



Synthesis, structure, and physical properties of $[\text{Sm}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_5\text{O}_2)_n(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n} \cdot (\text{H}_2\text{O})_{2n}$ with unprecedented ZnCl_5^{3-} species

Yi-Ming Xie^{a,*}, Wen-Tong Chen^b, Ji-Huai Wu^a

^a College of Materials Science and Engineering, The Key Laboratory for Functional Materials of Fujian Higher Education, Huaqiao University, Quanzhou, Fujian 362021, PR China

^b College of Chemistry and Chemical Engineering, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggongshan University, Ji'an, Jiangxi 343009, China

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ABSTRACT

A novel bimetallic 4f–3d metal–isonicotinic acid inorganic–organic hybrid complex $[\text{Sm}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_5\text{O}_2)_n(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n} \cdot (\text{H}_2\text{O})_{2n}$ (**1**) has been synthesized via hydrothermal reaction and structurally characterized by single-crystal X-ray diffraction. Complex **1** is characteristic of a one-dimensional polycationic chain-like structure and unprecedented ZnCl_5^{3-} species. Photoluminescent investigation reveals that the title complex displays interesting emissions in a wide region. Optical absorption spectra of **1** reveal the presence of an optical gap of 3.59 eV.

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1. Introduction

In recent years, the research of the trivalent lanthanide ions complexes continues to be an active research area, which may be ascribed to the remarkable physical properties of these complexes and their potential applications as magnetic functional materials, electroluminescent devices, catalysis, zeolite-like materials, and luminescent probes or labels in biological systems [1–6]. There is also an aesthetic perspective for the vast amount of inorganic–organic hybrid materials, the intriguing variety of the architectures and topologies that can be obtained by self-assembling metal ions, and multifunctional ligands attract chemists. So far, although the synthesis of inorganic–organic hybrid materials based on transition metals has become widespread [7–13], there are relatively few reports on lanthanide-based inorganic–organic hybrid materials despite their potential applications in luminescence and other fields [14]. To our knowledge, lanthanide-based inorganic–organic hybrid materials with aromatic carboxylic acids exhibit good thermal and luminescent stability for practical application. Besides, 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, semiconductive properties, and

the essential role in biological systems of zinc, and so forth. Furthermore, the isonicotinate anion is a quite interesting tecton in constructing extended structures because it is an asymmetrical divergent ligand with a nitrogen atom at one end and two oxygen atoms from the carboxylato group at the other end. The isonicotinate anion can link two metal centers by coordinating a metal center with the nitrogen atom and, to the other end, with one or two carboxylato oxygen atoms [15,16]. We believe 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 luminescence, semiconductivity, magnetism, electro- and photochemistry, catalysis, thermochromism and so on. Therefore, we recently became interested in the crystal engineering of LN–IIB-based inorganic–organic hybrid materials with isonicotinic acid as ligand. In this paper, we reported the synthesis, crystal structure, and semiconductive and luminescent properties of $[\text{Sm}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_5\text{O}_2)_n(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n} \cdot (\text{H}_2\text{O})_{2n}$ (**1**), which contains a novel one-dimensional polycationic chain and unprecedented ZnCl_5^{3-} anions.

2. Experimental

2.1. Materials and methods

All reactants of A.R. grade were obtained commercially and used without further purification. Fluorescence excitation and

* Corresponding author.

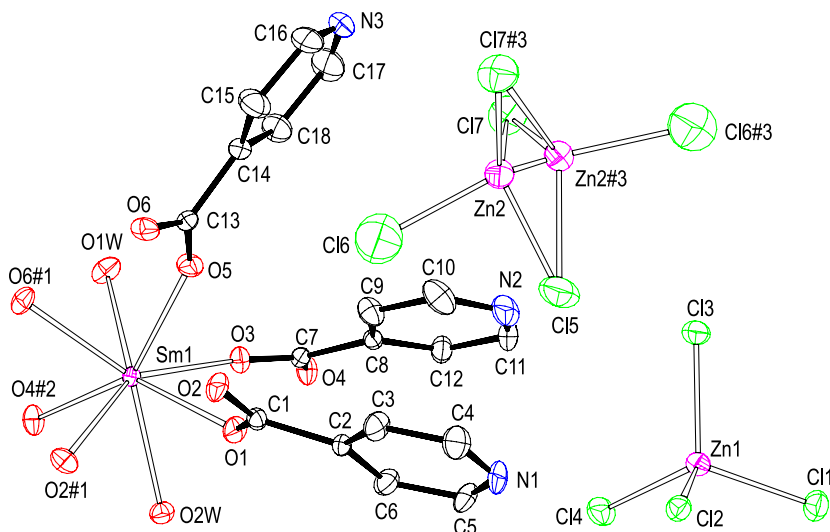
E-mail address: xym8790@yahoo.com.cn (Y.-M. Xie).

Table 1
Crystal data and structure refinement details for **1**

Formula	C ₃₆ H ₄₇ Cl ₁₃ N ₆ O ₂₀ Sm ₂ Zn ₃
<i>Mr</i>	1841.46
Color	Colorless
Crystal size/mm ³	0.35 0.20 0.10
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	23.840(2)
<i>b</i> (Å)	20.5726(8)
<i>c</i> (Å)	15.369(3)
β (deg)	127.126(2)
<i>V</i> (Å ³)	6010(1)
<i>Z</i>	4
$2\theta_{\max}$ (deg)	50.12
Reflections collected	18132
Independent, observed reflections (<i>R</i> _{int})	5265, 4589 (0.0210)
<i>d</i> _{calcd.} (g/cm ³)	2.035
μ (mm ⁻¹)	3.754
<i>T</i> (K)	293(2)
<i>F</i> (000)	3600
<i>R</i> ₁ , <i>wR</i> ₂	0.0303, 0.0680
<i>S</i>	1.010
Largest and mean Δ/σ	0.001, 0
$\Delta\rho$ (max/min) (e/Å ³)	1.789/−1.857

Table 2
Selected bond lengths (Å) and bond angles (deg) for **1**

Sm(1)–O(1)	2.380(2)	Zn(2)–Cl(7)#3	2.152(1)
Sm(1)–O(2)#1	2.363(2)	Cl(1)–Zn(1)–Cl(2)	107.80(3)
Sm(1)–O(3)	2.386(2)	Cl(1)–Zn(1)–Cl(3)	109.01(4)
Sm(1)–O(4)#2	2.408(2)	Cl(1)–Zn(1)–Cl(4)	113.20(3)
Sm(1)–O(5)	2.424(2)	Cl(2)–Zn(1)–Cl(3)	109.62(3)
Sm(1)–O(6)#1	2.411(2)	Cl(2)–Zn(1)–Cl(4)	106.86(3)
Sm(1)–O(1W)	2.469(2)	Cl(3)–Zn(1)–Cl(4)	110.27(3)
Sm(1)–O(2W)	2.526(2)	Cl(5)–Zn(2)–Cl(6)	88.85(8)
Zn(1)–Cl(1)	2.268(1)	Cl(5)–Zn(2)–Cl(7)	105.72(7)
Zn(1)–Cl(2)	2.3123(8)	Cl(5)#3–Zn(2)–Cl(7)	118.54(8)
Zn(1)–Cl(3)	2.2681(9)	Cl(6)–Zn(2)–Cl(5)#3	102.12(8)
Zn(1)–Cl(4)	2.2661(9)	Cl(6)–Zn(2)–Cl(7)	106.62(6)
Zn(2)–Cl(5)	2.209(2)	Cl(7)#3–Zn(2)–Cl(5)	136.77(6)
Zn(2)–Cl(5)#3	2.273(2)	Cl(7)#3–Zn(2)–Cl(5)#3	113.94(6)
Zn(2)–Cl(6)	2.271(2)	Cl(7)#3–Zn(2)–Cl(6)	108.73(7)
Zn(2)–Cl(7)	2.442(1)	Cl(7)#3–Zn(2)–Cl(7)	106.29(7)

Symmetry codes: #1: $-x+1, y, -z+\frac{1}{2}$; #2: $-x+\frac{1}{2}, -y-\frac{1}{2}, -z$; #3: $-x+1, y, -z+\frac{3}{2}$.**Fig. 1.** ORTEP plot of **1** with 30% thermal ellipsoids. Lattice water molecules, hydrogen atoms, and disordered Cl7B are omitted for clarity. The occupancies of Zn2 and Cl5 are equal to 0.5. (Symmetry codes: #1: $1-x, y, \frac{1}{2}-z$; #2: $\frac{1}{2}-x, -\frac{1}{2}-y, -z$; #3: $1-x, y, \frac{3}{2}-z$.)

emission spectra of solid-state sample were collected on a computer-controlled JY FluoroMax-3 spectrometer with high resolution (excitation slit width, 3 nm; emission slit width, 5 nm) at room temperature. The UV–vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV–vis spectrometer equipped with an integrating sphere in the wavelength range of 190–1100 nm. BaSO₄ plate was used as a reference (100% reflectance), on which the finely ground powder of the samples were coated. The absorption spectra were calculated from reflection spectra by the Kubelka–Munk function [17]: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm , and R is the reflectance.

2.2. Synthesis of $[\text{Sm}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]_{2n} \cdots (\text{H}_5\text{O}_2)_n(\text{ZnCl}_5)_n(\text{ZnCl}_4)_{2n} \cdots (\text{H}_2\text{O})_{2n}$ (**1**)

The title complex was prepared by mixing SmCl₃·6H₂O (1 mmol, 0.365 g), ZnCl₂ (1 mmol, 0.136 g), isonicotinic acid (1 mmol, 0.123 g), and 10 mL distilled water in a 25 mL teflon-lined stainless steel autoclave and heated at 180 °C for 7 days. After being slowly cooled to room temperature at 6 °C/h, colorless crystals suitable for X-ray analysis were obtained. The yield was 76% (based on samarium).

2.3. Crystal structure determination

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The hydrogen atom positions were generated theoretically, except for those on the lattice water molecules that is yielded by the difference Fourier maps, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structure was refined using a full-matrix least-squares refinement on F^2 . All

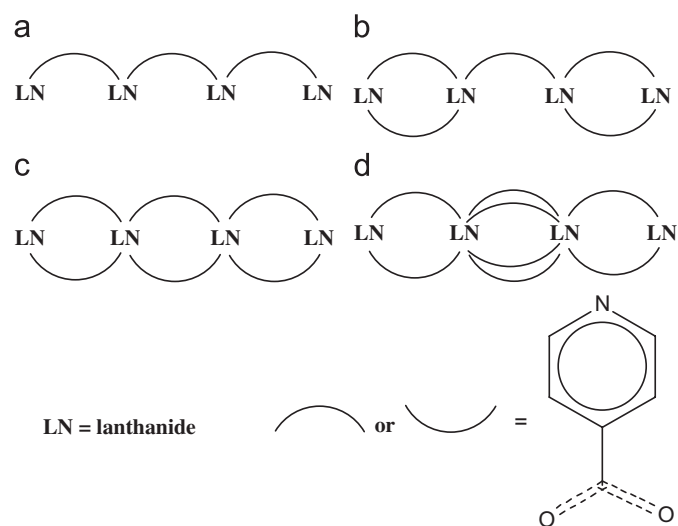
non-hydrogen atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 669669. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 33-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

Table 1 presents relevant crystallographic and refinement data. X-ray diffraction analysis reveals that the structure of the title complex consists of $[\text{Sm}(\text{C}_6\text{NO}_2\text{H}_5)_3(\text{H}_2\text{O})_2]^{5+}$ cationic moieties, H_5O_2^+ cations, ZnCl_3^{2-} and ZnCl_4^{2-} anions, and isolated water molecules, as shown in Fig. 1. The Zn1 atom is tetrahedrally bounded by four chlorine atoms to form a ZnCl_4^{2-} anion, while the Zn2 atom is coordinated by five chlorine atoms to form a ZnCl_5^{3-} anion. In contrast to the numerous complexes containing ZnCl_4^{2-} anion [18], no complex containing ZnCl_5^{3-} anion was reported thus far, although one complex containing ZnCl_6^{4-} anion has been reported [19]. Therefore, it is first time to document ZnCl_5^{3-} moieties. The bond lengths of Zn–Cl range from 2.152(1) to 2.442(1) Å with an average value of 2.273(2) Å, which are normal and comparable with the counterparts found in the literature [20]. The Zn2 atom is positional disordered and the occupancy of Zn2 must be set to 0.5 to get rational structure model and thermal displacement parameters. The samarium atom is octahedrally coordinated by eight oxygen atoms, of which two are from two water molecules and six are from 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 Sm–O_{isonicotinic acid} range from 2.363(2) to 2.424(2) Å with an average value of 2.395(2) Å, which is obviously shorter than that of Sm–O_{water} being of 2.469(2) and 2.526(2) Å, indicating that isonicotinic acid ligand has a stronger affinity to Sm^{3+} ion than that of water. The samarium atoms are alternately bridged by two or four μ_2 -isonicotinic acid ligands

in a 2-4-2 (the number indicates the number of the bridges) mode to construct a one-dimensional polycationic chain with the Sm...Sm distances of ca. 4.975 and 4.586 Å, respectively (Fig. 2 and Scheme 1d). It is noteworthy that, up to date, the types of the chains formed by LN and isonicotinic acid that have been documented are mainly 1-1-1, 2-1-2, and 2-2-2 types (Scheme 1a–c, respectively). However, the 2-4-2 type is very rare. In **1**, no $\pi\cdots\pi$ stacking interactions were established between the adjacent isonicotinic acid ligands. The one-dimensional polycationic chains, ZnCl_4^{2-} moieties, ZnCl_5^{3-} anions, and the water molecules are linked by hydrogen bonds to yield a three-dimensional network (Fig. 3). It is proposed that O3W hydrogen bonds to its symmetry-related O3W' to form a H_5O_2^+ moiety. Other crystallographic independent water molecules cannot form the H_5O_2^+ moiety, because they cannot hydrogen bond to their symmetry-related water molecules. The position of the proton between O3W and its symmetry-related O3W' could not be structurally located



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

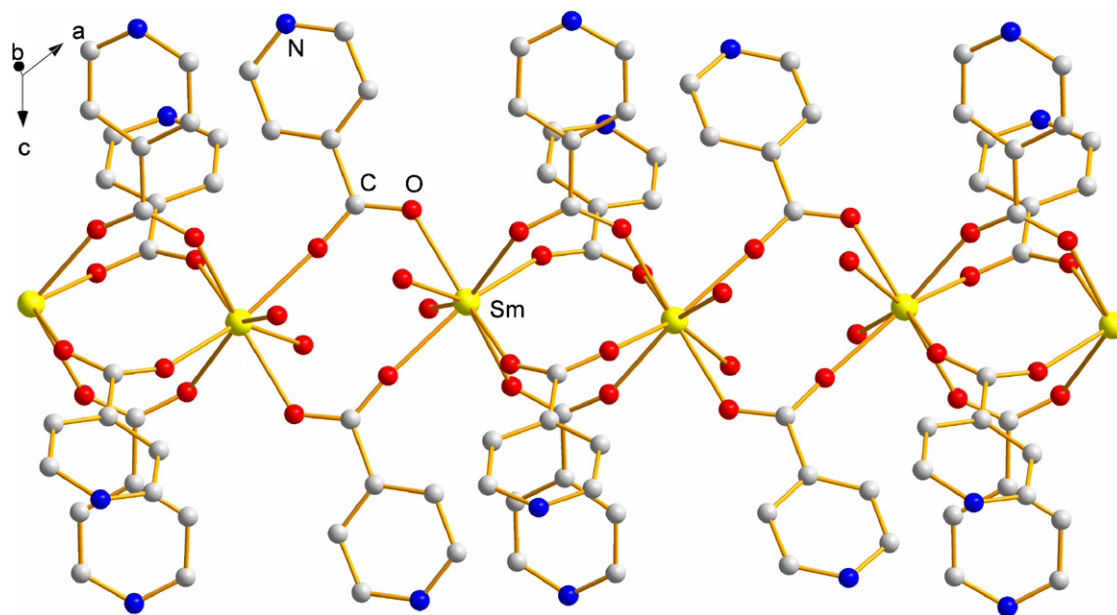


Fig. 2. The one-dimensional polycationic chain of **1**.

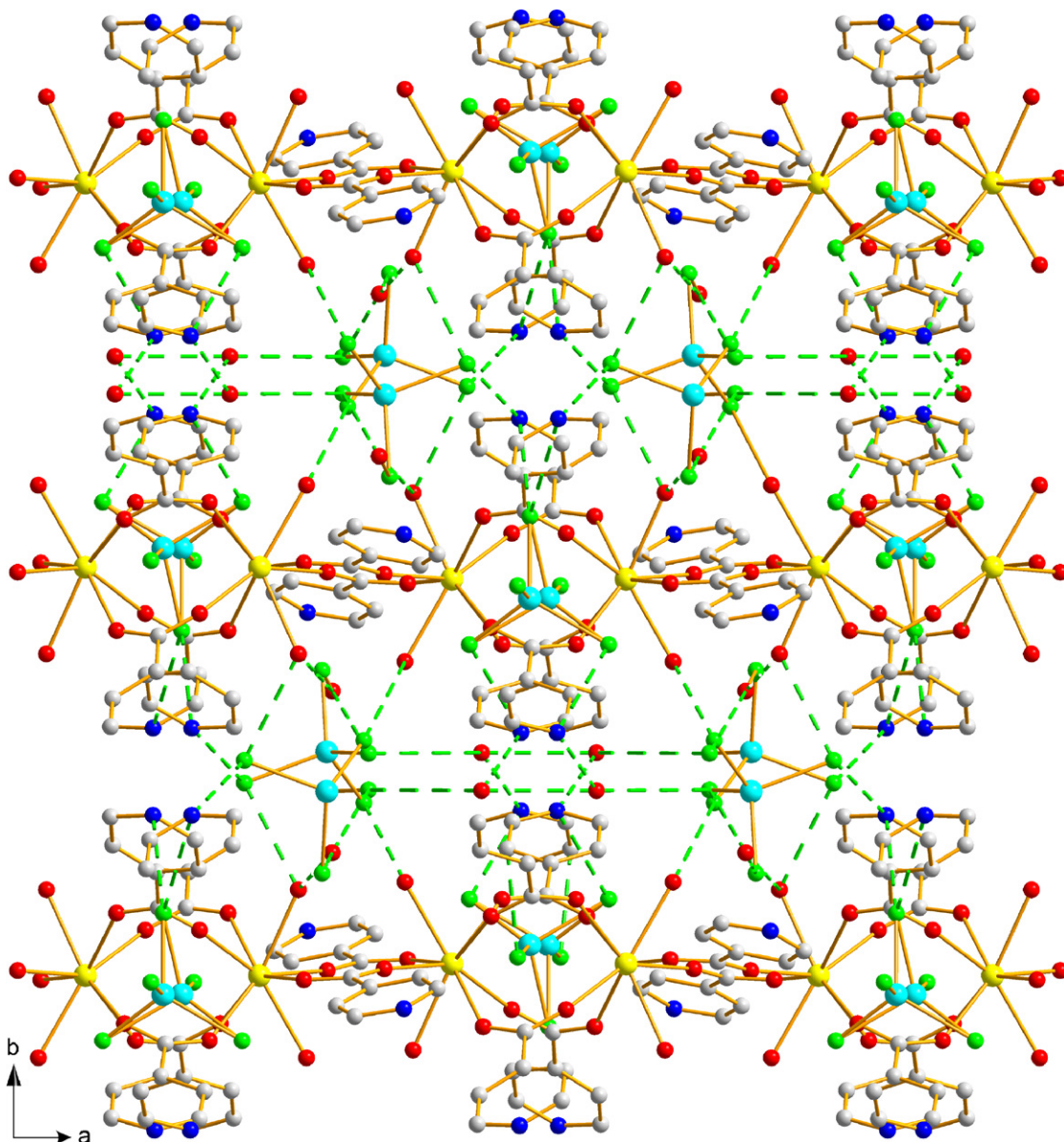


Fig. 3. Packing diagram of **1** with the dashed lines representing hydrogen bonds (Å): O1W...C11(1/2-x, -1/2+y, 1/2-z) 3.193(2), O2W...C12(x, -y, -1/2+z) 3.225(2), O2W...O4W 2.746(3), O3W...C14(1/2-x, -1/2-y, 1-z) 3.236(2), O3W...O3W(1-x, y, 1/2-z) 2.993(4), O3W...N3 2.867(4), O4W...C13(x, y, -1+z) 3.211(3), O4W...C14(x, -y, -1/2+z) 3.246(3), N1...C12 3.196(3), N1...C15 3.253(3), and N3...C17 3.273(4).

due to the existence of the heavy samarium and zinc atoms. However, the existence of H_5O_2^+ has been confirmed by the ESI-MS spectra showing H_5O_2^+ at $m/z = 37.0211$.

Taking into account the excellent luminescent property of Sm^{3+} ion, 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 takes place in the ultraviolet, violet, and blue regions in the range of 350–450 nm. The excitation bands of complex **1** possess three main peaks, 393, 410, and 421 nm, respectively. We further measured the corresponding emission spectra by selective excitation with the different excitation wavelengths of the title complex, and they show the similar emission position except for little distinction of luminescent intensities. Which indicates that all the excitation bands are effective. For complex **1**, the emission spectra show three main and intense emission bands in blue and green regions with the maximum wavelengths of 460, 472, and 495 nm upon photoexcitation at 393, 410, and 421 nm,

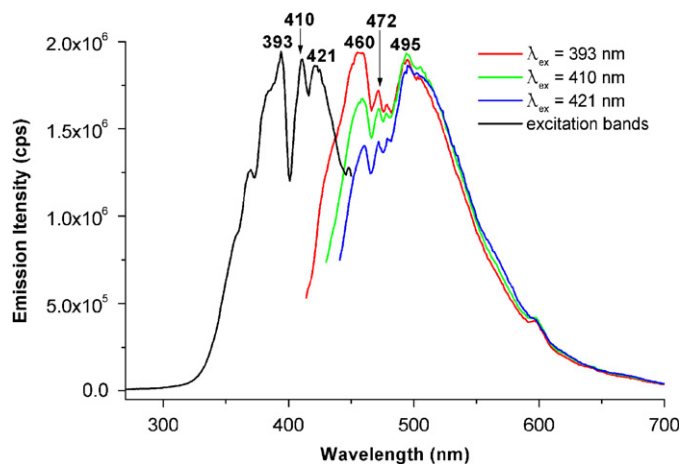


Fig. 4. Solid-state emission and excitation spectra of **1** at room temperature. Black line: emission spectrum; color line: excitation spectrum.

respectively. The changes of the emission spectra on the high-energy side on passing from an excitation wavelength of 393–421 nm are significant. This is probably due to the fact that higher energy excitation wavelength can lead to stronger emission on the high-energy side, in other words, emission intensity on the high-energy side is more easily affected by excitation wavelength than that on the low-energy side. To understand the nature of the luminescence of **1**, the luminescent spectra of pure isonicotinic acid were also measured under the same condition. For pure isonicotinic acid, the emission spectra show one intense emission band in blue region with the maximum wavelength of 455 nm upon photoexcitation at 397 nm (Fig. 5). The obvious discrepancy of the luminescent spectra of **1** and pure isonicotinic acid suggests that the emission spectra of **1** should not be assigned as an intraligand π - π^* transition. To our knowledge, the characteristic emission bands of Sm^{3+} are around 561, 596, 643, and 701 nm, which originate from ${}^4G_{5/2} \rightarrow {}^6H_J$ ($J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}$) of Sm^{3+} ions and, among them, the emission intensity of ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (locates at about 596 nm) is usually the strongest [21]. For complex **1**, most of these characteristic emission bands of Sm^{3+} cannot be found in Fig. 4, except for the small shoulder band of 596 nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$), indicating that in complex **1** all the characteristic emission bands of Sm^{3+} are very weak and maybe covered by the strong emission bands of 460, 472 and 495 nm. Based on the above discussions, for complex **1**, the three main emission bands of 460, 472 and 495 nm should probably be assigned to the LMCT transition (charge transfer from isonicotinic acid ligand to samarium metal). Moreover, the existence of the ligand-based emissions in the luminescent spectra of **1** suggests that the isonicotinic acid ligand is not perfect enough for the sensitization of the Sm^{3+} ion. However, the existence of the small shoulder band of 596 nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$) of Sm^{3+} ion indicates that the intramolecular energy transfer process still exist between the triplet state of isonicotinic acid ligand to the resonant emissive energy level of Sm^{3+} ion, i.e. “antenna effect”.

To our knowledge, for most Sm^{3+} containing complexes they show obvious characteristic emission bands of Sm^{3+} [21,22] while in complex **1** the characteristic emission bands of Sm^{3+} are very weak and not obvious. This discrepancy is probably attributed to the low energy transfer efficiency of the isonicotinic acid ligand in complex **1**. It is proposed that the low energy transfer efficiency between the isonicotinic acid ligand and the Sm^{3+} ion is caused by the fact that the lowest triplet state energy level of the isonicotinic acid ligand does not match enough to the resonance level of Sm^{3+} ion.

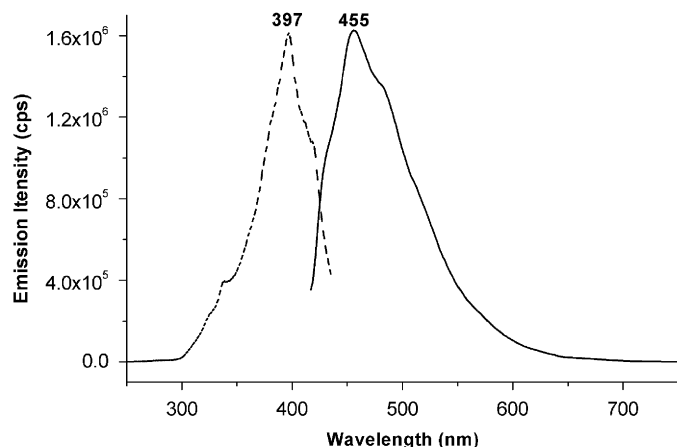


Fig. 5. Solid-state emission and excitation spectra of pure isonicotinic acid at room temperature. Solid line: emission spectrum; dashed line: excitation spectrum.

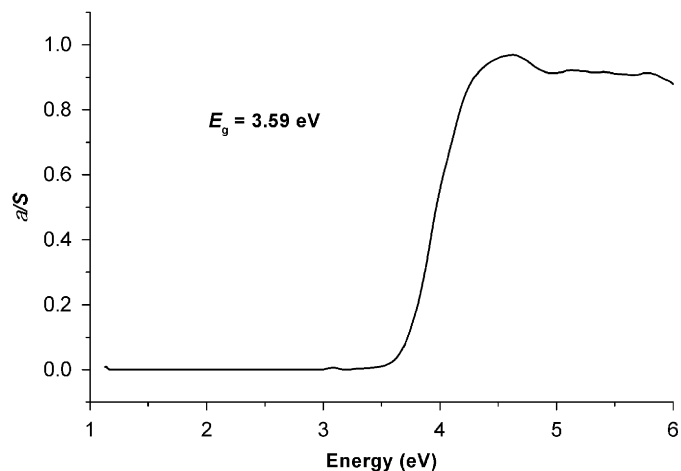


Fig. 6. Solid-state diffuse reflectance spectrum of **1**.

Optical absorption spectrum of **1** reveals the presence of an obviously optical gap of 3.59 eV (Fig. 6), which suggests that complex **1** may be a potential wide-gap semiconductor and is consistent with the color of the crystal, as the cases found in the Ref. [23]. The gradual slope of the optical absorption edge for **1** is indicative of the existence of indirect transitions [24]. The optical absorption of **1** is likely originated from the charge-transfer excitations mainly from the p -like valence band of the chloride ligands to the $4s$ -like conduction band of the zinc center, similar to those reported in the Refs. [25].

4. Conclusion

In brief, we have successfully prepared a metal–isonicotinic acid inorganic–organic hybrid complex via hydrothermal reaction. The crystal structure of the title complex is characteristic of a novel one-dimensional polycationic chain-like structure and unprecedented ZnCl_2^{2-} species. The title complex shows intense luminescence in a wide region. Optical absorption spectra show that the title complex may be a candidate for potential photoelectric material. It is believed that more and more LN–IIB-based inorganic–organic hybrid complexes with good semiconductive and luminescent properties can be developed.

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