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## Synthesis, structure, semiconductive and photoluminescent properties of $[\{\text{Eu}(\text{NC}_5\text{H}_4\text{COOH})_3(\text{H}_2\text{O})_2\}(1.5\text{ZnCl}_4)\cdot(2\text{H}_2\text{O})]_n$

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**Abstract:** A novel bimetallic 4f–3d metal-isonicotinic acid inorganic–organic hybrid complex  $[\{\text{Eu}(\text{NC}_5\text{H}_4\text{COOH})_3(\text{H}_2\text{O})_2\}(1.5\text{ZnCl}_4)\cdot(2\text{H}_2\text{O})]_n$  (**1**) was synthesized *via* a hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Complex **1** crystallizes in the space group  $C2/c$  of the monoclinic system with eight formula units in a cell:  $a = 23.878(8)$  Å,  $b = 20.573(6)$  Å,  $c = 15.358(5)$  Å,  $\beta = 127.276(5)^\circ$ ,  $V = 6003(3)$  Å<sup>3</sup>,  $C_{18}H_{23}Cl_6EuN_3O_{10}Zn_{1.5}$ ,  $M_r = 904.11$  g/mol,  $\rho = 2.001$  g/cm<sup>3</sup>,  $S = 1.077$ ,  $\mu(\text{MoK}\alpha) = 3.846$  mm<sup>-1</sup>,  $F(000) = 3536$ ,  $R = 0.0270$  and  $wR = 0.0672$ . Complex **1** has a characteristic, one-dimensional polycationic chain-like structure. A photoluminescent investigation revealed that the title complex displays intense emissions in the orange and red regions. The luminescence spectra show that the red emission is stronger than the orange emission. Optical absorption spectra of **1** revealed the presence of an optical gap of 3.56 eV.

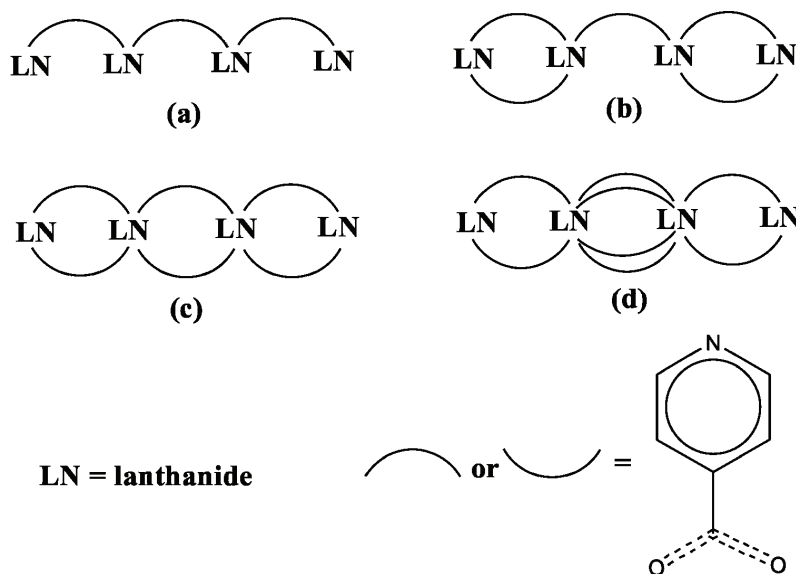
**Keywords:** crystal structure; europium; lanthanide; photoluminescence; semiconductor.

### INTRODUCTION

In recent years, inorganic–organic hybrid complexes containing trivalent lanthanides have attracted increasing attention for use as the active species in luminescent materials, magnetic functional materials, catalysts, electroluminescent devices, zeolite-like materials, and so forth.<sup>1–5</sup> Moreover, for a vast number of inorganic–organic hybrid materials, the intriguing variety of the architectures and topologies that can be obtained by the self-assembly of the metal ions and multifunctional ligands has attracted the attention of chemists. Hitherto, although the synthesis of inorganic–organic hybrid materials based on transition metals has become widespread,<sup>6–12</sup> there are relatively few reports on lanthanide-based inorganic–organic hybrid materials, despite their potential applications in lumines-

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cence and other fields.<sup>13</sup> To the best of our knowledge, lanthanide-based inorganic–organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. In addition, transition metal complexes containing group 12 (IIB) elements are particularly attractive for many reasons, such as, the variety of coordination numbers and geometries provided by the  $d^{10}$  configuration of the IIB metal ions, the well-known toxicity of cadmium and mercury, their semiconductor properties and the essential role in biological systems of zinc, *etc.* Taking the above into account, it was deemed that LN-IIB-based (LN = lanthanide) inorganic–organic hybrid materials with aromatic carboxylic acids as ligands may have novel structural topologies and properties, such as photoluminescence, semiconductivity, magnetism, electro- and photochemistry, catalysis, thermochromism and so forth. Therefore, our group recently became interested in the crystal engineering of LN-IIB-based inorganic–organic hybrid materials with isonicotinic acid as the ligand (Scheme 1). In this paper, the synthesis, crystal structure, and semiconductive and photoluminescent properties of  $[\{\text{Eu}(\text{NC}_5\text{H}_4\text{COOH})_3(\text{H}_2\text{O})_2\}(1.5\text{ZnCl}_4)\cdot(2\text{H}_2\text{O})\}_n$  (**1**) are reported.



Scheme 1. Important chain-like structural types of isonicotinic acid bridging LN centres: a) 1-1-1; b) 2-1-2; c) 2-2-2; d) 2-4-2 types, in which the number indicates the number of the bridges.

## EXPERIMENTAL

### *Chemicals and instruments*

All reactants of A.R. grade were obtained commercially and used without further purification. The fluorescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer. The UV–Vis spectra were recorded at room temperature in the

wavelength range 190–1100 nm using a computer-controlled PE Lambda 900 UV–Vis spectrometer equipped with an integrating sphere. A BaSO<sub>4</sub> plate was used as the reference (100 % reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from the reflection spectra by the Kubelka-Munk function:<sup>14,15</sup>  $\alpha/S = (1 - R)^2/2R$ , where  $\alpha$  is the absorption coefficient,  $S$  is the scattering coefficient, which is practically wavelength independent when the particle size is larger than 5  $\mu\text{m}$ , and  $R$  is the reflectance.

*Preparation of [Eu(NC<sub>5</sub>H<sub>4</sub>COOH)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>](1.5ZnCl<sub>4</sub>)·(2H<sub>2</sub>O)]<sub>n</sub>*

The title complex was prepared by mixing EuCl<sub>3</sub>·6H<sub>2</sub>O (1.0 mmol, 0.37 g), ZnCl<sub>2</sub> (1.0 mmol, 0.14 g), isonicotinic acid (1.00 mmol, 0.123 g) and 10 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 3 days. After slow cooling to room temperature at 6 °C/h, colourless crystals suitable for X-ray analysis were obtained. The yield was 88 % (based on europium).

*Crystallography*

The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-*K* $\alpha$  radiation ( $\lambda = 0.71073$  Å) using the  $\omega$  scan technique. CrystalClear software was used for data reduction and empirical corrections for absorption.<sup>16</sup> The structure was solved by the direct method using the Siemens SHELXTL™, version 5, package of crystallographic software.<sup>17</sup> The difference Fourier maps based on these atomic positions yielded the other non-hydrogen atoms. The hydrogen atom positions were generated theoretically, except for those of the lattice water molecules, which were obtained by difference Fourier maps allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but they were not refined. The structures were refined using a full-matrix least-squares refinement on  $F^2$ . All atoms were refined anisotropically. The crystallographic data are given in Table I and selected bond distances and bond angles are given in Table II (CCDC 666795).

TABLE I. Crystal data<sup>a</sup> and structure refinement details for **1**

Property	Value
Formula	C <sub>18</sub> H <sub>23</sub> Cl <sub>6</sub> EuN <sub>3</sub> O <sub>10</sub> Zn <sub>1.5</sub>
Formula weight, g mol <sup>-1</sup>	904.11
Colour	Colourless
Crystal size, mm <sup>3</sup>	0.40; 0.30; 0.20
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> / Å	23.878(8)
<i>b</i> / Å	20.573(6)
<i>c</i> / Å	15.358(5)
$\beta$ / °	127.276(5)
<i>V</i> / Å <sup>3</sup>	6003(3)
<i>Z</i>	8
$2\theta_{\text{max}}$ / °	50.12
Index ranges	$-22 \leq h \leq 28$ , $-24 \leq k \leq 24$ , $-18 \leq l \leq 17$
Reflections collected	18023
Independent, observed reflections ( $R_{\text{int}}$ )	5236, 4947 (0.0232)
$d_{\text{calcd.}}$ / gcm <sup>-3</sup>	2.001
$\mu$ / mm <sup>-1</sup>	3.846

TABLE I. Continued

Property	Value
$T / K$	293(2)
$F(000)$	3536
$R1, wR2$	0.0270, 0.0672
$S$	1.077
Largest and mean $\Delta/\sigma$	0.002, 0
$\Delta\rho(\text{max, min}) / e\text{\AA}^{-3}$	1.906, -1.494

TABLE II. Selected interatomic distances and bond angles  $\text{\AA}^\circ$  for **1**

Eu1–O1	2.376(2)	O5–C13	1.246(2)
Eu1–O2#1	2.357(2)	O6–C13	1.251(2)
Eu1–O3	2.363(2)	Cl1–Zn1–Cl2	107.75(3)
Eu1–O4#2	2.389(2)	Cl3–Zn1–Cl1	109.04(3)
Eu1–O5	2.412(2)	Cl3–Zn1–Cl2	109.62(2)
Eu1–O6#1	2.395(2)	Cl4–Zn1–Cl1	113.25(3)
Eu1–O1W	2.453(2)	Cl4–Zn1–Cl2	106.81(3)
Eu1–O2W	2.513(2)	Cl4–Zn1–Cl3	110.28(3)
Zn1–Cl1	2.2696(9)	Cl5–Zn2–Cl6	89.77(6)
Zn1–Cl2	2.3139(9)	Cl5–Zn2–Cl7	105.22(6)
Zn1–Cl3	2.2663(9)	Cl6–Zn2–Cl7	107.96(5)
Zn1–Cl4	2.266(1)	Cl7#3–Zn2–Cl5	135.10(5)
Zn2–Cl5	2.205(2)	Cl7#3–Zn2–Cl6	107.12(6)
Zn2–Cl6	2.261(2)	Cl7#3–Zn2–Cl7	108.22(6)
Zn2–Cl7	2.396(1)	C1–O1–Eu1	132.9(1)
Zn2–Cl7#3	2.396(1)	C1–O2–Eu1#1	157.0(1)
O1–C1	1.246(2)	C7–O3–Eu1	171.4(1)
O2–C1	1.239(2)	C7–O4–Eu1#2	126.2(2)
O3–C7	1.258(3)	C13–O5–Eu1	144.9(2)
O4–C7	1.246(2)	C13–O6–Eu1#1	137.3(1)

## RESULTS AND DISCUSSION

*Crystal structure*

X-ray diffraction analysis revealed that the structure of the title complex consisted of  $\{\text{Eu}(\text{NC}_5\text{H}_4\text{COOH})_3(\text{H}_2\text{O})_2\}^{3+}$  chains,  $[\text{ZnCl}_4]^{2-}$  and lattice water molecules, as shown in Fig. 1. The Zn1 atom is tetrahedrally bonded to four chlorine atoms to form the  $[\text{ZnCl}_4]^{2-}$ . The Zn2 atom is positionally disordered and the occupancy of Zn2 had to be set to 0.5 in order to obtain a rational structure model and thermal displacement parameters. The bond lengths of Zn–Cl range from 2.205(2) to 2.396(1) Å with an average value of 2.297(2) Å, which are normal and similar to the counterparts found in the literature.<sup>18–21</sup> The europium atom is coordinated to eight oxygen atoms, of which two are from the two water molecules and six are from the six isonicotinic acid ligands, yielding a distorted square anti-prism with the top and bottom planes defined by O(2)(1– $x$ ,  $y$ , 1/2– $z$ ), O(1), O(5), O(6)(1– $x$ ,  $y$ , 1/2– $z$ ), and O(2W), O(3), O(1W) and O(4)(1/2– $x$ , –1/2– $y$ ,

$-z$ ) atoms, respectively. The bond lengths of  $\text{Eu}-\text{O}_{\text{isonicotinic acid}}$  range from 2.357(2) to 2.412(2) Å, with an average value of 2.382(2) Å, which is obviously shorter than that of  $\text{Eu}-\text{O}_{\text{water}}$ , being of 2.453(2) and 2.513(2) Å, indicating that the isonicotinic acid ligand has a stronger affinity to the Eu(III) ion than water. For the requirement of charge balance, all isonicotinic fragments are protonated at the nitrogen atom. The europium atoms are alternately bridged by two or four  $\mu_2$ -isonicotinic acid ligands in a 2-4-2 (the number indicates the number of the bridges) mode to construct a 1D polycationic chain with  $\text{Eu}\cdots\text{Eu}$  distances of 4.986(2) and 4.568(1) Å, respectively (Fig. 2 and Scheme 1d). It is noteworthy that, to date, the documented types of chains formed by LN and isonicotinic acid are mainly 1-1-1, 2-1-2 and 2-2-2 types (Schemes 1a, 1b and 1c, respectively). There are five kinds of hydrogen bonds in **1**, *i.e.*,  $\text{O}\cdots\text{Cl}$ ,  $\text{O}\cdots\text{O}$ ,  $\text{O}\cdots\text{N}$ ,  $\text{N}\cdots\text{Cl}$  and  $\text{Cl}\cdots\text{Cl}$  hydrogen bonds, including  $\text{O1W}\cdots\text{Cl1}$  ( $1/2-x, -1/2+y, 1/2-z$ ),  $\text{O2W}\cdots\text{Cl2}$  ( $x, -y, -1/2+z$ ),  $\text{O2W}\cdots\text{O4W}$ ,  $\text{O3W}\cdots\text{Cl4}$  ( $1/2-x, -1/2-y, 1-z$ ),  $\text{O3W}\cdots\text{O3W}$  ( $1-x, y, 3/2-z$ ),  $\text{O3W}\cdots\text{N3}$ ,  $\text{O4W}\cdots\text{Cl3}$  ( $x, y, -1+z$ ),  $\text{O4W}\cdots\text{Cl4}$  ( $x, -y, -1/2+z$ ),  $\text{N1}\cdots\text{Cl2}$ ,  $\text{N1}\cdots\text{Cl5}$ ,  $\text{N2}\cdots\text{Cl3}$  and  $\text{HC15}\cdots\text{Cl6}$ , with the hydrogen bond distances being of 3.205(2), 3.235(2), 2.727(3), 3.245(2), 2.983(3), 2.858(3), 3.234(3), 3.236(3), 3.191(3), 3.286(3), 3.318(3) and 3.027(3) Å, respectively. The 1D polycationic chains,  $[\text{ZnCl}_4]^{2-}$  moieties and the water molecules are linked *via* hydrogen bonds to yield a 3D network (Fig. 3).

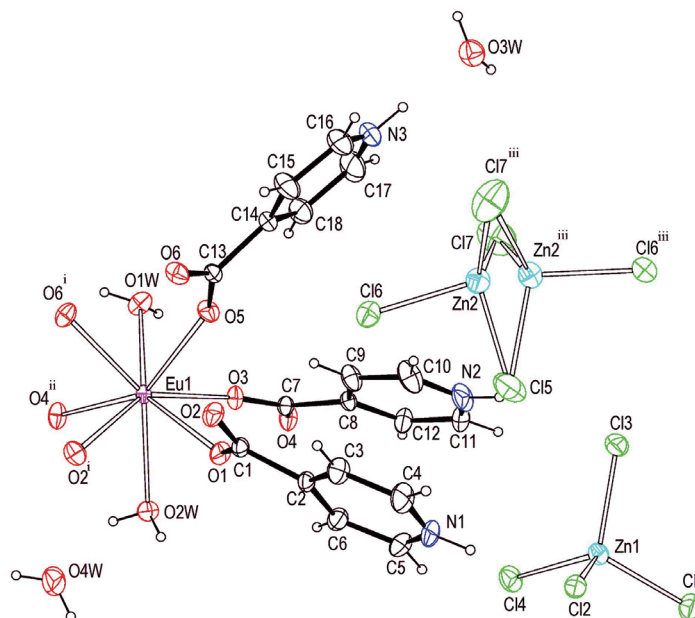


Fig. 1. ORTEP-plot of **1** with 30 % thermal ellipsoids. The small spheres represent hydrogen atoms. Disordered  $\text{Cl5}^{\text{iii}}$  are omitted for clarity. The occupancies of  $\text{Zn2}$ ,  $\text{Cl5}$  and  $\text{Cl6}$  are set to 0.5. Symmetry codes: i)  $1-x, y, 1/2-z$ ; ii)  $1/2-x, -1/2-y, -z$ ; iii)  $1-x, y, 3/2-z$ .

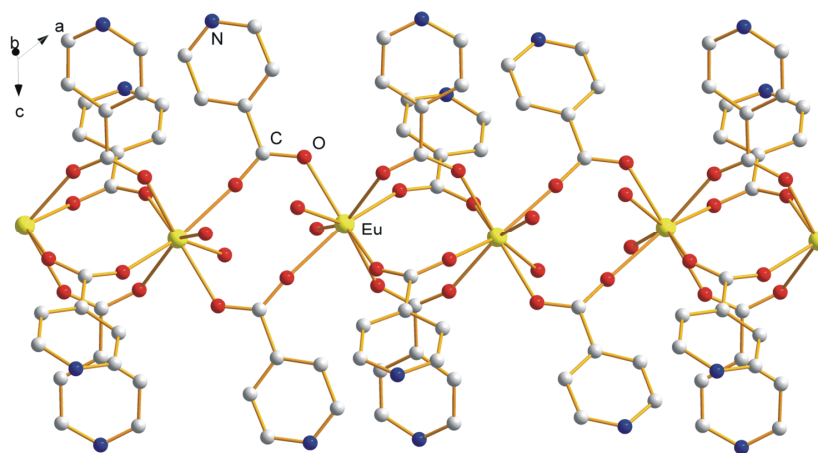


Fig. 2. The 1D cationic chain-like structure of **1**.

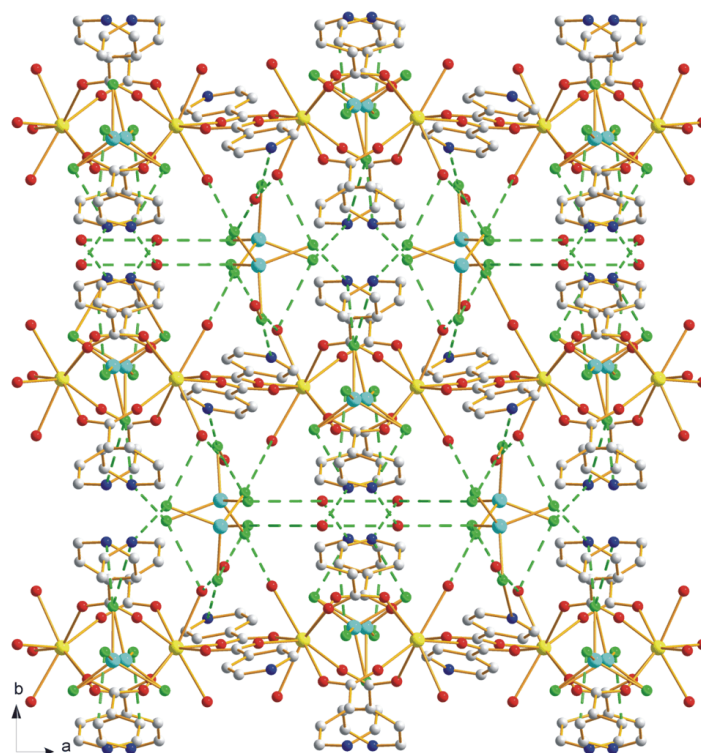


Fig. 3. Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å):

O1W...C11 ( $1/2-x, -1/2+y, 1/2-z$ ), 3.205(2); O2W...C12 ( $x, -y, -1/2+z$ ), 3.235(2);  
 O2W...O4W, 2.727(3); O3W...C14 ( $1/2-x, -1/2-y, 1-z$ ), 3.245(2); O3W...O3W ( $1-x, y, 3/2-z$ ),  
 2.983(3); O3W...N3 2.858(3); O4W...C13 ( $x, y, -1+z$ ) 3.234(3); O4W...C14 ( $x, -y, -1/2+z$ ),  
 3.236(3); N1...C12, 3.191(3); N1...C15, 3.286(3); N2...C13, 3.318(3) and C15...C16, 3.027(3).

To our knowledge, isonicotinic acid is a quite interesting tecton in constructing extended structures because it is an unsymmetrical, divergent ligand with a nitrogen atom at one end and two oxygen atoms from the carboxylato group at the other. Isonicotinic acid can link two metal centres by coordinating to a metal centre with the nitrogen atom and to the other one with one or two carboxylato oxygen atoms.<sup>22,23</sup> Therefore, an attempt was made to employ isonicotinic acid as a ligand to bridge LN and IIB metal centres. Unfortunately, the isonicotinic acid only coordinated to LN centres, while the IIB atoms did not link to the isonicotinic acid ligand. The reason for this can probably be ascribed to the experimental conditions. It is believed that the isonicotinic acid ligand would bridge LN and IIB atoms together if the changing experimental conditions, such as temperature and solvent, were changed. Further systematic experimental and theoretical investigations on this system are currently in progress.

#### *Photoluminescent properties*

Taking into account the excellent luminescent property of the  $\text{Eu}^{3+}$ , the luminescence of **1** was investigated at room temperature (Fig. 4). The solid-state excitation spectra of the title complex show that the effective energy absorption mainly occurs in the long wavelength ultraviolet region in the range 280–360 nm (inner plot of Fig. 4). The excitation bands of complex **1** under the red emission of 613 nm possess two main bands, at 288 and 346 nm. The corresponding emission spectra were further measured by selective excitation with the different excitation wavelengths of the title complex and they showed a similar emission position with only small differences in the luminescent intensities, which indicates that the excitation bands are all effective energy sensitizer for the luminescence of the  $\text{Eu}^{3+}$ . The emission spectrum is shown in the outer plot of Fig. 4. For complex **1**, the emission spectra show two main and intense emission bands under excitation by 346 nm: 592 and 613 nm light, corresponding to the characteristic emission of  ${}^5D_0-{}^7F_J$  transitions ( $J = 1,2$ ) of the  $\text{Eu}^{3+}$ . This indicates that effective energy transfer occurred and that conjugated systems formed between the ligands and the chelated lanthanide ions in **1**. Moreover, the absence of a ligand-based emission in the fluorescence spectra of **1** also suggests that energy transfer from the ligand to the lanthanide centre is effective. Among the red luminescent intensity of  ${}^5D_0-{}^7F_2$ , the electric dipole transition is the strongest and the orange emission intensity of the  ${}^5D_0-{}^7F_1$  magnetic dipole transition becomes stronger by the overlap of the  ${}^5D_0-{}^7F_0$  transition. For the title complex, the spectra were not ideal enough because the two bands of the emission spectra corresponding to the emissions originating from the  ${}^5D_0-{}^7F_J$  transitions ( $J = 1,2$ ) of the  $\text{Eu}^{3+}$  were not completely separated; they meet at 602 nm. The overlap of the two transitions and the small shoulder band of the  ${}^5D_0-{}^7F_2$  transition suggest that the isonicotinic acid ligand is not perfect for the sensitization of  $\text{Eu}^{3+}$ .

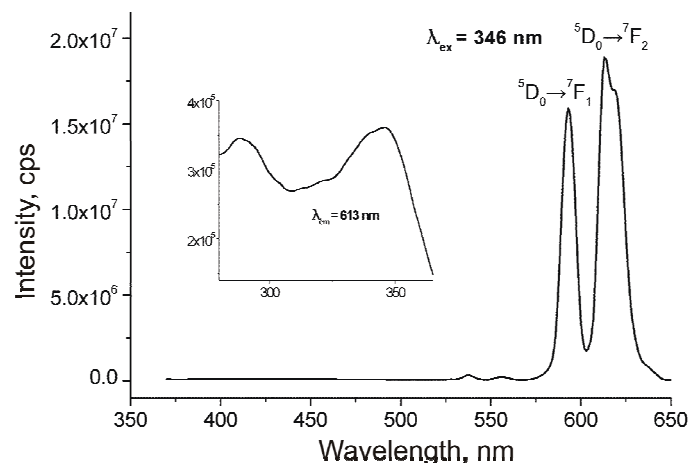


Fig. 4. Luminescent spectra of the title complex: outer plot, emission spectrum and inner plot, excitation spectrum.

#### *Solid-state diffuse reflectance spectrum*

The optical absorption spectrum of **1** revealed the presence of an obvious optical gap of 3.56 eV (Fig. 5), which suggests that complex **1** may be a potential wide-gap semiconductor, which is consistent with the colour of the crystal, as for cases found in the literature.<sup>24</sup> The steep slope of the optical absorption edge for **1** is indicative of the existence of direct transitions.<sup>25</sup> The optical absorption of **1** most likely originates from charge-transfer excitations, mainly from the p-like valence band of the chloride ligands to the 4s-like conduction band of the zinc centre, similar to those reported in the literature.<sup>26–28</sup>

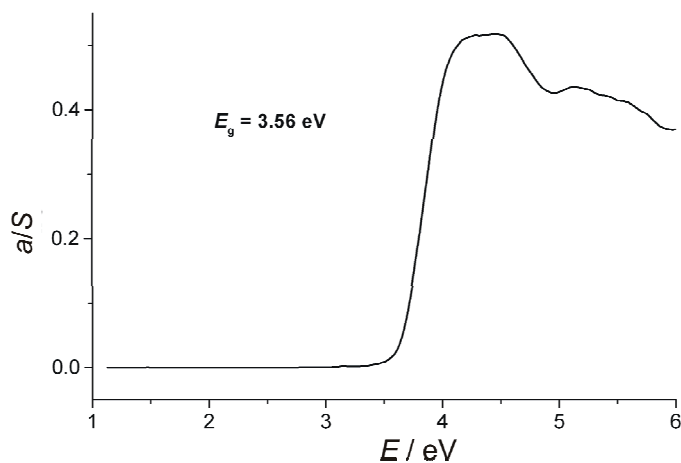


Fig. 5. Solid-state diffuse reflectance spectrum of **1**.



## CONCLUSIONS

In brief, a metal-isonicotinic acid inorganic-organic hybrid complex was prepared *via* a hydrothermal reaction. The crystal structure of the title complex is characteristic for a novel one-dimensional polycationic chain-like structure. The title complex shows intense red luminescence at around 613 nm, corresponding to the  ${}^5D_0-{}^7F_2$  transition under UV excitation. Therefore, it may be expected that the title lanthanide functional complex could lead to the fabrication of high-quality colour displays and be rather useful as a source of monochromatic emission in photonic crystals. The optical absorption spectra show that the title complex may be a candidate for potential photoelectric materials.

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## ИЗВОД

СИНТЕЗА, СТРУКТУРА, ПОЛУПРОВОДНИЧКА И ФОТОЛУМИНИСЦЕНТНА СВОЈСТВА [ $\{\text{Eu}(\text{NC}_5\text{H}_4\text{COOH})_3(\text{H}_2\text{O})_2\}(1,5\text{ZnCl}_4)\cdot(2\text{H}_2\text{O})\}_n$ ]

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Хидротермалном реакцијом добијен је нови диметални 4f-3d метал-изоникотинска киселина органско-неоргански хибридни комплекс [ $\{\text{Eu}(\text{NC}_5\text{H}_4\text{COOH})_3(\text{H}_2\text{O})_2\}(1,5\text{ZnCl}_4)\cdot(2\text{H}_2\text{O})\}_n$  (**1**) и структурно окарактерисан X-рендгенском дифракционом анализом на моно-кристалу. Комплекс кристалише у просторној групи  $C2/c$  моноклиничког система са 8 формулских јединица у ћелији:  $a = 23,878(8) \text{ \AA}$ ,  $b = 20,573(6) \text{ \AA}$ ,  $c = 15,358(5) \text{ \AA}$ ,  $\beta = 127,276(5)^\circ$ ,  $V = 6003(3) \text{ \AA}^3$ ,  $\text{C}_{18}\text{H}_{23}\text{Cl}_6\text{EuN}_3\text{O}_{10}\text{Zn}_{1,5}$ ,  $M_r = 904,11 \text{ g/mol}$ ,  $\rho = 2,001 \text{ g/cm}^3$ ,  $S = 1,077$ ,  $\mu(\text{MoK}\alpha) = 3,846 \text{ mm}^{-1}$ ,  $F(000) = 3536$ ,  $R = 0,0270$  и  $wR = 0,0672$ . Комплекс је карактеристичан по једно-димензионалној поликатјонској ланчастој структури. Фотолуминисцентна испитивања потврдила су да наведени комплекс показује интензивну емисију у наранџастој и црвеној области. Луминисцентни спектри показују јачу црвену него наранџасту емисију. Оптички апсорпциони спектар комплекса **1** има оптички пад од 3,56 eV.

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## REFERENCES

1. M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am Chem. Soc.* **116** (1994) 1151
2. K. M. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **45** (1997) 283
3. M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reinecke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **34** (2001) 319
4. J. Kido, Y. Okamoto, *Chem. Rev.* **102** (2002) 2357
5. R. Reyes, E. N. Hering, M. Cremona, C. F. B. Silva, H. F. Brito, C. A. Achete, *Thin Solid Films* **23** (2002) 420
6. M. J. Zaworotko, *Chem. Soc. Rev.* (1994) 283
7. G. B. Gardner, D. Venkataraman, J. S. Moore, S. Lee, *Nature* **374** (1995) 792
8. C. Janiak, *Angew. Chem. Int. Ed. Engl.* **36** (1997) 1431
9. O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. L. Groy, *Acc. Chem. Res.* **31** (1998) 474

10. S. R. Batten, R. Robson, *Angew. Chem., Int. Ed. Engl.* **37** (1998) 1460
11. W. Lin, O. R. Evans, R. G. Xiong, Z. Wang, *J. Am. Chem. Soc.* **120** (1998) 13272
12. O. R. Evans, R. G. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem. Int. Ed. Engl.* **38** (1999) 536
13. T. M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O. M. Yaghi, *J. Am. Chem. Soc.* **121** (1999) 1651
14. W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, 1966
15. G. Kortüm, *Reflectance Spectroscopy*, Springer Verlag, New York, 1969
16. Rigaku, CrystalClear, version 1.35, Rigaku Corporation, 2002
17. Siemens, SHELXTL™, version 5, Reference Manual, Siemens Energy & Automation Inc., Madison, WI, 1994
18. A. Bino, F. A. Cotton, Z. Dori, M. Shaia-Gottlieb, M. Kapon, *Inorg. Chem.* **27** (1988) 3592
19. A. J. Dickie, D. C. R. Hockless, A. C. Willis, J. A. McKeon, W. G. Jackson, *Inorg. Chem.* **42** (2003) 3822
20. Z. Tao, Q.-J. Zhu, S.-F. Xie, W. G. Jackson, Z.-Y. Zhou, X.-G. Zhou, *Polyhedron* **22** (2003) 1603
21. A. Dogan, B. Sarkar, A. Klein, F. Lissner, T. Schleid, J. Fiedler, S. Zalis, V. K. Jain, W. Kaim, *Inorg. Chem.* **43** (2004) 5973
22. J. Y. Lu, A. M. Babb, *Chem. Commun.* (2001) 821
23. M. E. Chapman, P. Ayyappan, B. M. Foxman, G. T. Yee, W. Lin, *Cryst. Growth Des.* **1** (2001) 159
24. E. A. Axtell, Y. Park, K. Chondroudis, M. G. Kanatzidis, *J. Am. Chem. Soc.* **120** (1998) 124
25. F. Q. Huang, K. Mitchell, J. A. Ibers, *Inorg. Chem.* **40** (2001) 5123
26. J.-H. Liao, M. G. Kanatzidis, *Chem. Mater.* **5** (1993) 1561
27. T. J. McCarthy, X. Zhang, M. G. Kanatzidis, *Inorg. Chem.* **32** (1993) 2944
28. E. A. Axtell, Y. Park, K. Chondroudis, M. G. Kanatzidis, *J. Am. Chem. Soc.* **120** (1998) 124.