, two aqua ligands, and three lattice water molecules. All atoms occupy general positions. The Eu^{3+} ion is bonded to eight oxygen atoms, and the Eu–O bond lengths range from 2.318(2) to 2.523(2) Å. All pyridyl nitrogen atoms do not coordinate to the metals. There are three crystallographically independent ligands, which behave differently. Two of them link the Eu^{3+}

**Figure 1.** Asymmetric unit of polymer **1**.

ions ($\mu\text{-}1\kappa\text{O}:2\kappa\text{O}'$, (A) in Chart 1), whereas the last one acts as a simple chelating ligand ($\kappa^2\text{O},\text{O}'$, (B) in Chart 1).

Figure 2 illustrates the repeat unit of coordination polymer **1**, which consists of two subunits: two Eu^{3+} ions and two carboxylate groups (subunit 1) and another two Eu^{3+} ions and two carboxylate groups (subunit 2). Both subunits are loops made up of eight atoms (two Eu^{3+} ions and six ligand atoms) and have the $\text{Eu}^{3+}\cdots\text{Eu}^{3+}$ separation of 4.9001(2) or 4.8274(2) Å. Moreover, these subunits are twisted significantly from each other. The subunits are linked in the [100] direction to form a 1-D chain, in which the metal ions behave as knots (Figure 3). All of the hydrogen atoms in the aqua ligands and lattice water molecules participate in the hydrogen bonds of the O–H \cdots O or O–H \cdots N type. Figure 4 shows the packing diagram of polymer **1**, in which various

**Chart 1**

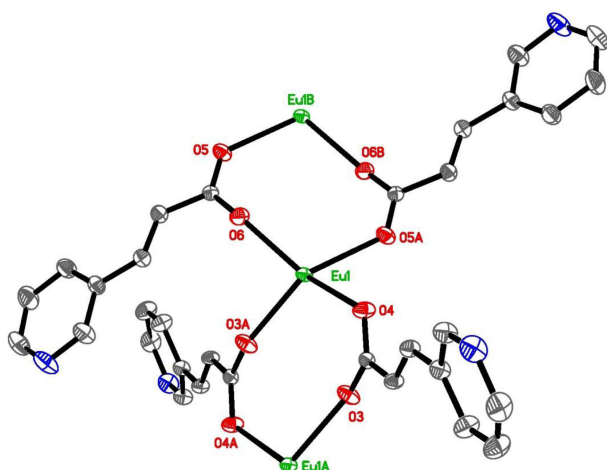


Figure 2. Repeat unit consisting of two subunits in polymer 1.

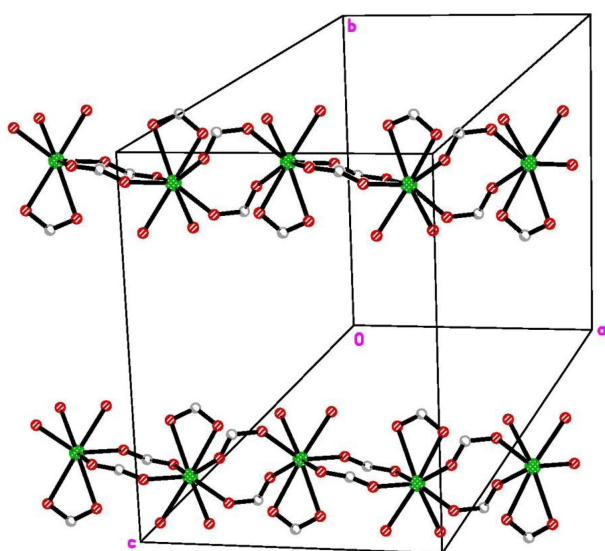


Figure 3. A1-D loop-connected chain structure of polymer 1, in which the subunits are linked along the *a*-axis by sharing the metal ions (knots). For clarity, the moiety --CH=CH--(3-py) of each ligand is omitted.

hydrogen bonds connect the 1-D chains in the $[010]$ direction to create a 2-D network.

In 2006, Wen and co-workers prepared a 1-D zigzag chain coordination polymer of europium, $[\text{Eu}(\text{L})_3(\text{H}_2\text{O})]$, from HL, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and NaOH under hydrothermal conditions.²⁴ This polymer differs in the number of aqua ligands and lattice water molecules from polymer 1, and such differences result in distinct chemical formulas and crystal structures of the two polymers.

Polymers 2 (Figure 5) and 3 (Figure 6) are isostructural with polymer 1. The Tb^{3+} ion is bonded to eight oxygen atoms in polymer 2, and the Tb--O bond lengths range from 2.380(2) to 2.497(2) Å. The Gd^{3+} ion in polymer 3 is also 8-coordinate with the Gd--O bond lengths in the range of 2.297(3)–2.510(3) Å. Like polymer 1, polymers 2 and 3 have a 1-D loop-connected chain framework, and the hydrogen bonds lead to the formation of a 2-D network.

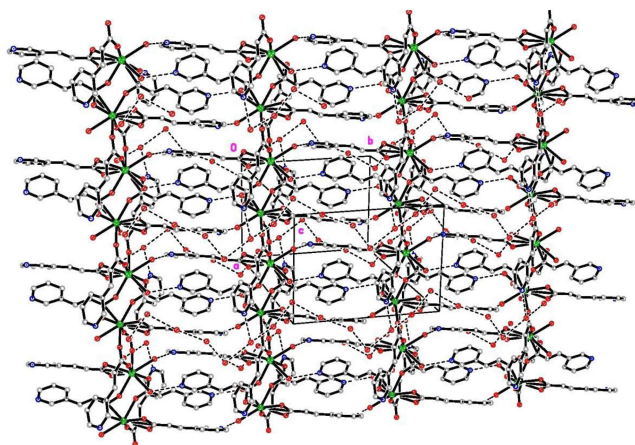


Figure 4. Packing diagram of polymer 1, which shows a 2-D network formed by hydrogen bonds (dotted lines) approximately along the *b*-axis.

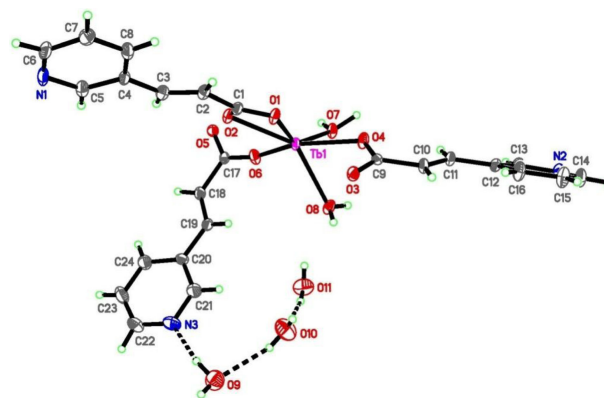


Figure 5. Asymmetric unit of polymer 2.

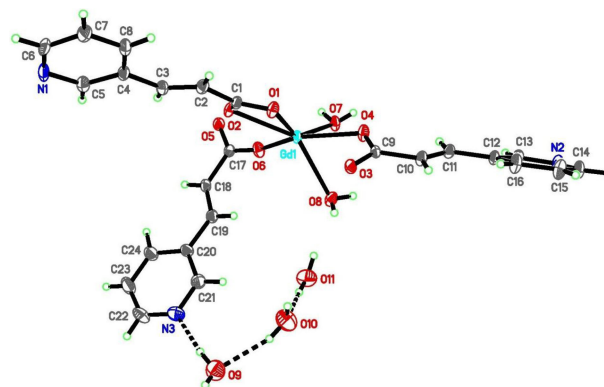


Figure 6. Asymmetric unit of polymer 3.

Thermogravimetric Analysis. Figure 7 shows TGA curves for polymers 1–3, which show practically the same pattern. All polymers exhibit two major weight losses and then decompose abruptly above approximately 450 °C. In the case of coordination polymer 1, the first weight loss occurs at 650–120 °C, corresponding to the loss of three lattice water molecules (calculated: 7.8%; observed: 8.0%). The second weight loss in the range of 300–324 °C is due to the elimination of two aqua ligands (calculated: 5.2%;

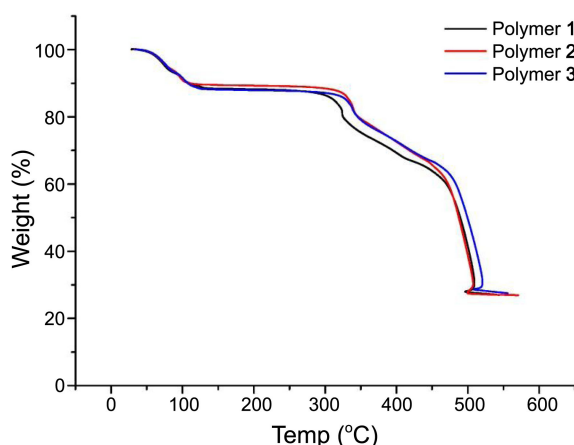


Figure 7. TGA curves for polymers 1-3.

observed: 5.6%). Polymer 2 first loses its weight at 60-100 °C, which can be ascribed to the loss of the lattice water molecules (calculated: 7.8%; observed: 7.7%). The second weight loss occurs in the range of 320-340 °C owing to the elimination of the aqua ligands (calculated: 5.2%; observed: 5.4%). For polymer 3, the first (8.1%) and second (4.9%) weight losses appear at 60-104 and 320-340 °C, respectively.

Solid-state Photoluminescence. Lanthanide metal ions, especially Eu^{3+} and Tb^{3+} ions, typically exhibit sharp and narrow bands due to $f-f$ transitions in their luminescence (emission) spectra. The Eu^{3+} ion has the ${}^7\text{F}_0$ ground state and the long-lived ${}^5\text{D}_0$ excited state. The Tb^{3+} ion has the ${}^7\text{F}_6$ ground state and the long-lived ${}^5\text{D}_4$ excited state.³⁵ Because polymers 1 and 2 contain Eu^{3+} and Tb^{3+} ions, respectively, their luminescence was examined in the solid state at room temperature. In consistent with our expectation, only polymer 1 exhibited photoluminescence, but polymer 2 did not. In fact, the photoluminescence spectra of polymer 2 do not display any defined peaks. Unfortunately, we cannot give a reasonable explanation for the quenching of the photoluminescence of the Tb^{3+} ion in polymer 2. As a comparison, we previously observed the well-defined emission spectra of $[\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (a starting compound for polymer 2) and $[\text{Tb}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L}')_2](\text{NO}_3)(\text{H}_2\text{O})$ {a discrete Tb complex related to polymer 2; $\text{L}' = (4\text{-pyH})^+\text{-CH}_2\text{CH}_2\text{-SO}_3$ }, both of which exhibit practically the same intense green luminescence.²⁵

Figure 8 shows the solid-state emission spectra of polymer 1 and $[\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (a starting compound for polymer 1), which display practically the same pattern. Both compounds are excited at 360 nm and exhibits red luminescence. Polymer 1 exhibits the transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ at 591, 612, 699 nm, respectively, which can be explained on the basis of the Eu^{3+} energy-level structure.³⁵ The emission peak of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition is a magnetic-dipole transition and its intensity may depend on the crystal field strength acting on the Eu^{3+} ion.³⁶ The strongest peak at 612 nm is the electric-dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, and it is absent if the Eu^{3+} ion lies on the inversion center.³⁷ This observation is consistent with the crystal

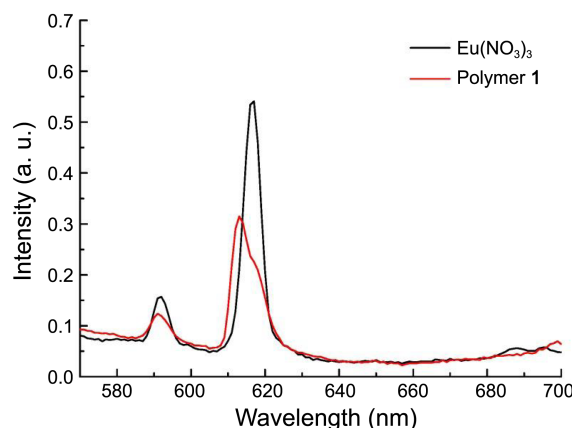


Figure 8. Solid-state emission spectra of polymer 1 and $[\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ at room temperature.

structure of polymer 1, in which the Eu^{3+} ion occupies a general position. Moreover, the intensity of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition is stronger than that of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, which also supports the acentric coordination environment of the Eu^{3+} ions in polymer 1. The fact that no emission peaks other than the characteristic peaks of Eu^{3+} ions appear in the emission spectrum indicates that the ligand does not sensitize the Eu^{3+} ions in polymer 1.

Conclusion

We prepared three novel isostructural lanthanide coordination polymers, $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$ {Ln = Eu (1), Tb (2), Gd (3); $\text{L} = \text{trans}-(3\text{-py})\text{-CH=CH-COO}$ } in H_2O by microwave heating. The reactions were completed for 1 min and highly reproducible. In all polymers, lanthanide metal ions are 8-coordinate. The nitrogen atoms in the pyridyl terminals do not coordinate to the metals, but participate in the intermolecular $\text{O-H}\cdots\text{N}$ hydrogen bonds. All of the hydrogen atoms in the aqua ligands and lattice water molecules are involved in the hydrogen bonds of the $\text{O-H}\cdots\text{O}$ or $\text{O-H}\cdots\text{N}$ type. Polymers 1-3 contain two repeat subunits that are linked to form a 1-D loop-connected chain. Various types of hydrogen bonds connect the 1-D chains to create a 2-D network. Polymer 1 exhibited red luminescence in the solid state, whereas polymers 2 and 3 did not exhibit luminescence in the visible region.

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