



Photoluminescence and semiconductor properties of two novel lanthanide-mercury compounds with one-dimensional chain-like structures

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ABSTRACT

Two novel lanthanide-mercury compounds $[\text{Ln}(\text{IA})_3(\text{H}_2\text{O})_2]_n(\text{Hg}_3\text{Cl}_9) \cdot 4n\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ (**1**) and Tb (**2**); $\text{IA} =$ isonicotinic acid) have been synthesized under solvothermal conditions and structurally characterized by single-crystal X-ray diffraction. Both complexes exhibit one-dimensional (1D) chain-like structure with a novel isolated $(\text{Hg}_3\text{Cl}_9)^{3-}$ anion. Solid-state diffuse reflectance spectroscopy reveals the presence of wide optical band gaps of 2.81 eV and 3.47 eV, suggesting that they are potentially wide band gap organic semiconductor materials. Solid-state photoluminescence measurements uncover that they show red or green light emission bands, respectively. The emission bands can be assigned to the characteristic emission of the 4f electrons intrashell transitions of $^5D_0 \rightarrow ^7F_J$ (Eu^{3+} , $J = 2$ and 4) and $^5D_4 \rightarrow ^7F_J$ (Tb^{3+} , $J = 6, 5, 4$ and 3), respectively. Energy transfer mechanism is explained by the energy level diagram of Eu^{3+} ion, Tb^{3+} ion and isonicotinic acid ligand. The title compounds have remarkable CIE chromaticity coordinates of (0.6438, 0.3559) and (0.3172, 0.4773). This suggests that they may be potential candidates with red or green light emitting materials for white light emitting diodes (LEDs).

1. Introduction

Up to date, scientists have accomplished a lot of investigations on lanthanide compounds, for the sake of exploring the potential applications in various areas like light-emitting diodes (LEDs), magnetic materials, luminescent probes, electrochemical displays, and so on [1–3]. The attractive physicochemical properties of lanthanide compounds mainly originate from the abundant 4f electrons of the lanthanide ions. Lanthanide compounds can usually show strong photoluminescence if the transitions of the 4f electrons can efficiently happen. However, the transitions of the 4f electrons are generally difficult to occur, due to low absorption coefficient of lanthanide ions. This will lead to weak or even no photoluminescence emissions.

Choosing organic ligands with conjugated motifs is an effective way to enhance the absorption coefficient for achieving strong photoluminescence emissions. Organic ligands like heterocyclic derivatives and aromatic carboxylic acids are often chosen to design and prepare lanthanide compounds, because these organic ligands can absorb ultraviolet light and then transfer the absorbed energy to lanthanide ions; this is so-called antenna effect [4,5]. The factors affecting an

efficient emission of lanthanide ions are the distance between the antenna and the lanthanide ion, the intersystem crossing quantum yield of the “antenna” ligand, as well as the energy match (exactly the energy difference) between the triplet state energy of “antenna” ligand and the resonant energy level of lanthanide ions. Amongst these factors, the energy match plays the most important role. Efficient photoluminescence emissions of lanthanide ions are possible only when a good energy match is attained; this is the energy match mechanism [6]. Based on the energy transfer and the energy match mechanism, people can predict the photoluminescent performance of a lanthanide compound.

To our knowledge, the semiconductor properties of lanthanide compounds have been rarely explored yet in comparison with lots of studies on photoluminescence properties [7]. As a matter of fact, semiconductor compounds have gained more and more attention as useful photocatalysts for handling with the problems of environmental pollution and energy shortage in the future [8,9]. Amongst the huge family of semiconductor compounds, some lanthanide organic semiconductor compounds have also been studied due to their potential applications in the areas of sensors [10,11], single molecule magnets

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(SMMs) [12,13] and organic field-effect transistors (OFETs) [14,15]. Based on the above considerations, we recently become interest in investigating novel lanthanide compounds with interesting structures and physicochemical properties. We report in this work the syntheses, crystal structures, photoluminescence and semiconductor properties, as well as energy transfer mechanism of two novel lanthanide-mercury compounds, $[\text{Ln}(\text{IA})_3(\text{H}_2\text{O})_2]_n(\text{Hg}_3\text{Cl}_9)_n \cdot 4n\text{H}_2\text{O}$ (Ln = Eu (**1**) and Tb (**2**); IA = isonicotinic acid). Both of them were prepared through solvothermal reactions and featured a 1D chain-like structure with a novel isolated $(\text{Hg}_3\text{Cl}_9)^{3-}$ anion.

2. Experimental

2.1. Materials and instrumentation

The reagents $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, HgCl_2 and isonicotinic acid were analytical reagent grade and obtained from SigmaAldrich. Elemental microanalyses of carbon, hydrogen and nitrogen were carried out on an Elementar Vario EL elemental analyzer. Photoluminescence measurements with solid-state samples were conducted on a F97XP photoluminescent spectrometer. The solid-state UV/Vis diffuse reflectance spectroscopy was carried out at room temperature in the wavelength span of 190–900 nm on a computer-controlled TU1901 UV/Vis spectrometer attached with an integrating sphere. The barium sulfate powder plate was applied as references for 100% reflectance, on which the finely ground powder samples, were coated.

2.2. Synthesis of $[\text{Eu}(\text{IA})_3(\text{H}_2\text{O})_2]_n(\text{Hg}_3\text{Cl}_9)_n \cdot 4n\text{H}_2\text{O}$ (**1**)

We loaded the mixture of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 366 mg), HgCl_2 (3 mmol, 816 mg), isonicotinic acid (3 mmol, 369 mg) and 10 mL distilled water into a 25 mL Teflon-lined stainless steel vessel, then put the vessel into an oven and heated it to 433 K. The vessel was kept at this temperature for 7 days. Once the oven was slowly cooled down to room temperature, the vessel was opened up and colorless prismatic crystals that can be used for single-crystal X-ray diffraction were collected. The yield was 45% (based on $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{Cl}_9\text{EuHg}_3\text{N}_3\text{O}_{12}$: C, 13.95; H, 1.76; N, 2.71. Found: C, 14.12; H, 1.79; N, 2.76.

2.3. Synthesis of $[\text{Tb}(\text{IA})_3(\text{H}_2\text{O})_2]_n(\text{Hg}_3\text{Cl}_9)_n \cdot 4n\text{H}_2\text{O}$ (**2**)

Complex **2** was synthesized according to the same procedure for complex **1**, except for using $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (1 mmol, 374 mg) instead of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The yield was 48% (based on $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{Cl}_9\text{Hg}_3\text{N}_3\text{O}_{12}\text{Tb}$: C, 13.88; H, 1.75; N, 2.70. Found: C, 13.98; H, 1.80; N, 2.79.

2.4. Crystal structure determination

A suitable crystal was carefully selected and adhered onto the tip of a glass fiber. The fiber was mounted to a SuperNova CCD diffractometer. The graphite monochromated Mo-K α radiation with $\lambda = 0.71073 \text{ \AA}$ was applied for the data collection. The diffraction data were collected at 293(2) K with the use of the ω scan mode. The CrystalClear software was used for the data reduction and empirical absorption corrections [16]. The crystal structures of both compounds were solved by means of the direct methods. The final structures were refined on F^2 by full-matrix least-squares with the Siemens SHELXTLTM V⁵ crystallographic software package [17]. All non-hydrogen atoms were found on difference Fourier maps and refined anisotropically, while hydrogen atoms were theoretically generated and allowed to ride on their parent atoms. The crystal data as well as the details of data collection and refinement are shown in Table 1, while selected bond lengths and bond angles are displayed in Table S1. Hydrogen bonding interactions are given in Table 2.

Table 1

Crystal data and structure refinement details.

compound	1	2
formula	$\text{C}_{18}\text{H}_{27}\text{Cl}_9\text{EuHg}_3\text{N}_3\text{O}_{12}$	$\text{C}_{18}\text{H}_{27}\text{Cl}_9\text{Hg}_3\text{N}_3\text{O}_{12}\text{Tb}$
<i>F</i> _w	1550.21	1557.17
color	colorless	colorless
crystal size(mm)	$0.38 \times 0.04 \times 0.03$	$0.30 \times 0.05 \times 0.04$
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	9.6342(3)	9.5995(3)
<i>b</i> (Å)	12.8306(6)	12.8103(5)
<i>c</i> (Å)	16.6704(7)	16.6739(8)
α (°)	105.553(4)	105.588(4)
β (°)	95.871(3)	95.691(3)
γ (°)	96.894(3)	96.945(3)
<i>V</i> (Å ³)	1951.28(14)	1941.85(13)
<i>Z</i>	2	2
$2\theta_{\text{max}}$ (°)	50	50
reflections collected	20,802	21,382
independent, observed	6684, 5707 (0.0322)	6804, 5726 (0.0311)
reflections (<i>R</i> _{int})		
<i>d</i> _{calc.} (g/cm ³)	2.638	2.663
μ (mm ^{−1})	14.019	14.293
<i>F</i> (000)	1416	1420
<i>T</i> (K)	293(2)	293(2)
<i>R</i> ₁ , <i>wR</i> ₂	0.0323, 0.0682	0.0330, 0.0647
<i>S</i>	1.004	1.003
largest and Mean Δ/σ	0.004, 0	0.003, 0
$\Delta\rho$ (max, min) (e/Å ³)	1.633, −1.171	1.556, −1.184

Table 2

Hydrogen bonding interactions.

Compound 1				
<i>D</i> – <i>H</i> ... <i>A</i>	<i>D</i> – <i>H</i> , Å	<i>H</i> ... <i>A</i> , Å	<i>D</i> ... <i>A</i> , Å	<i>D</i> – <i>H</i> ... <i>A</i> , °
O2W–H2WA...O4W	0.82	2.06	2.817(10)	154
N2–H2B...Cl8	0.86	2.41	3.195(6)	152
O1W–H1WB...Cl5 ⁱ	0.92	2.35	3.142(5)	144
O2W–H2WB...O6W ⁱⁱ	0.92	2.00	2.871(8)	156
O5W–H5WA...N1	0.93	1.80	2.704(8)	164
C7–H7A...Cl2 ⁱⁱⁱ	0.93	2.74	3.529(8)	143
C11–H11A...Cl3	0.93	2.80	3.588(8)	144
Symmetric codes: (i) <i>x</i> , 1+ <i>y</i> , <i>z</i> ; (ii) <i>x</i> , −1+ <i>y</i> , <i>z</i> ; (iii) 1+ <i>x</i> , <i>y</i> , <i>z</i> .				
Compound 2				
<i>D</i> – <i>H</i> ... <i>A</i>	<i>D</i> – <i>H</i> , Å	<i>H</i> ... <i>A</i> , Å	<i>D</i> ... <i>A</i> , Å	<i>D</i> – <i>H</i> ... <i>A</i> , °
N1–H1B...O5W	0.86	1.83	2.686(10)	177
O2W–H2WA...O4W	0.82	2.07	2.827(10)	154
N2–H2B...Cl8	0.86	2.44	3.220(7)	152
O1W–H1WB...Cl5 ⁱ	0.92	2.31(5)	3.140(6)	153
N3–H3A...O6W	0.86	2.02	2.858(9)	164
O2W–H2WB...O6W ⁱⁱ	0.90	2.02	2.860(9)	156
O5W–H5WA...O3W ⁱ	0.90	1.99	2.836(13)	155
O6W–H6WA...O3W ⁱⁱⁱ	0.90	2.19	2.819(12)	127
O3W–H3WA...O6W ^{iv}	0.90	2.40	2.819(12)	110
C7–H7A...Cl2 ^v	0.93	2.71	3.510(8)	145
C11–H11A...Cl3	0.93	2.80	3.590(7)	143

Symmetric codes: (i) *x*, 1+*y*, *z*; (ii) *x*, −1+*y*, *z*; (iii) *x*, 2+*y*, 1+*z*; (iv) *x*, −2+*y*, −1+*z*; (v) 1+*x*, *y*, *z*.

3. Results and discussion

3.1. Crystal structures

The results of the single crystal X-ray diffraction analysis reveal that both title complexes are isostructural and crystallized in the triclinic $P\bar{1}$ space group. It should be pointed out that there are two formula units existing in the crystal structure and this is a so-called $Z' > 1$ structure [18,19]. Therefore, in this section only complex **1** is chosen for the description of their crystal structures. The crystal structure of complex **1** is characterized by a 1D chain-like motif. The asymmetric unit of

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