

# NIR luminescence of one-dimensional tartaric acid derivatives neodymium coordination polymers



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## ARTICLE INFO

### Article history:

Received 10 May 2016  
Received in revised form 12 September 2016  
Accepted 14 September 2016  
Available online 29 September 2016

### Keywords:

L-di-2-thenoyltartaric acid  
L-di-*p*-toluoyl-tartaric acid  
Neodymium  
Coordination polymers  
NIR luminescence

## ABSTRACT

A series of four neodymium coordination polymers (CPs), namely,  $\{[\text{Nd}_2\text{L}_3(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})_4]\}_n$  (**1**),  $\{[\text{Nd}_2\text{L}_3(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})_3]\cdot 4\text{CH}_3\text{OH}\cdot \text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Nd}_2\text{L}_3(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})_3]\cdot 4\text{CH}_3\text{OH}\cdot \text{H}_2\text{O}\}_n$  (**3**) and  $[\text{NdL}'_3(\text{CH}_3\text{OH})_3]_n$  (**4**) have been isolated by facile reactions of ligands ( $\text{H}_2\text{L} = \text{L-di-2-thenoyltartaric acid}$  and  $\text{H}_2\text{L}' = \text{L-di-}p\text{-toluoyl-tartaric acid}$ ) with  $\text{NdCl}_3\cdot 6\text{H}_2\text{O}$  at ambient temperature depending on the reaction conditions. X-ray crystallographic analysis reveals that all complexes **1–4** feature one-dimensional (1D) network structure in which the  $\text{Nd}^{3+}$  ions are bridged by carboxylate groups of ligands by five types of coordinated modes. Complexes **1–3** feature one-dimensional (1D) ladder-like chain structure and complex **4** features one-dimensional (1D) linear structure owing to the ligands coordination modes. NIR luminescence analysis reveal that all complexes **1–4** exhibit three characteristic bands around 890, 1054 and 1326 nm of  $\text{Nd}^{3+}$  ion in which complex **3** shows the longest lifetime and highest quantum yield. The energy transfer processes among ligands, the  $\text{Nd}^{3+}$  ion and the auxiliary ligand in complexes **1–4** has been investigated.

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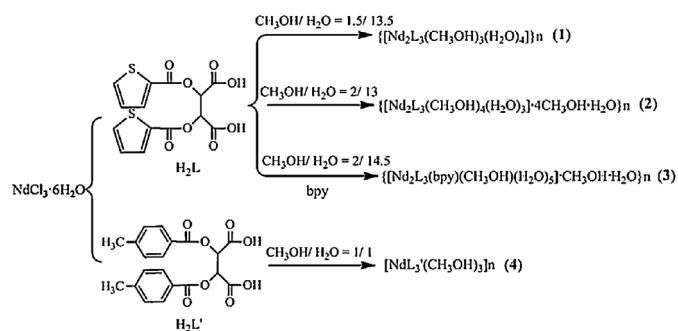
## 1. Introduction

Near-infrared (NIR) luminescence of lanthanide complexes, such as  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Ho}^{3+}$  ion, have received increasing attention for their potential applications in telecommunications, optical communications, optical amplifiers and drug delivery [1–11]. Particularly, NIR emission from  $\text{Nd}^{3+}$  ion around 890, 1054 and 1326 nm demonstrates efficient transmission in biological tissues since NIR luminescence ranging from 0.8 to 1.5  $\mu\text{m}$  has few interferences with biomaterials [12–14]. Therefore, more and more studies on NIR luminescence of  $\text{Nd}^{3+}$  ions have been documented. Since the direct excitation of the  $\text{Nd}^{3+}$  ions is inefficient because of the low molar absorption coefficient of the parity-forbidden  $f-f$  transitions, organic ligands must be employed on enhancing the NIR luminescence in terms of lifetime and quantum yield [15,16]. It is reported that the aromatic-conjugated carboxylates can satisfy the coordination number and the valence state requirements simultaneously promising longer lifetimes and higher efficiency in comparison with  $\beta$ -diketones and nitrogen macrocyclic groups.

E.g. J. Cepeda et al. have reported the two novel  $\text{Nd}^{3+}$  complexes  $\{[\text{Nd}_9(\mu_4\text{-pzdc})_9(\text{NO}_3)_2(\text{H}_2\text{O})_{25}](\text{NO}_3)_7\cdot 8\text{H}_2\text{O}\}_n$  and  $\{[\text{Nd}_6(\mu_4\text{-pzdc})_5(\mu_3\text{-pzdc})_2(\mu\text{-pzdc})(\text{H}_2\text{O})_{10}](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}\}_n$  with 3D structures featuring intrinsic and strong NIR luminescence by doping  $\text{Nd}^{3+}$  ion in pyrazine-2,5-dicarboxylic acid [17]. M. Mazzanti et al. have reported two  $\text{Nd}^{3+}$  coordination complexes  $(\text{Et}_3\text{NH})_3[\text{Nd}(\text{H}_{1/2}\text{hqa})_3]_2\cdot (\text{Et}_3\text{NHOTf})$  and  $\text{K}_3[\text{Nd}(\text{hqa})_3]\cdot 8\text{MeOH}$  with 2D structures in which the  $\text{Nd}^{3+}$  ion could be effectively sensitized by the 8-hydroxyquinoline-2-carboxylic acid emitting NIR luminescence with longer lifetime [18]. On the basis of a number of previous reported [19–23], it is known that the main ligand, the auxiliary ligand and the structure of the complexes synergistic dominate the NIR luminescence of complexes. However, it is still a great challenge choosing the appropriate main ligand and auxiliary ligand to effectively sensitize the lanthanide ions as well as construct an optimized structure to enhance the NIR luminescence of lanthanide coordination polymers. Herein, attempting to develop the effective NIR luminescence of  $\text{Nd}^{3+}$  complexes, the L-di-2-thenoyltartaric acid and L-di-*p*-toluoyl-tartaric acid containing rigid aromatic structure which may give rise to high stability and high carrier mobility as well as the rigid azacyclo-auxiliary ligands were employed in the reactions with  $\text{NdCl}_3\cdot 6\text{H}_2\text{O}$ . As a result, a series four complexes **1–4** with two

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Scheme 1. The synthetic route of complexes 1–4.

types of one-dimensional (1D) structure have been isolated (Scheme 1). Their synthesis, crystal structures and NIR luminescence have been investigated.

## 2. Experimental details

### 2.1. Materials and instrumentations

The  $\text{H}_2\text{L}$  ligand was synthesized according to the literature [21].  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  were prepared by the reactions of  $\text{Nd}_2\text{O}_3$  and hydrochloric acid. The  $\text{H}_2\text{L}'$  ligand and other chemicals were commercially available sources of analytical grade and used without further purification. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 analyzer. FT-IR spectra were collected on a Perkin-Elmer Spectrum 100 spectrophotometer by using KBr pellets in the range of  $4000\text{--}500\text{ cm}^{-1}$ . UV spectra (in methanol solution) were recorded on a Perkin-Elmer Lambda 35 spectrophotometer. Thermogravimetric analyses (TGA) were conducted on a Perkin-Elmer STA 6000 heated from  $30\text{ }^\circ\text{C}$  to  $800\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Powder X-ray diffraction (PXRD) data were performed on a Rigaku D/Max-3B X-ray diffractometer with  $\text{CuK}\alpha$  as the radiation source ( $\lambda = 0.15406\text{ nm}$ ) in the angular range  $2\theta = 5\text{--}50^\circ$  at room temperature. The steady-state NIR emission spectrometer equipped with a Hamamatsu R5509-72 supercooled photomultiplier tube at 193 K and a TM 300 emission monochromator with NIR grating blazed at 1000 nm. The corrected spectra were obtained via a calibration curve supplied with the instrument. Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instrument (FLS 920) with microsecond pulse lamp as the excitation.

### 2.2. Synthesis of complexes 1–4

Synthesis of  $\{[\text{Nd}_2\text{L}_3(\text{CH}_3\text{OH})_3(\text{H}_2\text{O})_4]\}_n$  (**1**). A solution of  $\text{H}_2\text{L}$  (0.0833 g, 0.225 mmol) and triethylamine (0.0227 g, 0.225 mmol) in methanol (3.5 mL) ( $\text{pH} \approx 6$ ), mixed with a solution of  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (0.0707 g, 0.2 mmol) in  $\text{H}_2\text{O}$  (1.5 mL), the mixture was placed in a test tube (15 mm  $\times$  150 mm) after being stirred for two hours at room temperature, then 10 mL methanol was layered on the mixture. The tube was sealed and allowed to stand at room temperature. Purple crystals suitable for X-ray determination were obtained in about one week. Yield: 63 mg, 53.8%. Elemental analysis (%) Calcd for  $\text{C}_{45}\text{H}_{44}\text{Nd}_2\text{O}_{31}\text{S}_6$  ( $M_r = 1561.68$ ): C 34.61, H 2.84; Found: C 34.52, H 2.78. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3501 (m), 3104 (w), 1713 (s), 1614 (s), 1524 (w), 1416 (s), 1364 (w), 1263 (s), 1096 (m), 1017 (m), 748 (m). UV-vis [ $\text{CH}_3\text{OH}$ ,  $\lambda$ ]: 249, 269 nm.

Synthesis of  $\{[\text{Nd}_2\text{L}_3(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})_3] \cdot 4\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}\}_n$  (**2**). A solution of  $\text{H}_2\text{L}$  (0.0833 g, 0.225 mmol) and triethylamine (0.0222 g, 0.22 mmol) in methanol (3 mL) ( $\text{pH} \approx 5.9$ ), mixed with a solution of  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (0.0538 g, 0.15 mmol) in  $\text{H}_2\text{O}$  (2 mL), the mixture was placed in a test tube (15 mm  $\times$  150 mm) after being

stirred for two hours at room temperature, then 10 mL methanol was layered on the mixture. The tube was sealed and allowed to stand at room temperature. Purple crystals suitable for X-ray determination were obtained in about one week. Yield: 66 mg, 51.1%. Elemental analysis (%) Calcd for  $\text{C}_{50}\text{H}_{64}\text{Nd}_2\text{O}_{36}\text{S}_6$  ( $M_r = 1721.89$ ): C 34.88, H 3.75; Found: C 35.02, H 3.71. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3395 (m), 3105 (w), 1703 (s), 1607 (s), 1525 (w), 1416 (s), 1365 (w), 1264 (s), 1096 (m), 749 (m). UV-vis [ $\text{CH}_3\text{OH}$ ,  $\lambda$ ]: 249, 269 nm.

Synthesis of  $\{[\text{Nd}_2\text{L}_3(\text{bpy})(\text{CH}_3\text{OH})(\text{H}_2\text{O})_5] \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}\}_n$  (**3**). A solution of  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (0.0538 g, 0.15 mmol) and 4,4'-bipyridyl (bpy, 0.0234 g, 0.15 mmol) in  $\text{H}_2\text{O}$  (2 mL) and methanol (1 mL), after being stirred at room temperature for two hours, then added to a solution of  $\text{H}_2\text{L}$  (0.0833 g, 0.225 mmol) and triethylamine (0.0227 g, 0.225 mmol) in methanol (3.5 mL) ( $\text{pH} \approx 6$ ), the mixture was placed in a test tube (15 mm  $\times$  150 mm) after stirred at room temperature for two hours, then 10 mL methanol was layered on the mixture. The tube was sealed and allowed to stand at room temperature. Purple crystals suitable for X-ray determination were obtained in about one week. Yield: 59 mg, 45.7%. Elemental analysis (%) Calcd for  $\text{C}_{54}\text{H}_{52}\text{Nd}_2\text{O}_{32}\text{S}_6\text{N}_2$  ( $M_r = 1721.85$ ): C 37.67, H 3.04; Found: C 37.75, H 3.09. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3504 (m), 3096 (w), 2973 (w), 1711 (s), 1604 (s), 1524 (w), 1417 (s), 1365 (w), 1268 (s), 1094 (m), 749 (m). UV-vis [ $\text{CH}_3\text{OH}$ ,  $\lambda$ ]: 248, 268 nm.

Synthesis of  $[\text{NdL}'_3(\text{CH}_3\text{OH})_3]_n$  (**4**). Triethylamine (0.24 mmol, 0.0243 g) was added to a solution of L-DTTA (0.0773 g, 0.20 mmol) in methanol (4 mL) to  $\text{pH} \approx 6$ , then  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (0.0466 g, 0.13 mmol) in  $\text{H}_2\text{O}$  (4 mL) was diffused slowly into the solution in a test tube (15 mm  $\times$  150 mm). The tube was sealed and allowed to stand at room temperature. Purple crystals suitable for X-ray determination were obtained in about one week. Yield: 0.0310 mg, 61.54%. Elemental analysis (%) Calcd for  $\text{C}_{63}\text{H}_{60}\text{O}_{27}\text{Nd}$  ( $M_r = 1394.25$ ): C 54.31, H 4.34; Found: C 54.01, H 4.25. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3530 (w), 3441 (w), 1718 (s), 1619 (s), 1410 (s), 1260 (s), 1180 (s), 694 (w), 752 (s). UV-vis [ $\text{CH}_3\text{OH}$ ,  $\lambda$ ]: 205, 239 nm.

### 2.3. X-ray crystallography

Single-crystal X-ray diffraction data for complexes 1–4 were collected on a OxfordXcalibur Gemini Ultra diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) at room temperature. Empirical absorption corrections based on equivalent reflections were applied. The structures of complexes 1–4 were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$  using SHELXS-97 crystallographic software package [22,23]. All non-hydrogen atoms were refined anisotropically. Pertinent crystal data and structural refinement for complexes 1–4 are listed in Table 1. The selected bond lengths and bond angles for complexes 1–4 are summarized in Table S1. CCDC No. for complexes 1–4 is from 1441239 to 1441242.

## 3. Results and discussion

### 3.1. Synthesis

Complexes 1–3 were synthesized by the reaction of L-di-2-thenoyltartaric acid ( $\text{H}_2\text{L}$ ) with  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  under different reaction conditions (Scheme 1), e.g. different stoichiometry of  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  for complexes 1 and 2, and different auxiliary ligand (bpy) for complexes 1, 2 and 3. Complex 4 was prepared by reactions of  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  with different main ligand L-di-*p*-toluoyltartaric acid ( $\text{H}_2\text{L}'$ ) in comparison with complexes 1–3. Notably, diverse forms of coordination modes were observed in complexes 1–4, respectively, which dominated the final structure of complexes 1–4 (Fig. 2).

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