



# Semiconducting lanthanide polymers of pyridine-2,6-dicarboxylate: Hydrothermal synthesis, structural characterization, electrical conductivity and luminescence properties

Burak Ay<sup>a,\*</sup>, Emel Yildiz<sup>a</sup>, İbrahim Kani<sup>b</sup>

<sup>a</sup>Çukurova University, Department of Chemistry, Arts and Science Faculty, 01330 Adana, Turkey

<sup>b</sup>Department of Chemistry, Anadolu University, 26470 Eskişehir, Turkey

## ARTICLE INFO

### Article history:

Received 13 November 2017

Accepted 23 December 2017

Available online 30 December 2017

### Keywords:

Hydrothermal synthesis

Insoluble Nd(III) and La(III) coordination polymers

Luminescence

Electrical conductivity

MOFs

## ABSTRACT

This paper describes the hydrothermal synthesis of two novel lanthanide coordination polymers (CPs)  $(\text{H}_2\text{pip})_n[\text{Ln}_2(\text{pydc})_4(\text{H}_2\text{O})_2]_n$  (Ln = La (**1**) and Nd (**2**),  $\text{H}_2\text{pydc}$  = 2,6-pyridinedicarboxylic acid,  $\text{H}_2\text{pip}$  = piperazine). The synthesized polymers were structurally characterized by the elemental analysis, ICP-OES, IR spectroscopy, TGA, single-crystal X-ray diffraction and powder X-ray diffraction (PXRD) analysis. For the morphological analysis field emission scanning electron microscopy (FESEM) was used. CPs are isomorphous, showing three-dimensional Ln–O–Ln chains. Ln(III) ions in **1–2** adopt nine-coordinated mode to construct a mono-capped square antiprism coordination environments. The electrical conductivity and luminescence properties of insoluble **1–2** have been investigated. CPs exhibited luminescence emission bands at 612 nm for **1** and 624 nm for **2** at room temperature when excited at 320 nm.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Design and synthesis of metal–organic frameworks (MOFs) have drawn special attention owing to their diverse and intriguing structures. Especially, lanthanide based MOFs (Ln-MOFs) have been an area of rapid growth due to their various potential applications such as catalysis, sensors, adsorption, luminescence, separation, gas storage, ion exchange [1–10], and so on. A great number of study have been done for the synthesis of Ln-MOFs and still continues [11–14]. Lanthanides have high coordination numbers (varies from 7 to 13), and water molecules are often coordinated beside the ligands. These ions are hard Lewis acids and display strong affinity for O-donor ligands [15]. Some polydentate ligands, such as multicarboxylic acids, pyridinecarboxylates and pyrazinecarboxylates are employed to construct Ln-MOFs [16]. Among the types of these ligands, pyridinecarboxylates are able to stabilize lanthanide ions can provide diverse structures with different coordination modes in the construction of supermolecular frameworks.  $\text{H}_2\text{pydc}$  and its deprotonated anions ( $\text{Hpydc}^-$  and  $\text{pydc}^{2-}$ ) are highly effective ligands for the construction of Ln-MOFs [17–19]. It behaves as multifunctional ligands to act as bridging ligands, and has got five potential coordination sites

involving the –O atoms of the –COOH groups and the –N atoms of the pyridine ring [20]. Moreover, the angle between pyridine ring and two carboxylate groups is  $120^\circ$ . With this rigid angle  $\text{H}_2\text{pydc}$ , and its deprotonated anions offer various coordination modes to form unusual and unexpected CPs under hydrothermal conditions.

In this study, we have designed two novel Ln-MOFs,  $(\text{H}_2\text{pip})_n[\text{La}_2(\text{pydc})_4(\text{H}_2\text{O})_2]_n$  (**1**) and  $(\text{H}_2\text{pip})_n[\text{Nd}_2(\text{pydc})_4(\text{H}_2\text{O})_2]_n$  (**2**) ( $\text{H}_2\text{pydc}$  = 2,6-pyridinedicarboxylic acid,  $\text{H}_2\text{pip}$  = piperazine) incorporating  $\text{pydc}^{2-}$ , aqua ligands, and piperazine as a counter moieties. Solubility tests were performed for the **1** and **2**. The test showed that the synthesized coordination polymers are insoluble in all common organic and inorganic solvents (Table S1). Due to the this feature, electrical conductivity and luminescence properties of the MOFs were investigated in solid phase.

## 2. Experimental

### 2.1. Materials and methods

All chemicals and solvents were purchased from commercial sources and used without further purification. All hydrothermal syntheses were carried out in 23 mL PTFE-lined stainless steel containers under autogenous pressure. A Perkin-Elmer RX-1 FT-IR with KBr pellets spectrometer in the range of  $4000\text{--}400\text{ cm}^{-1}$

\* Corresponding author. Fax: +90 322 338 60 70.

E-mail address: [bay@cu.edu.tr](mailto:bay@cu.edu.tr) (B. Ay).

**Table 1**  
Crystal data and structure refinement for **1** and **2**.

Code	<b>1</b>		<b>2</b>	
Empirical formula	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>9</sub> La		C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>9</sub> Nd	
Formula weight	529.91 g/mol		535.24 g/mol	
Temperature (K)	296(2)		296(2)	
Wavelength (Å)	0.71073		0.71073	
Crystal system	triclinic		triclinic	
Crystal size	0.21 × 0.38 × 0.19 mm		0.17 × 0.28 × 0.31 mm	
Space group	P-1		P-1	
Unit cell dimensions	<i>a</i> = 7.0177(10) Å	<i>α</i> = 112.95(5)°	<i>a</i> = 6.9370(2) Å	<i>α</i> = 112.803(10)°
	<i>b</i> = 10.9132(16) Å	<i>β</i> = 96.256(5)°	<i>b</i> = 10.8872(3) Å	<i>β</i> = 95.7460(10)°
	<i>c</i> = 12.4544(18) Å	<i>γ</i> = 95.013(5)°	<i>c</i> = 12.3184(3) Å	<i>γ</i> = 95.0290(10)°
Volume (Å <sup>3</sup> )	864.2(2)		845.17(4)	
Z	1		2	
Density (calculated) (g/cm <sup>3</sup> )	1.942		2.096	
Absorption coefficient (mm <sup>-1</sup> )	2.503		3.134	
<i>F</i> (000)	492		520	
Theta range for data collection	1.80 to 28.4°		1.81 to 28.33°	
Index ranges	-9 ≤ <i>h</i> ≤ 9, -14 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 16		-9 ≤ <i>h</i> ≤ 9, -14 ≤ <i>k</i> ≤ 14, -16 ≤ <i>l</i> ≤ 16	
Reflections collected	32257		38387	
Unique reflections	4081 [R(int) = 0.0203]		4216 [R(int) = 0.0251]	
Coverage of independent reflections	93.5%		98%	
Max. and min. transmission	0.6046 and 0.3910		0.6140 and 0.4430	
Data/restraints/parameters	4081/0/274		4216/0/275	
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.010		0.966	
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0232, <i>wR</i> <sub>2</sub> = 0.0915		<i>R</i> <sub>1</sub> = 0.0177, <i>wR</i> <sub>2</sub> = 0.0662	
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0237, <i>wR</i> <sub>2</sub> = 0.0924		<i>R</i> <sub>1</sub> = 0.0177, <i>wR</i> <sub>2</sub> = 0.0664	
Largest diff. peak and hole (e-Å <sup>-3</sup> )	0.785 and -0.807		1.037 and -0.650	

**Table 2**  
Selected bond lengths [Å] and angles [°] for **1–2**.

<b>1</b>			
La1–O2	2.5804(4)	O2–La1–O5	72.05 (1)
La1–O5	2.6060(4)	O2–La1–O3	122.42 (1)
La1–O3	2.5202(4)	O2–La1–N1	60.96 (1)
La1–N1	2.6413(4)	O2–La1–O9	139.76 (1)
La1–O9	2.6398(4)	O5–La1–O3	98.75 (1)
O2–C1	1.2625(1)	O5–La1–N1	83.70 (1)
O5–C8	1.2933(1)	O5–La1–O9	69.30 (1)
O7–C14	1.2644(1)	O3–La1–N1	61.56 (1)
O1–C1	1.2458(2)	O3–La1–O9	74.82 (1)
O3–C7	1.2546(1)	N1–La1–O9	123.91 (1)
O4–C7	1.2409(2)	La1–O2–C1	124.31 (1)
N1–C2	1.3304(2)	La1–O5–C8	117.08 (2)
N1–C6	1.3353(2)	La1–O3–C7	126.15 (1)
O6–C8	1.2272(2)	La1–N1–C2	120.53 (1)
<b>2</b>			
Nd1–O7	2.4286 (17)	Nd1–O2–C1	124.21 (15)
Nd1–O3	2.4643 (17)	Nd1–O5–C14	124.30 (16)
Nd1–O5	2.5161 (16)	Nd1–O3–C7	125.36 (16)
Nd1–O2	2.5250 (16)	Nd1–O7–C8	127.32 (18)
Nd1–O1	2.5363 (17)	Nd1–N2–C2	120.78 (15)
Nd1–O5	2.5580 (16)	Nd1–N2–C6	119.38 (15)
Nd1–O9	2.560 (2)	Nd1–N1–C13	120.83 (15)
Nd1–N1	2.5620 (18)	Nd1–N1–C9	119.47 (17)
Nd1–N2	2.5744 (18)	O2–Nd1–O5	75.44 (6)
O2–C1	1.264 (3)	O5–Nd1–O3	150.66 (6)
O5–C14	1.294 (3)	O3–Nd1–N2	62.86 (6)
O5–Nd1	2.5580 (16)	N1–Nd1–O9	120.91 (7)
O1–Nd1	2.5364 (17)	N2–Nd1–N1	116.42 (6)
C15–N3	1.484 (4)	N2–Nd1–O9	122.58 (7)

was used for the IR analysis of the compounds. Thermo Flash 2000 CHNS analyzer was used for the elemental analysis. The melting points of the coordination polymers were determined using a Galenkamp MPD 350 BM 2.5 capillary melting point apparatus. Quantitative lanthanide analyses were performed with Perkin-Elmer Optima 2100DV ICP-OES instrument. Perkin Elmer Pyris Diamond TG/DTA equipment was used for the TG analyses. The FESEM images of the compounds were recorded using Carl Zeiss, SUPRA-55. Rigaku Miniflex system with CuK $\alpha$  radiation ( $\lambda = 1.54059 \text{ \AA}$ )

was used for the PXRD studies. The electrical conductivity properties of the coordination polymers were determined by four-point probe method with an Electrometer Entek Electronic FPP-470. Perkin-Elmer LS 55 Luminescence Spectrometer was used for the solid state phosphorescence excitation and emission spectra. LEICA EZ4W stereo microscope was used for the high definition views of the MOFs.

## 2.2. Synthesis of (H<sub>2</sub>pip)<sub>n</sub>[La<sub>2</sub>(pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>

A solution of lanthanum (III) nitrate hexahydrate (0.130 g, 0.30 mmol), 2,6-pyridinedicarboxylic acid (0.150 g, 0.90 mmol), piperazine (0.078 g, 0.90 mmol), and H<sub>2</sub>O (5 mL, 278 mmol) with the mole ratio of 1:3:3:927 was stirred before heating at 170 °C for 84 h under hydrothermal conditions. The initial and final pH values were measured as 4.80 and 6.75, respectively. The heterogeneous solution mixture was separated from the solid phase and the crystals washed by the water and dried at room temperature. Colorless crystals (Fig. S1-a) suitable for X-ray diffraction were isolated in 93.3% yield (based on La). *Anal. Calc.* for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>9</sub>La: C, 36.25; H, 2.47; N, 7.93. *Found*: C, 36.02; H, 2.64; N, 7.50%. The ICP analysis (%) showed that **1** contained La: 26.17; *Calcd.*: La: 26.20. IR data (cm<sup>-1</sup>): 3640(w), 3238(w), 3083(m), 1649(s), 1615(s), 1588(s), 1443(m), 1373(s), 1280(m), 1179(m), 1072(m), 1018(m), 910(w), 765(m), 726(s), 596(m), 521(m), 432(w), 417(m).

## 2.3. Synthesis of (H<sub>2</sub>pip)<sub>n</sub>[Nd<sub>2</sub>(pydc)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub>

The preparation of **2** was similar to that of **1** except that Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.132 g, 0.30 mmol) was used instead of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The initial and final pH values were measured as 5.00 and 6.30, respectively. The crystals were obtained under hydrothermal conditions. Violet crystals (Fig. S1-b) suitable for X-ray diffraction were isolated in 76% yield (based on Nd). *Anal. Calc.* for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>9</sub>Nd: C, 35.88; H, 2.45; N, 7.85. *Found*: C, 35.01; H, 2.54; N, 7.20%. The ICP analysis (%) showed that **2** contained Nd: 26.37; *Calcd.*: Nd: 26.93. IR data (cm<sup>-1</sup>): 3645(m), 3328(w), 3043(m), 1653(m), 1615(m), 1589(m), 1445(m), 1372(s), 1339(m), 1268(m), 1073(m), 1020

Download English Version:

<https://daneshyari.com/en/article/7763337>

Download Persian Version:

<https://daneshyari.com/article/7763337>

[Daneshyari.com](https://daneshyari.com)