ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 9, pp. 573–578. © Pleiades Publishing, Ltd., 2015.

Synthesis, Structural, and Luminescence of Two Coordination Polymers[1]

L. Lu[a, *], W. P. Wu[a], A. Q. Ma[b, **], B. Xie[a], and Y. Wu[a]

[a] *School of Chemistry and Pharmaceutical Engineering, Sichuan University of Science and Engineering, Zigong, 643000 P.R. China*

[b] *Guangdong Medical College, School of Pharmacy, Dongguan, 523808 P.R. China*

*e-mail: *lulusczg@126.com, **maqandght@126.com*

Received February 2, 2015

Abstract—A organic compound and its lanthanide coordination polymer with chemical formulae HL^1, $\{[La(L^1)_3(H_2O)_2] \cdot 2H_2O \cdot 2,2'\text{-Bipy}\}$ (**I**), (HL^1 = 3-(4-hydroxyphenyl)propanoic acid, 2,2'-Bipy = 2,2'-bipyridine) have been synthesized and structurally characterized. Organic compound HL^1 shows 1D supramolecular chain constructing from intermolecular hydrogen-bonded interaction. Complex **II** has 1D infinite chain with a $[La(L^1)_3]_n$ dimeric repeat unit with lanthanide in a nine-coordinate environment. Furthermore, the luminescent properties of the two compounds were discussed in detail (CIF files CCDC nos. 1045032 (HL^1), 1045033 (**I**)).

DOI: 10.1134/S1070328415080035

INTRODUCTION

Coordination polymers have attracted intense attention in recent years because of their intriguing structures and potential applications as functional materials [1–3]. Many efforts has been paid to the rational design of MOFs for the specific needs of applications. A conventional strategy of using long exo-multidentate ligands has been successful to construct frameworks with porosity [4]. Moreover, the flexible carboxylic acids are good candidates for the construction of new coordination polymers as the carboxyl groups can form C–O–M–O cyclic mode with central metal ions, thus, improving the stability of transition metal complexes [4].

Luminescent lanthanide complexes have gained recognition owing to potential applications in biochemistry and materials science [5–7]. Lanthanide ions are excellent luminescent centers and the luminescent properties are influenced by ligands. Compared to first-row transition metals, lanthanides have a larger coordination sphere and more flexible coordination geometry, easily coordinating to various carboxylates and N-containin ligands to form complexes with diverse stereochemistries [8, 9]. Aromatic carboxylic acid, with versatile binding and coordination modes, are widely employed in construction of luminescent lanthanide coordination polymers, which usually exhibit high thermal stability and intense fluorescence because of a large conjugated π-electron system [10–12]. In this report, we employed a flexible carboxylate 3-(4-hydroxyphenyl)propanoic acid (HL^1), to build complexes. We anticipated that increase architecture complexity may be introduced by using chelating aromatic N-donor linker and there is an opportunity to drive the new modes of network assembly required to satisfy the unique constraints imposed by linker geometries. Furthermore, such types of the carboxylate and carboxyl groups of HL^1 are always actively involved in H-bonding interactions, which might turn out to be significant structure-controlling factors [12, 13]. The reaction of HL^1 with La(III) and the well-known dipyridyl linker of 2,2'-Bipy under mild conditions resulted the formation of a new complex $\{[La(L^1)_3(H_2O)_2] \cdot 2H_2O \cdot 2,2'\text{-Bipy}\}$ (**I**), characterized by single crystal X-ray diffraction. Furthermore, the luminescent properties of compounds HL^1 and **I** were discussed in detail.

EXPERIMENTAL

Materials and methods. All reagents were purchased from commercial sources and used as received. IR spectra were recorded with a PerkinElmer Spectrum One spectrometer in the region 4000–400 cm^{-1} using KBr pellets. TGA was carried out with a Metter-Toledo TA 50 in dry dinitrogen (60 mL min^{-1}) at a heating rate of 5°C min^{-1}. X-ray powder diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60 kV, 300 mA for CuK_α radiation (λ = 1.5406 Å) with a scan speed of 2°C/min and a step size of 0.013° in 2θ. Luminescence spectra for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter.

---

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement information for compound HL^1 and **I**

Parameter	Value	
	HL^1	**I**
Formula weight	166.17	862.64
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Crystal color	Colorless	Colorless
a, Å	11.275(9)	15.6119(3)
b, Å	5.330(4)	9.3468(2)
c, Å	14.019(11)	26.9308(5)
β, deg	105.937(14)	106.539(1)
V, Å^3	810.1(11)	3767.19(13)
Z	4	4
ρ_{calcd}, g/cm^3	1.362	1.521
μ, mm^{-1}	0.102	1.201
F(000)	352	1760
θ Range, deg	1.88–25.20	3.21–27.50
Reflection collected	3966	56943
Independent reflections (R_{int})	3966 (0.0241)	56943 (0.0552)
Reflections with $I > 2\sigma(I)$	1093	5675
Number of parameters	117	480
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0438, 0.1196	0.0371, 0.0767
R_1, wR_2 (all data)**	0.0594, 0.1388	0.0747, 0.0896
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.188, –0.175	0.794, –0.767

* $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, ** $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2\}^{1/2}$.

Syntheses of HL^1. A mixture of HL^1 (0.0149 g), 2,2'-Bipy (0.0220 g), CH_3CH_2OH (5 mL) and deionised water (5 mL) was stirred for 30 min in air. The resulting solution was kept at room temperature for one week, the crystals formed were filtered off, washed with water and dried in air.

For $C_9H_{10}O_3$ (M = 166.17)

anal. calcd., %:	C, 65.05;	H, 6.07.
Found, %:	C, 65.11;	H, 5.92.

Syntheses of I was cattied out by the same synthetic method that for HL^1 except that $La(NO_3)_3 \cdot 6H_2O$ (0.2 mmol) was introduced into the reactive system.

For $C_{52}H_{52}N_4O_{16}La_2$ (1213.78)

anal. calcd., %:	C, 51.52;	H, 5.02;	N, 3.25.
Found, %:	C, 51.32;	H, 5.07;	N, 3.04.

IR (KBr; ν, cm^{-1}): 3288 v.s, 1904 m, 1534 v.s, 1421 v.s, 1242 v, 1085 m, 826 m,748 m, 523 m.

X-ray crystallography. Single crystal X-ray diffraction analysis of the title compounds were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using ϕ–ω scan technique at room temperature. Data were processed using the Bruker SAINT package and the structures solution and the refinement procedure was performed using SHELX-97 [14]. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The hydrogen atoms of lattice water molecule in compounds were located using the different Fourier method. Table 1 shows crystallographic data of HL^1 and **I**. Selected bond distances and bond angles are listed in Table 2. Some H-bonded parameters are listed in Table 3.

Supplementary material for structures HL^1 and **I** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1045032 (HL^1), 1045033 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 2. Selected bond distances (Å) and angles (deg) of structures HL^1 and **I**

Bond	*d*, Å	Bond	*d*, Å
		I	
C(1)–O(1)	1.378(3)	C(9)–O(2)	1.203(3)
C(9)–O(3)	1.290(3)		
		II	
La(1)–O(1*w*)	2.584(3)	La(1)–O(2)	2.540(3)
La(1)–O(2*w*)	2.576(3)	La(1)–O(4)	2.642(3)
La(1)–O(5)	2.576(3)	La(1)–O(7)	2.539(3)
Angle	ω, deg	Angle	ω, deg
		I	
C(1)O(1)H(4*A*)	112 (4)	C(1)O(1)H(4*B*)	103(4)
C(9)O(3)H(3*A*)	111.00	H(4*A*)O(1)H(4*B*)	144(6)
		II	
O(1*w*)La(1)O(2)	66.95(9)	O(1*w*)La(1)O(2*w*)	72.30(9)
O(1*w*)La(1)O(4)	133.44(9)	O(1*w*)La(1)O(7)	77.43(8)
O(2)La(1)O(2*w*)	138.04(9)	O(2)La(1)O(4)	71.63(9)
O(2)La(1)O(5)	70.56(9)	O(2)La(1)O(7)	86.44(8)
O(2*w*)La(1)O(4)	149.78(9)	O(2*w*)La(1)O(7)	75.23(9)
O(4)La(1)O(5)	49.33(9)	O(4)La(1)O(7)	120.60(8)
O(5)La(1)O(7)	71.46(9)		

Table 3. Hydrogen bonding distances (Å) and angles (deg) for **I**, **II**

		I	
O(3)···O(2)	2.639(7)	O(1)···O(1)	2.899(2)
O(3)–H(3*A*)···O(2)	174	O(1)–H(4*A*)···O(1)	178
		II	
O(3)···N(2)	2.803(5)	O(6)···O(3*w*)	2.600(1)
O(9)···O(8)	2.7312	O(1*w*)···O(9)	2.9807
O(1*w*)···O(3*w*)	2.7265	O(2*w*)···O(5)	2.692(2)
O(2*w*)···O(6)	2.828(6)	O(3*w*)···O(4*w*)	2.682(5)
O(4*w*)···N(1)	2.911(7)		
O(3)–H(3)···N(2)	160.00	O(6)–H(6)···O(3*w*)	138.00
O(9)–H(9)··O(8)	167.00	O(1*w*)–H(11)···O(9)	157.00
O(1*w*)–H(11)···O(3*w*)	159.00	O(2*w*)–H(21)···O(5)	168.00
O(2*w*)–H(22)···O(6)	139.00	O(2*w*)–H(32)···O(4)*w*	162.00
O(4*w*)–H(2*A*)···N(1)	155.00		

RESULTS AND DISCUSSION

The adjacent carboxylate groups form a dermic unit through H-bonded interaction (Table 3), then the phenolic groups taking as donor extend the discrete unit into a 1D chain, as shown in Fig. 1. To investigate the complexity on the L^1–2,2'-Bipy system, the lanthanum ion was deliberately introduced. A new compound **I** was obtained. Complex **I** displays a 1D polymer with $[La(L^1)_3]$ dimeric repeat units. The asymmetric unit of **I** consists of one La(III), three L^1 anions, two coordinative water molecules, one free 2,2'-Bipy and two lattice water molecules, as shown in Fig. 2a. The La(III) is nine-coordinate by seven O-donors of six different L^1 ligands and two coordinative water molecules. The La(III) can be described as having a cap square antiprism geometry (Fig. 2b) with La–O bond

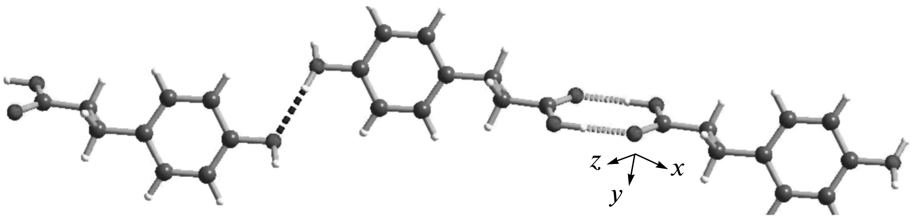

Fig. 1. View of the 1D packing framework directing by weak interactions in HL^1.

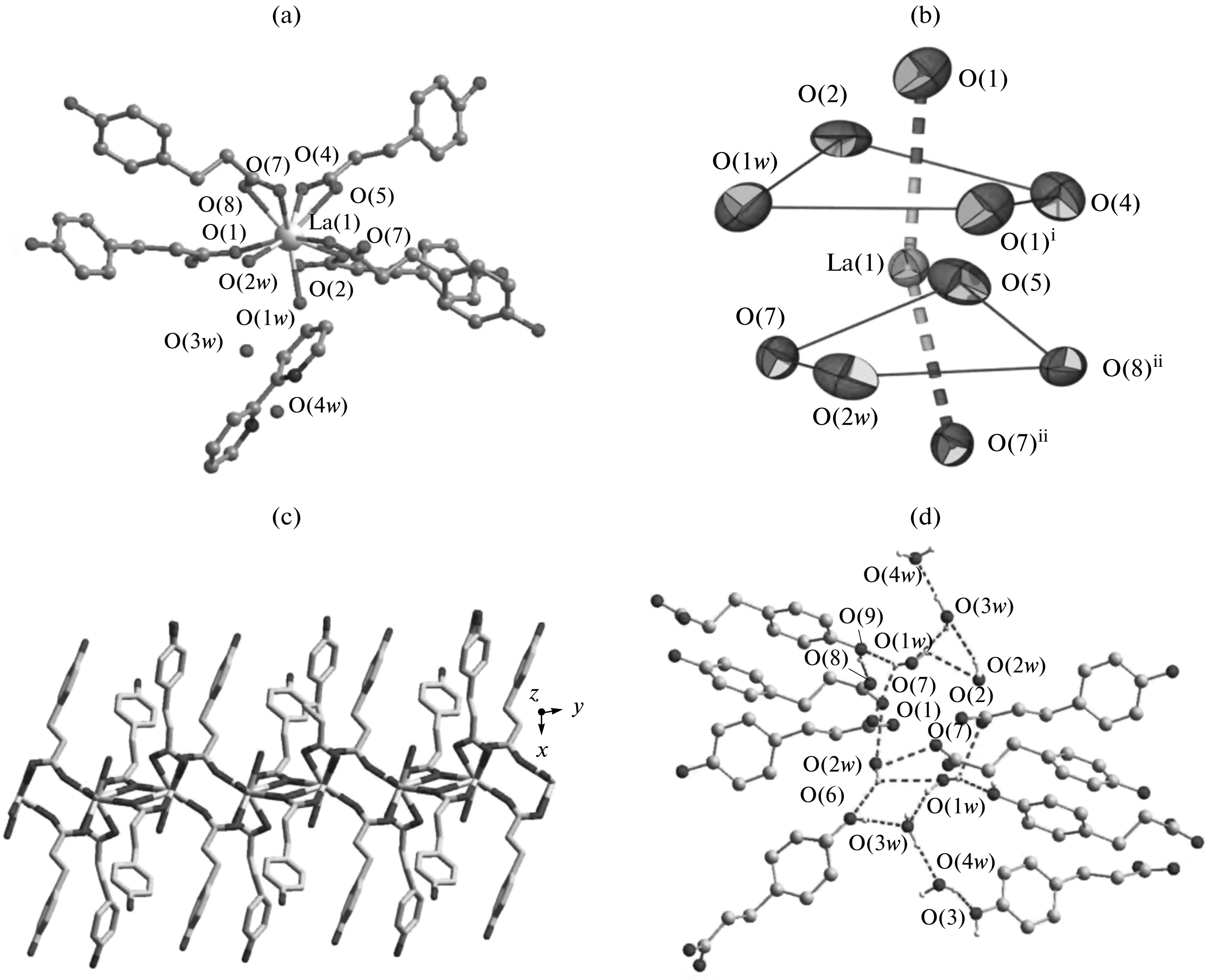

Fig. 2. The coordination geometries of the metal centers and the ligands geometries in **I** (displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity) (a); SAP geometry surrounding La ion (b); view of the 1D O–C–O–La–O–C–O– chain (c); (d) view of the packing motif directing by weak interactions.

distances ranging from 2.576(3) to 3.006(3) Å, all of which are within the range of those observed for other La(II) complexes with oxygen donors. In the polymeric structure of **I**, the L^1 ligand shows η^1-η^1-μ_2, η^2-η^1-μ_2 and η^0-η^0-μ_1 modes to link two La^{3+} ions, in which similar with other La-based complexes with carboxylate ligands. The carboxylates of L^1 connect La(III) centers to form a zigzag chain parallel to the *y* axis (Fig. 2c).

In addition, careful analysis reveals that the hydrogen bonded interaction association of solvent water molecules, phenolic groups, free 2,2'-Bipy and carboxylate groups in **I** leads to the formation of 2D supramolecular network (Table 3). The oxygen atoms

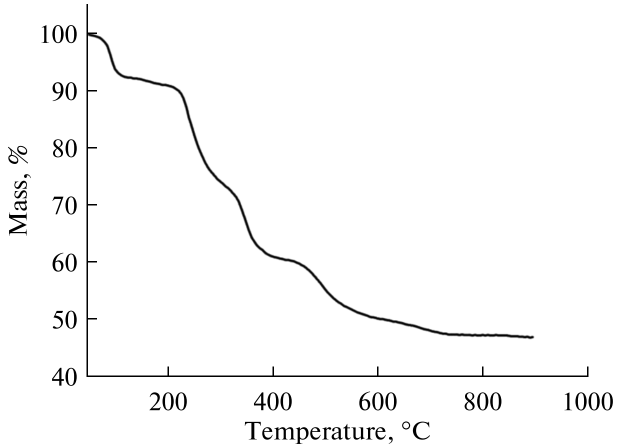

Fig. 3. The TGA curve in **I**.

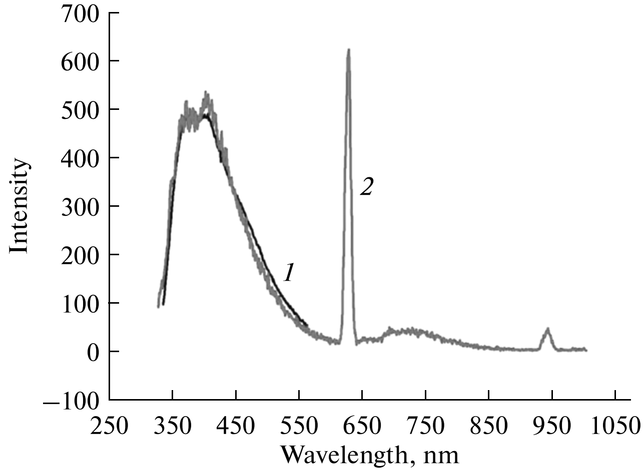

Fig. 4. View of the fluorescent emission spectra of HL^1 (*1*) and **I** (*2*).

(O(1*w*), O(2*w*), O(3*w*) and O(4*w*)) of water molecule could take as acceptors to bind with O(3), O(6) and O(9) from phenolic groups. The oxygen atom (O(4*w*)) from free water molecule acting as donor binds to N(1) from free 2,2'-Bipy. Also, each water molecule acting as donors or/and acceptors bind to others water molecules, leading to a tetrameric water cluster. The O(7) and O(8) from carboxylate groups taking as acceptors involve in O(1*w*) and O(2*w*), respectively. It should be noted that there is not any packing interaction between rings from adjacent 2,2'-Bipy molecules, as shown in Fig. 2d.

In the FT–IR spectra, compound **I** shows a broad band centered around 3300 cm^{-1} attributable to the O–H stretching frequency of the water molecules. The asymmetric stretching vibrations ν(COO$^-$) appear around 1540 cm^{-1} for **I**, and the symmetric stretching vibrations ν(COO$^-$) are observed 1420 cm^{-1}. For the complex, the difference between the asymmetric and symmetric stretches, $\Delta\nu_{as}(COO^-) - \nu_s(COO^-)$, are on the order of 150 cm^{-1} indicating that carboxyl groups are coordinated to the metal in a bidentate modes [15], consistent with the observed X-ray crystal structure of **I**.

To study the stability of the polymer, thermogravimetric analyses (TGA) of complex **I** was performed (Fig. 3). The TGA diagram shows two main weight loss steps. The first weight loss began at 35°C and completed at 180°C. The observed weight loss of 8.5% is corresponding to the loss of the coordinative water molecule (calcd. 8.4%). Soon after, the deposition of all the ligands starts on. The second weight loss occurs in the range 216–760°C, which can be attributed to the elimination of L^1 and bipy ligands.

Additionally, to confirm the phase purity and stability of compound **I**, the original samples were characterized by XRPD method. Although the experimental patterns have a few unindexed diffractions lines and some are slightly broadened in comparison to those simulated from single-crystal models, it can still to be considered that the bulk synthesized materials and as-grown crystal are homogeneous for compound **I**.

Metal-organic hybrid coordination polymers with lanthanide metal centers have been widely investigated for their fluorescence properties. The lanthanides only exhibit weak emissions under direct excitation due to their low molar absorptivity [16]. Lanthanide-centered emission can be sensitized by coordinating ligands with π-systems, which can efficiently absorb and transfer the energy. 1D fluorescence of HL^1 and **I** were investigated at room temperature under excitation and emission wavelengths of 315 nm with the same interval of 5 nm, respectively. As shown in Fig. 4, emission peaks of **I** at 400, 625 and 921 nm can be obtained under the excitation wavelength, which corresponds to $^5D_0 \rightarrow {}^7F_n$ (n–4) transitions of La(III), respectively, indicating a moderately efficient ligand-to-metal energy transfer [17, 18]. The emission band at 625 nm ($^5D_0 \rightarrow {}^7F_2$) is the strongest emission, and the intensity increases as the site symmetry of La(III) decreases. Emission peak $^5D_0 \rightarrow {}^7F_1$ at 400 nm is a magnetic dipole transition and its intensity should vary with the crystal field strength acting on La(III). The intensity ratio $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$, which is equal to ~1.3, indicates that La^{3+} ions have a low-symmetry coordination environment [19], consistent with the single-crystal X-ray analysis. The luminescent intensity of Ln(III) relies on the efficiency of energy transfer from the ligand to Ln(III) [20]. Presence of lattice and coordination water decreases the luminescent emission intensity of lanthanide coordination polymers, as the thermal oscillation of water molecules consume some excitation energy absorbed by "antenna" ligands. There are more lattice or coordination water molecules in **I**, thus the emission intensities are much weaker than those due to less activation in **I**.

ACKNOWLEDGMENTS

The authors acknowledge financial assistance from Sichuan University of Science and Engineering (nos. 2014PY01, and 2015PY03), and the Education Committee of Sichuan Province (no. 14ZB0220, 15ZB0222, 15ZB0214).

REFERENCES

1. Chen, B.L., Xiang, S.C., and Qian, G.D., *Acc. Chem. Res.*, 2010, vol. 43, p. 111.
2. Carlucci, L., Ciani, G., and Proserpio, D.M., *Coord. Chem. Rev.*, 2003, vol. 246, p. 247.
3. Raymond, J. and Blankenship, R.E., *Coord. Chem. Rev.*, 2008, vol. 252, p. 377.
4. Sun, C.Y., Gao, S., and Jin, L.P., *Eur. J. Inorg. Chem.*, 2006, vol. 12, p. 2411.
5. Liu, J.Q., Wang, Y.Y., Liu, P., Dong, Z., et al., *CrystEngComm*, 2009, vol. 11, p. 207.
6. Mondal, R., Bhunia, M.K., and Dhara, K., *CrystEngComm*, 2008, vol. 10, p. 1167.
7. Farha, O.K., Malliakas, C.D., Kanatzidis, M.G., and Hupp, J.T., *J. Am. Chem. Soc.*, 2010, vol. 132, p. 950.
8. Du, M., Li, C.P., and Guo, J.H., *CrystEngComm*, 2009, vol. 11, p. 1536.
9. Wuest, J.D., *Chem. Commun.*, 2005, p. 5830.
10. MacGillivray, L.R., *J. Org. Chem.*, 2008, vol. 73, p. 3311.
11. Kumar, A., Hüch, V., and Ram, V.J., *CrystEngComm*, 2013, vol. 15, p. 7019.
12. Badjic, J.D., Nelson, A., Cantrill, S.J., et al., *Acc. Chem. Res.*, 2005, vol. 38, p. 723.
13. Schmidbaur, H. and Schier, A., *Chem. Soc. Rev.*, 2008, vol. 37, p. 1931.
14. Sheldrick, G.M., *SHELXL-97, Program for Structure Determination and Refinement*, Göttingen (Germany): Univ. of Göttingen, 1997.
15. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley Interscience, 1997.
16. Ma, D.Y., Guo, H.F., Qin, L., et al., *J. Coord. Chem.*, 2012, vol. 65, p. 3424.
17. de Bettencourt Dias, A. and Viswanathan S., *Chem. Commun.*, 2004, p. 1024.
18. Bunzli, J.C.G., in *Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice*, Bunzli, J.C.G. and Choppin, G.R., Eds., Elsevier Scientific Publishers, Amsterdam, The Netherlands, 1989, pp. 219–293.
19. Wong, K.L., Law, G.L., Yang, Y.Y., and Wong, W.T., *Adv. Mater.*, 2006, vol. 18, p. 1051.
20. Lu, W.G., Jiang, L., and Lu, T.B., *Cryst. Growth Des.*, 2010, vol. 10, p. 4310.