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Syntheses, Structure, and Luminescent Property of a New 2D Nd(III) Coordination Polymer Based on 4′-(4-Carboxyphenyl)-4,2′:6′,4″-Terpyridine

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Abstract—A new lanthanide coordination polymer (Ln-CP) based on Nd(III), $[Nd_2(Cptpy)_2(Glu)_2(H_2O)_2]_n \cdot 5n(H_2O)$ (**I**) (HCptpy = 4'-(4-carboxyphenyl)-4,2':6',4"-terpyridine and H_2Glu = glutaric acid), have been hydrothermally synthesized and characterized by elemental analysis, IR, single crystal X-ray diffraction (CIF file CCDC no. 1857154) and thermal analyses. Single crystal X-ray analysis (CIF file CCDC no. 1857154) reveals that compound **I** displays a (4,5)-connected 2D topological net and the Schläfli symbol of $(3.4^3.5^2)(3^2.4^4.5^2.6^2)$, which is further extended into a 3D supramolecular network by hydrogen bonds. Additionally, the near-infrared (NIR) luminescence of **I** was investigated in the solid state at room temperature.

Keywords: neodymium, terpyridine derivative, luminescent property

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INTRODUCTION

Currently, the particular field of materials science related to coordination polymers (CPs) is being widely studied owing to the well-known multiple properties such as high surface areas, well-defined porosity and tunable chemical functionality, as well as their potential application as gas storage and separation, sensing, catalysis and so on [1–4]. However, the rational design and synthesis of CPs with fine characterizations and properties remains a great challenge in coordination chemistry [5, 6]. As far as we know, the selection of the metal center, ligand, and/or ancillary ligand can direct the dimensionality, topology, and accessibility to the functionality center. Meanwhile, we are interested in the lanthanide MOFs (Ln-MOFs) with new structures constructed from the semi-rigid ligands with N,O-donor (polypyridine carboxylate), mainly because of their unusual coordination characteristics, magnetisms and optical properties arising from 4*f* electrons, especially for luminescence properties [7, 8].

Taking above factors into consideration, the bisfunctional trigonal ligand, 4'-(4-carboxyphenyl)-4,2':6',4"-terpyridine (HCptpy) is applied in the field of coordination chemistry [9–15] according to the following consideration: (a) HCptpy, as a semi-rigid bridging ligand, can link metal atoms via coordination bond to construct high dimensional and honeycomb porous coordination polymer; (b) it has a large π-conjugated nonlinear structure with N,O donors that can offer additional hydrogen bonding and π–π interactions to consolidate the whole framework structures. Herein, we present hydrothermal synthesis and crystal structures of a new 2D Nd polymeric frameworks, namely $[Nd_2(Cptpy)_2(Glu)_2(H_2O)_2]_n \cdot 5n(H_2O)$ (**I**), as well as its near-infrared (NIR) luminescence and thermal stability.

EXPERIMENTAL

Materials and measurements. HCptpy was prepared according to literature methods with some modifications [16, 17], other chemicals were of reagent grade and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 Fourier transform infrared spectrometer in the 400–4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on an elementar Vario EL III elemental analyzer. The solid-state photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer in the range of 200–1400 nm. Thermal gravimetry (TG) analyses were carried out with a Universal V2.6 DTA system at a rate of 10°C/min in a nitrogen atmosphere. Powder X-ray diffraction (PXRD) measurements were mea-

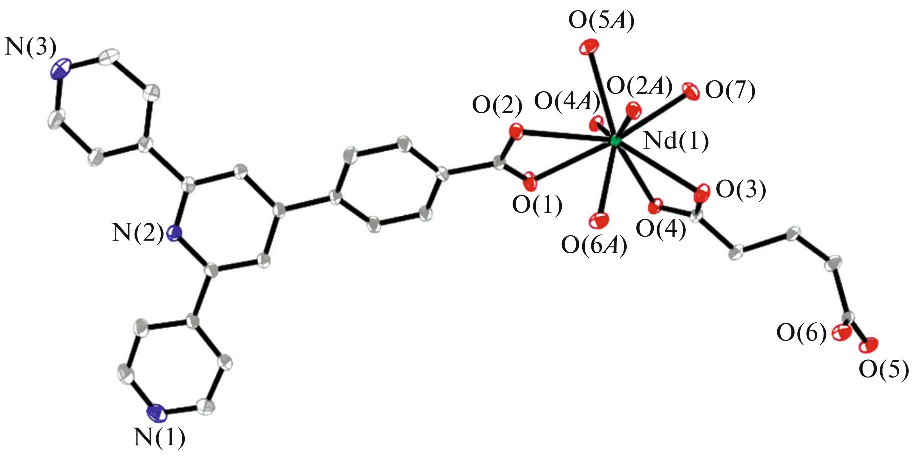

Fig. 1. Coordination environment of the Nd^{3+} ion in **I**.

sured on a Bruker D8 ADVANCE X-ray powder diffractometer (CuK_α, 1.5418 Å).

Synthesis of compound I. A mixture of $Nd(NO_3)_3 \cdot 6H_2O$ (0.0439 g, 0.1 mmol), HCptpy (0.0353 g, 0.1 mmol), and H_2Glu (0.0132 g, 0.1 mmol) in distilled water (10 mL) that adjusted the pH value to 6.0 with 0.5 mol L^{-1} NaOH aqueous solution was placed in a Teflon-lined stainless steel vessel (25 mL), heated to 160°C for 72 h and then cooled to room temperature at a rate of 5°C/h. The crystalline products of **I** were obtained, washed with distilled water (5 mL), and dried in air to give 0.0121 g (yield 17.7% based on Nd).

For $C_{54}H_{44}N_6O_{19}Nd_2$

Anal. calcd., %	C 47.22	H 2.98	N 5.97
Found, %	C 47.36	H 3.24	N 6.12

IR (KBr; ν, cm^{-1}): 3587 w, 3418 s, 2975 w, 2353 w, 1538 s, 1446 s, 1411 s, 1356 w, 1308 w, 1221 w, 1058 w, 880 w, 813 w, 754 w, 660 m.

X-ray crystallography. The crystallographic parameters for complex **I** at T = 296 K were as follows: $C_{54}H_{44}N_6O_{19}Nd_2$, Fw = 1369.43, blue, block, crystal size 0.28 × 0.18 × 0.12 mm, triclinic system, space group $P\bar{1}$, a = 8.0367(5), b = 9.1025(6), c = 18.6716(13) Å, α = 95.7250(10)°, β = 94.3660(10)°, γ = 102.6270(10)°, V = 1319.46(15) $Å^3$, Z = 1, ρ_{calcd} = 1.723 g cm^{-3}, μ = 203 mm^{-1}, 6616 reflections collected, 4611 unique ($R_{int} = 0.0159$), $R_1 = 0.0258$, $wR_2 = 0.0612$ ($I > 2\sigma(I)$), GOOF = 1.051. Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied by the SADABS program. The structure was solved by direct methods [18] and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program [19]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and refined as riding models. The selected bond distances and bond angles for **I** are listed in Table 1.

Supplementary material for complexes has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1857154; deposit@ccdc.cam.ac.uk or https://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

X-ray single crystal structural analysis reveals that compound **I** crystallizes in the triclinic system with, $P\bar{1}$ space group and is a 2D layer structure. The asymmetric unit of **I** contains one crystallographically independent Nd^{3+} ion, one $(Cptpy)^-$ ligand, one $(Glu)^{2-}$ anion, one coordinated water molecule and two and a half lattice water molecules. As shown in Fig. 1, Nd(1) center is nona-coordinated with three oxygen atoms (O(1), O(2), O(2*A*)) of two different $(Cptpy)^-$ anion, five oxygen atom (O(3), O(4), O(4*B*), O(5*C*), O(6*D*)) from four different $(Glu)^{2-}$ anion and one oxygen atom (O(7)) from one coordination water, forming a distorted muffin geometry (C_s with $S_Q(P)$ = 1.189 [20, 21]) (Fig. 2a). The bond lengths of Nd–O are in the range of 2.435(2)–2.677(2) Å, which are in accordance with reported values of Nd(III) compounds in literatures [22, 23]. In **I**, three pyridyl and one phenyl rings of the HCptpy ligand are non-coplanar, two outer pyridyl and one phenyl groups are twisted with respect to the central pyridyl ring, the dihedral angles between the central and outer pyridyl and phenyl rings are 4.20° (N(1) pyridyl ring), 9.26° (N(3) pyridyl ring) and 29.02° (phenyl ring), respectively.

Notably, the $(Cptpy)^-$ ligand adopts a μ_2-η^1:η^2 bridging coordination mode and the auxiliary $(Glu)^{2-}$ ligand employs a μ_4-η^1:η^1:η^1:η^2 coordination fashion.

Table 1. Selected bond distances (Å) and bond angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Nd(1)–O(2)$^{\#1}$	2.435(2)	Nd(1)–O(5)$^{\#2}$	2.438(2)
Nd(1)–O(6)$^{\#3}$	2.444(2)	Nd(1)–O(7)	2.473(3)
Nd(1)–O(4)$^{\#4}$	2.494(2)	Nd(1)–O(4)	2.532(2)
Nd(1)–O(1)	2.536(2)	Nd(1)–O(3)	2.568(2)
Nd(1)–O(2)	2.677(2)	Nd(1)–Nd(1)$^{\#1}$	4.0285(4)
N(1)–C(1)	1.323(5)	N(1)–C(5)	1.332(6)
N(2)–C(10)	1.337(5)	N(2)–C(6)	1.341(4)
N(3)–C(11)	1.326(6)	N(3)–C(15)	1.331(6)
O(1)–C(22)	1.253(4)	O(2)–C(22)	1.278(4)
O(2)–Nd(1)$^{\#1}$	2.435(2)	O(3)–C(23)	1.241(4)
O(4)–C(23)	1.294(4)	O(4)–Nd(1)$^{\#4}$	2.494(2)
O(5)–C(27)	1.262(4)	O(5)–Nd(1)$^{\#5}$	2.438(2)
O(6)–C(27)	1.247(4)	O(6)–Nd(1)$^{\#3}$	2.444(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(2)$^{\#1}$Nd(1)O(5)$^{\#2}$	75.72(8)	O(2)$^{\#1}$Nd(1)O(6)$^{\#3}$	74.21(8)
O(5)$^{\#2}$Nd(1)O(6)$^{\#3}$	136.09(8)	O(2)$^{\#1}$Nd(1)O(7)	93.93(8)
O(5)$^{\#2}$Nd(1)O(7)	74.82(9)	O(6)$^{\#3}$Nd(1)O(7)	138.14(9)
O(2)$^{\#1}$Nd(1)O(4)$^{\#4}$	153.04(8)	O(5)$^{\#2}$Nd(1)O(4)$^{\#4}$	78.04(8)
O(6)$^{\#3}$Nd(1)O(4)$^{\#4}$	130.95(8)	O(7)Nd(1)O(4)$^{\#4}$	73.18(9)
O(2)$^{\#1}$Nd(1)O(4)	133.70(7)	O(5)$^{\#2}$Nd(1)O(4)	141.35(8)
O(7)Nd(1)O(4)	78.17(8)	O(4)$^{\#4}$Nd(1)O(4)	67.93(8)
O(2)$^{\#1}$Nd(1)O(1)	122.00(7)	O(5)$^{\#2}$Nd(1)O(1)	99.77(8)
O(6)$^{\#3}$Nd(1)O(1)	71.03(9)	O(7)Nd(1)O(1)	141.67(9)
O(4)$^{\#4}$Nd(1)O(1)	68.61(8)	O(4)Nd(1)O(1)	84.78(7)
O(2)$^{\#1}$Nd(1)O(3)	83.34(7)	O(5)$^{\#2}$Nd(1)O(3)	137.25(8)
O(6)$^{\#3}$Nd(1)O(3)	68.95(8)	O(7)Nd(1)O(3)	69.87(9)
O(4)$^{\#4}$Nd(1)O(3)	112.71(7)	O(4)Nd(1)O(3)	50.90(7)
O(1)Nd(1)O(3)	122.87(8)	O(2)$^{\#1}$Nd(1)O(2)	76.10(8)
O(5)$^{\#2}$Nd(1)O(2)	70.41(8)	O(6)$^{\#3}$Nd(1)O(2)	71.81(8)
O(7)Nd(1)O(2)	145.18(8)	O(4)$^{\#4}$Nd(1)O(2)	100.78(7)
O(4)Nd(1)O(2)	132.42(7)	O(1)Nd(1)O(2)	49.66(7)
O(3)Nd(1)O(2)	139.32(8)		

* Symmetry codes: $^{\#1}$ $-x + 1, -y + 1, -z + 1$; $^{\#2}$ $x - 1, y - 1, z$; $^{\#3}$ $-x + 2, -y + 2, -z + 1$; $^{\#4}$ $-x + 2, -y + 1, -z + 1$; $^{\#5}$ $x + 1, y + 1, z$.

Two neighboring Nd^{3+} ions are quadruply bridged by carboxylate groups from two (Cptpy)$^-$ and two (Glu)$^{2-}$ anions, respectively, to yield a binuclear Nd(III) unit with the Nd···Nd distance of 4.0285(4) Å (Fig. 2b). The binuclear units are bridged to each other by (Glu)$^{2-}$ anions to form a 1D chain structure (Fig. 3). Further, these 1D chains are bridged by (Glu)$^{2-}$ anions to give rise to an infinite 2D layer structure (Fig. 4). From the view of topology, if each nona-coordinated Nd^{3+} ion acts as five-connected node and (Glu)$^{2-}$ as 4-connected node, the 2D layer structure is simplified to a (4,5)-connected 2D topological network with the Schläfli symbol of (3.4^3.5^2)(3^2.4^4.5^2.6^2). Finally, the layers are extended into a 3D supramolecular network through hydrogen bonding interactions between the coordination water molecule and uncoordinated nitrogen atoms from the

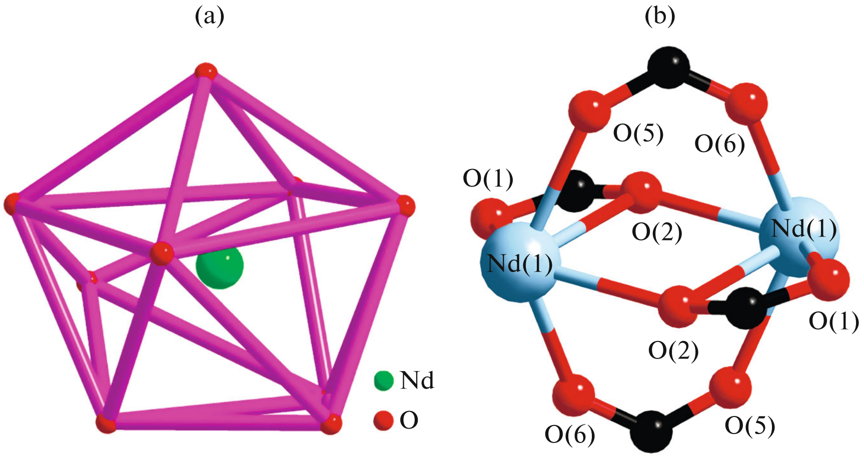

Fig. 2. The distorted tricapped trigonal prism coordination geometry of Nd(III) (a) and the bimetallic unit in **I** (b).

pyridyl ring of (Cptpy)$^-$ anion (O(7)–H(7*A*)···N(1)^i, 1.87 Å, 169°, symmetry code ^{i} *x, y, z* – 1), which is further firmed the whole backbone (Fig. 5).

In order to confirm the purities of the bulk samples, PXRD experiments was carried out for **I**. The experimental pattern is in good agreement with the corresponding simulated one, indicating that the synthesized bulk materials and the measured single crystals are the same.

The lanthanide coordination polymer may possess excellent luminescent property in terms of the line-like and high color-pure emission. Hence, the solid-state luminescent property of compound **I** are investigated at room temperature. As shown in Fig. 6, compound **I** exhibits characteristic emission bands of Nd^{3+}

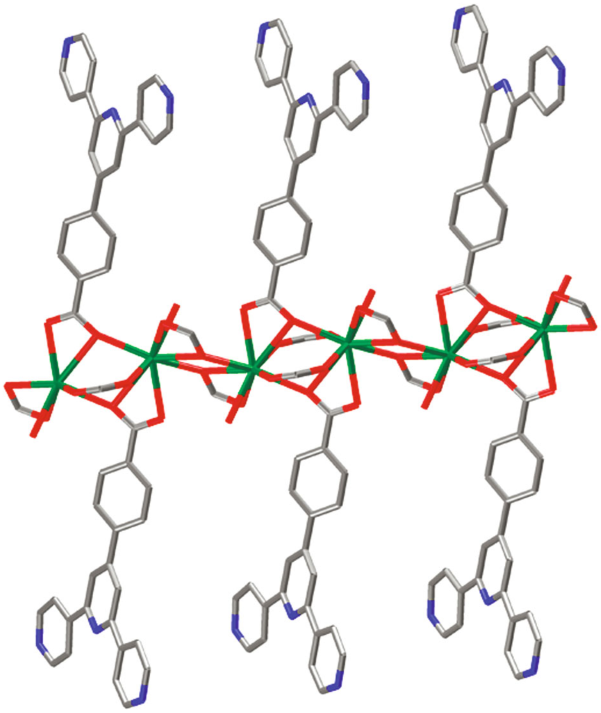

Fig. 3. View of the 1D chain of **I**.

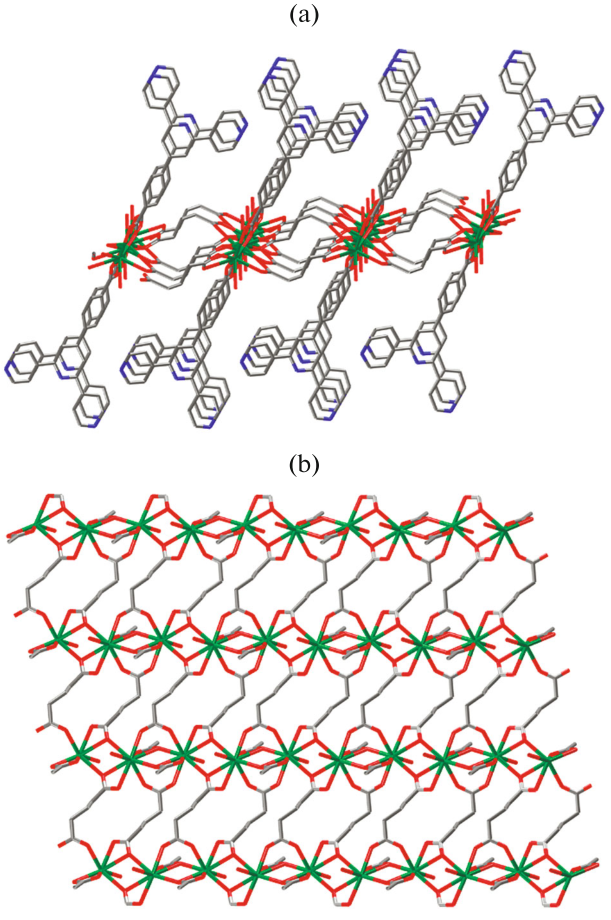

Fig. 4. View of the 2D layer structure of **I** in A (a) and C (b) direction.

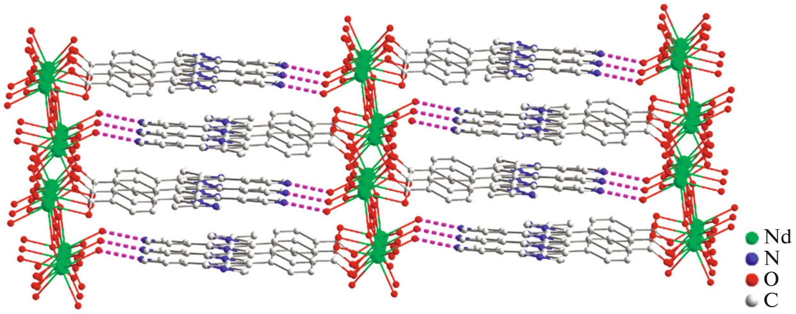

Fig. 5. The 3D supramolecular structure constructed by hydrogen bonding interaction.

ions in the NIR region, which indicating that the triplet state T1 of HCptpy ligand matches well with the excited state of Nd^{3+} cations and the energy transfer is efficient from ligand to Nd^{3+} cation. Upon excitation at 354 nm, we observed three emission bands at nearly 900, 1060 and 1335 nm, which are attributed to $^4F_{3/2} \to {}^4I_{J/2}$ ($J = 9, 11, 13$) transitions [24]. The second band, which is potentially applicable to laser emission and in vivo detection [25, 26].

In order to examine the thermal stability of the compound, TG analyses was carried out for **I** at 30–900°C. The TG curve of **I** shows an initial weight loss of 8.96% below 224°C (calcd. 9.20%) corresponds to the loss of two coordinated water molecule and five lattice water molecules. After 380°C, the weight loss of 25.27% until 507°C corresponds to the loss of one $(Cptpy)^-$ anion ligand (calcd. 25.70%) and does not stop until heating to 950°C. TG analysis results of the compound possess great thermal stability and the frameworks are stable up to around above 400°C.

IR spectra data of HCptpy ligand and compound **I** were measured in the range 400–4000 cm^{-1}. Compared with the free ligand, the absence of of any strong bands around 1700 cm^{-1} for **I** indicates that the carboxylate groups of organic-acid are completely deprotonated [27]. In the IR spectrum of **I**, the characteristic peaks of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ are observed at 1539–1446 and 1409–1352 cm^{-1}, respectively. The difference between $\nu_{as}(COO)$ and $\nu_s(COO)$ ($\Delta <$ 211 cm^{-1}) suggests that the carboxylate groups coordinate to the Nd^{3+} ions in bidentate-cheating coordination mode [28]. The result is in good agreement of the X-ray structural analyses.

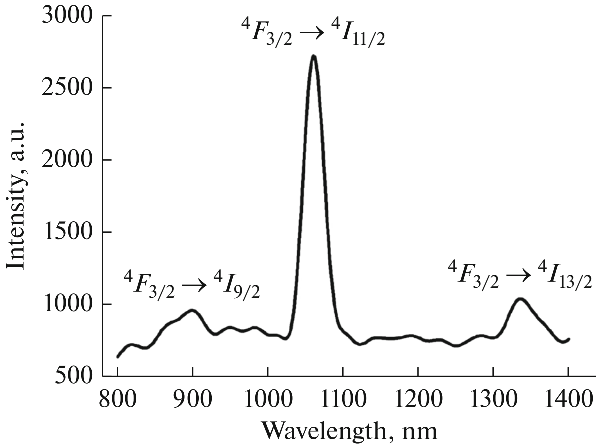

Fig. 6. Solid-state NIR emission spectra ($\lambda_{ex} = 354$ nm) of **I** at room temperature.

In summary, we have successfully synthesized a rare Ln-MOF based on Nd(III) binuclear nodes with 4'-(4-carboxyphenyl)-4,2':6',4''-terpyridine and glutaric acid via hydrothermal conditions. Compound **I** displays a (4,5)-connected 2D topological net and the Schläfli symbol of $(3.4^3.5^2)(3^2.4^4.5^2.6^2)$, which is further extended into a 3D supramolecular network by hydrogen bonds. Moreover, **I** displays interesting NIR luminescence property. This work provides a rational synthetic strategy for the construction of novel functional Ln-MOFs with terpyridyl carboxylic acid ligand with special symmetry.

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