Preparation and characterization of two lanthanide complexes with one-dimensional chain-like structures

Hui Luo\(^1\) and Wen-Tong Chen\(^{2,3}\)\(^\ast\)

Abstract
Two novel RE–Hg (RE = rare earth) complexes \([\text{RE}(\text{IA})_3(\text{H}_3\text{O})_2]_n \cdot 2n(\text{HgCl}_4) \cdot n(\text{HgCl}_5) \cdot n\text{H}_2\text{O} \cdot 3n\text{H}_2\text{O}\) (RE = Y, 1; Lu, 2; IA = isonicotinic acid anion) were synthesized through hydrothermal reactions and are structurally characterized by single-crystal X-ray diffraction. The two complexes are isostructures and are characteristic of a one-dimensional chain-like structure. Both complexes are characterized by a three-dimensional supramolecular network. Photoluminescence experiments using solid-state samples show that they possess emission bands in the blue or red region. They have remarkable CIE chromaticity coordinates of (0.1172, 0.182) and (0.623, 0.3765), respectively. As a result, they are potential candidates for light-emitting materials for light-emitting diodes. They show wide optical band gaps of 3.29 eV and 2.89 eV, as revealed by the solid-state UV/Vis diffuse reflectance spectra.

Keywords
Commission Internationale de l’Éclairage, mercury, photoluminescence, rare earth, semiconductor

Introduction
Rare earth materials have gained more and more attention in recent years because of their fascinating magnetic, semiconductor, and photoluminescence performance.\(^1\)–\(^9\) Many researchers have devoted their efforts toward the exploration of the design, preparation, and characterization of novel rare earth materials. To date, scientists have accomplished a large number of studies on rare earth materials in order to reveal the practical applications of such materials in the field of light-emitting diodes (LEDs), magnets, electrochemical displays, luminescent probes, and so on.\(^10\)–\(^13\) In comparison with the many studies on the magnetic and photoluminescence performance of the rare earth materials, reports on the semiconductor performance of the rare earth materials are still rare and needs to be explored further.

Zinc, cadmium, and mercury are group 12 (IIB) elements and they have also gained increasing interest for many decades due to the following reasons: their various coordination numbers, their photoluminescence and photoelectric performance, as well as the vital role played by zinc in the biosystem.\(^14\)–\(^15\) Moreover, IIB elements are also an important component for semiconductor materials. To date, many semiconductor materials using IIB element have been prepared.\(^16\)–\(^19\) We have focused on exploring photoluminescence and semiconductor materials for a long time. In recent years, our main aim was investigating RE–IIB (RE = rare earth) materials in order to obtain new insights into their structures, photoluminescence, and semiconductor performance. We report in the present work the syntheses, structures, photoluminescence, and semiconductor performance of two novel RE–Hg materials \([\text{RE}(\text{IA})_3(\text{H}_3\text{O})_2]_n \cdot 2n(\text{HgCl}_4) \cdot n(\text{HgCl}_5) \cdot n\text{H}_2\text{O} \cdot 3n\text{H}_2\text{O}\) (RE = Y, 1; Lu, 2; IA = isonicotinic acid anion) with a one-dimensional (1D) chain-like structure. It is noteworthy that these complexes are characterized by a three-dimensional (3D) supramolecular network.

\(\ast\) Corresponding author:
Wen-Tong Chen, Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, J’ian Key Laboratory of Photoelectric Crystal Materials and Device, Humic Acid Utilization Engineering Research Center of Jiangxi Province, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggangshan University, J’ian, P.R. China

\(1\) Health Science Center, Jinggangshan University, J’ian, P.R. China

\(2\) Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, J’ian Key Laboratory of Photoelectric Crystal Materials and Device, Humic Acid Utilization Engineering Research Center of Jiangxi Province, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggangshan University, J’ian, P.R. China

\(3\) Department of Ecological and Resources Engineering, Fujian Provincial Key Laboratory of Eco-Industrial Green Technology, Wuyi University, Wuyishan, P.R. China

© The Author(s) 2020

Article reuse guidelines:
SAGE journals use the Creative Commons license system. Please see the Copyright and Reprints page for further information.

Creative Commons Attribution-NonCommercial 4.0 License (https://creativecommons.org/licenses/by-nc/4.0/) which permits non-commercial use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (https://us.sagepub.com/en us/nam/open-access-at-sage).
Results and discussion

The title compounds 1 and 2 are isostructures and crystallize in the monoclinic system with four formula units in a cell, as revealed by single-crystal X-ray diffraction. In this section, only compound 2 is given as an example to describe the crystal structure. The asymmetric unit of compound 2 possesses one lutetium(III) ion, two mercury ions, seven chloride ions, two coordinating water molecules, and three isonicotinic acid ligands (Figure 1). The crystal structure of compound 2 contains one \([\text{Lu(IA)}_3\left(\text{H}_3\text{O}\right)_2]^{2+}\) cation, two \(\text{HgCl}_4^{2−}\) anions, one \(\text{HgCl}_5^{3−}\) anion, three \(\text{H}_3\text{O}^{+}\) cations, and one lattice water molecule. All of the crystallographically independent atoms, except for the \(\text{Cl}_7\) atom, reside at general positions. The Lu1 ion shows an eight-coordination environment, being bound by eight oxygen atoms of which six are from six isonicotinic acid ligands and two are from two coordinating water molecules, yielding a slightly distorted square antiprism. The bond lengths of Lu–O are between 2.272(4) Å and 2.430(4) Å, with an average value of 2.321(4) Å, which is comparable with those reported previously.20–22 The bond angles of O–Lu–O are in the range of 69.49(14)°–145.80(15)°. Hg1 is coordinated by four chloride ions to give a distorted \(\text{HgCl}_4^{2−}\) tetrahedron, while the Hg2 ion is surrounded by five chloride ions to form a \(\text{HgCl}_5^{3−}\) anion. The bond angles of Cl–Hg–Cl are in the range of 90.47(11)°–123.11(9)° and the bond lengths of Hg–Cl span of 2.293(3) Å–2.638(3) Å, which is normal and comparable with those found in the literature.23–25 Every two neighboring lutetium(III) ions connect together through isonicotinic acid ligands to yield a 1D Lu–(IA)–Lu–(IA)–Lu–(IA) chain, running along the \(c\) direction (Figure 2). The Lu–(IA)–Lu–(IA)–Lu–(IA) chains, \(\text{HgCl}_4^{2−}\) anions, \(\text{HgCl}_5^{3−}\) anions and lattice water molecules interconnect together through hydrogen bonding interactions to construct a 3D supramolecular network (Figure 3).

It is well known that rare earth materials usually exhibit photoluminescence performance, which endows these materials with important applications in the areas of LEDs, chemical sensors, electrochemical displays, and so on.26-27 To date, a large number of rare earth materials have been reported due to their fascinating photoluminescence performance.28-30 Furthermore, mercury materials and isonicotinic acid compounds can also display photoluminescence performance.31-33 Therefore, based on the
above considerations, we deem that both lanthanide complexes could display interesting photoluminescence performance. The photoluminescence performance for both complexes in the present work was studied in the solid state at room temperature. The results of the photoluminescence measurements are given in Figures 4 and 5. For compound 1, upon excitation at 332 nm, its photoluminescence emission spectrum showed one main peak at 492 nm and one shoulder peak at 470 nm; both of them located in the blue region. In contrast, when compound 2 was excited at a wavelength of 251 nm, its photoluminescence emission spectrum showed one main peak at 773 nm and two shoulder peaks at 701 nm and 819 nm; all of them located in the red region. The blue-light emission of compound 1 is in good agreement with the CIE (Commission Internationale de l’Éclairage) chromaticity coordinate (0.1172, 0.182), as shown in Figure 6. The red-light emission of compound 2 is also in good agreement with the CIE chromaticity coordinate (0.623, 0.3765), as shown in Figure 7. As a result, they are potential candidates as color converters for lighting and displays.

The group 12 or IIB elements are zinc, cadmium, and mercury; they are well known in the field of semiconductor materials. Both compounds 1 and 2 possess mercury and it is believed that they could exhibit semiconductor behavior. Hence, we obtained their solid-state UV/Vis diffuse reflectance spectra using solid-state samples at room temperature. Their diffuse reflectance spectra data were treated with the Kubelka–Munk function, which is known as the function \( \alpha/S = (1-R)^2/2R \), where \( \alpha \) refers to the absorption.
coefficient, $S$ is the scattering coefficient, and $R$ is the reflectance. Their optical band gap values could be found by extrapolating from the linear parts of the absorption edges of the $\alpha/S$ versus energy diagrams, as shown in Figure 8. As for compound 1, its solid-state UV/Vis diffuse reflectance spectrum shows that it possesses a wide optical band gap of 3.29 eV; while for compound 2, it has a wide optical band gap of 2.89 eV. As a result, both compounds are probably good candidates for wide optical band gap semiconductor materials. As for both compounds, their solid-state UV/Vis diffuse reflectance spectra display shallow slopes for the optical absorption edges, which suggest an indirect transition.\(^3\)\(^4\)

**Conclusion**

In summary, we have successfully synthesized two novel rare earth materials through hydrothermal reactions. The complexes are isostructures and are characteristic of a 1D chain-like structure as well as a 3D supramolecular network. Their solid-state photoluminescence emission bands are in the blue or red region. They have remarkable CIE chromaticity coordinates of (0.1172, 0.182) and (0.623, 0.3765), respectively. As a result, they are potential candidates for LEDs. They show wide optical band gaps of 3.29 eV and 2.89 eV, as revealed by the solid-state UV/Vis diffuse reflectance spectra.

**Experimental**

Reagents and chemicals were commercially purchased and directly used for the preparation of the title compounds. Elemental microanalyses of carbon, hydrogen, and nitrogen were carried out on an Elementar Vario EL elemental analyzer. The infrared spectra were measured on a Perkin-Elmer (PE) Spectrum-One Fourier-transform infrared (FTIR) spectrophotometer over the frequency range 4000 ~ 400 cm\(^{-1}\) by using the KBr pellet technique. Photoluminescence spectra were measured on an F97XP photoluminescent spectrometer. The solid-state UV/Vis diffuse reflectance spectra were measured on a TU1901 UV/Vis spectrometer with an integrating sphere.

**Synthesis of compound 1**

$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 304 mg), $\text{HgCl}_2$ (3 mmol, 369 mg), isonicotinic acid (3 mmol, 369 mg) and distilled water (10 mL) were loaded into a 25 mL Teflon-lined stainless steel vessel. This vessel was heated to 433 K and kept at this temperature for 10 days. The yield was 33% based on $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$. $\text{C}_{36}\text{H}_{45}\text{Cl}_{13}\text{Hg}_4\text{N}_6\text{O}_{20}\text{Y}_2$: calculated C, 18.61; H, 1.95; N, 3.62; found C, 18.68; H, 1.98; N, 3.66. Infrared (IR) (KBr) (cm\(^{-1}\)): 3456 (vs), 3101 (w), 2923 (w), 1964 (w), 1608 (vs), 1551 (s), 1499 (w), 1420 (vs), 1236 (m), 1058 (w), 1006 (w), 870 (w), 775 (s), 692 (s), 561 (w) and 456 (m).

**Synthesis of compound 2**

$\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 389 mg), $\text{HgCl}_2$ (3 mmol, 813 mg), isonicotinic acid (3 mmol, 369 mg) and distilled water (10 mL) were loaded into a 25 mL Teflon-lined stainless steel vessel. This vessel was heated to 433 K and kept at this temperature for 10 days. The yield was 40% based on $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$. $\text{C}_{36}\text{H}_{45}\text{Cl}_{13}\text{Hg}_4\text{Lu}_2\text{N}_6\text{O}_{20}$: calculated C, 17.33; H, 1.82; N, 3.37; found C, 17.37; H, 1.84; N, 3.41. IR (KBr) (cm\(^{-1}\)): 3457 (vs), 3089 (w), 2894 (w), 1962 (w), 1620 (vs), 1578 (s), 1498 (w), 1420 (vs), 1232 (m), 1053 (m), 1002 (w), 850 (w), 766 (s), 683 (s), 556 (w) and 420 (m).

**X-ray structure determination**

Carefully selected single crystals were adhered on the tip of a glass fiber and mounted in a SuperNova CCD diffractometer with the X-ray source being graphite monochromated Mo-$K\alpha$ radiation. The crystal data sets were measured using the $\omega$ scan mode. CrystalClear software was used for data reduction and empirical absorption correction. The crystal structures of both compounds were solved with direct methods and the final structures were refined on $\text{F}^2$ with full-matrix least-squares by employing Siemens SHEXLXTL\textsuperscript{TM} V5 crystallographic software. All non-hydrogen atoms were found based on difference Fourier maps and refined anisotropically. Crystal data as well as the details of data collection and refinement are presented in Table 1; selected bond lengths and bond angles are listed in Table 2. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1858911 and 1858912 for 1 and 2, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).
Table 1. Crystal data and structure refinement details.

| Compound | 1   | 2   |
|----------|-----|-----|
| Formula  | C$_2$H$_2$Cl$_2$Hg$_2$N$_2$O$_{20}$Y | C$_2$H$_2$Cl$_2$Hg$_2$Lu$_2$N$_2$O$_{20}$ |
| Mr       | 2124.22 | 2296.34 |
| Color    | Yellow | Colorless |
| Crystal size/mm$^3$ | 0.28 $\times$ 0.06 $\times$ 0.05 | 0.09 $\times$ 0.06 $\times$ 0.04 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | C2/c | C2/c |
| a (Å)     | 24.2541(5) | 24.1818(4) |
| b (Å)     | 20.7826(5) | 20.7599(4) |
| c (Å)     | 15.3123(3) | 15.2908(2) |
| $\beta$ (°) | 128.360(2) | 128.5800(10) |
| V (Å$^3$) | 6052.2(3) | 6000.74(18) |
| Z         | 4    | 4    |
| $2\theta_{\text{max}}$ (°) | 50 | 50 |
| Reflections collected | 16,957 | 17,502 |
| Independent reflections ($R_{int}$) | 5540 (0.031) | 5487 (0.019) |

\[
d_{\text{calc}} (g/cm^3) = 2.329 \\
\mu (mm^{-1}) = 10.13 \\
F (000) = 4008 \\
T (K) = 293 (2) \\
\rho R^2 = 0.054, 0.127 \\
S = 1.034 \\
\Delta \rho (\text{max}, \text{min}) (e/Å^3) = 3.45, -3.37, 1.55, -1.93
\]

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

Compound 1

| Bond length (Å) | Bond angle (°) |
|-----------------|----------------|
| Y(1) –O(3)     | 2.310(5)       |
| O(3) –Y(1) –O(5) | 145.72°       |

Compound 2

| Bond length (Å) | Bond angle (°) |
|-----------------|----------------|
| Lu(1) –O(3)     | 2.272(4)       |
| O(3) –Lu(1) –O(2) | 140.59°       |

References

1. Zheng TF, Yao SL, Cao C, et al. New J Chem 2017; 41: 8598.
2. Mendes RF, Ananias D, Carlos LD, et al. Cryst Growth Des 2017; 17: 5191.
3. Yao SL, Cao C, Tian XM, et al. ChemistrySelect 2017; 2: 10673.
4. Wen GX, Han ML, Wu XQ, et al. Dalton Trans 2016; 45: 15492.
5. Liu SJ, Cao C, Xie CC, et al. Dalton Trans 2016; 45: 9209.
6. Zhang P, Zhang L, Wang C, et al. J Am Chem Soc 2014; 136: 4484.
7. Li RP, Liu QY, Wang YL, et al. Inorg Chem Front 2017; 4: 1149.
8. Han S, Deng R, Xie X, et al. Angew Chem Int Ed 2014; 53: 11702.
9. Han S, Liu S, Wang Q, et al. Cryst Growth Des 2015; 15: 2253.
10. Wei JH, Yi JW, Han ML, et al. Chem Asian J 2019; 14: 3694.
11. Zheng TF, Cao C, Dong PP, et al. Polyhedron 2016; 113: 96.
12. Zhou Z, Gu JP, Qiao XG, et al. Sensor Actuat B-Chem 2019; 282: 437.
13. Liu SJ, Cao C, Yao SL, et al. Dalton Trans 2017; 46: 64.
14. Yang XG, Zhai ZM, Xu XM, et al. Dalton Trans 2019; 48: 10785.
15. Zhao Y, Wang YJ, Wang N, et al. Inorg Chem 2019; 58: 12700.
16. Zeng Y and Kelley DF. J Phys Chem C 2016; 120: 17853.
17. Zhao Y, Yang XG, Xu XM, et al. Inorg Chem 2019; 58: 6215.
18. Yoshida Y, Ito H, Nakamura Y, et al. Cryst Growth Des 2016; 16: 6613.
19. Qin JH, Huang YD, Zhao Y, et al. Inorg Chem 2019; 58: 15013.
20. Utochnikova VV, Solodukhin NN, Aslandukov AA, et al. Eur J Inorg Chem 2017; 1: 107.
21. Gao CH, Zhang L, Hou GF, et al. Chem Commun 2017; 78: 70.
22. Ridenour JA, Carter KP and Cahill CL. CrystEngComm 2017; 19: 1190.
23. Yi XG, Zhang ZX, Chen WT, et al. J Solid State Chem 2018; 266: 16.
24. Dong YT, Tu B, Xu H, et al. Wuji Huaxue Xuebao 2017; 33: 651.
25. Lin L, Zhong Q, Hong J, et al. Inorg Chim Acta 2018; 479: 30.
26. van Sark WGJHM, de Wild J, Rath JK, et al. Nanoscale Res Lett 2013; 8: 811.
27. Joos JJ, Poelman D and Smet PF. Phys Chem Phys 2015; 17: 19058.
28. Rogers JJ, MacKenzie KJD and Trompetter WJ. Appl Clay Sci 2018; 157: 1.
29. Khatua DK, Agarwal A, Kumar N, et al. Acta Mater 2018; 145: 429.
30. Zhu Y, Cui S, Wang Y, et al. Nanotechnology 2016; 27: 405202/1.
31. Mynbaev KD, Bazhenov NL, Dvoretsky AS, et al. J Electron Mater 2018; 47: 4731.
32. Yuan C, Xi H and Tao X. Inorg Chem Commun 2017; 86: 145.
33. Liu Y, Zhang Y, Hu GH, et al. Chem Eur J 2015; 21: 10391.
34. Huang FQ, Mitchell K and Ibers JA. Inorg Chem 2001; 40: 5123.