

一维链状 4-乙基苯甲酸镧配合物 [La(EBA)₃(EBAH)(H₂O)]_n 的合成、晶体结构和性质研究

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摘要: 水热法合成了配位聚合物 [La(EBA)₃(EBAH)(H₂O)]_n (EBA=4-乙基苯甲酸根, EBAH=4-乙基苯甲酸), 并通过 X-射线衍射单晶结构分析、红外光谱、紫外光谱、荧光光谱以及热重分析对配合物进行了结构和性质研究。配合物属三斜晶系, $P\bar{1}$ 空间群。该配合物具有一维链状结构。La³⁺离子与 9 个 O 原子配位, 其中 4 个 O 原子来自 4 个双齿桥联的 4-乙基苯甲酸根, 3 个 O 原子来自 2 个螯合-桥联的 4-乙基苯甲酸根, 1 个 O 原子来自 1 个中性的 4-乙基苯甲酸, 1 个 O 原子来自配位水分子。La³⁺离子处于九配位扭变的三帽三角棱柱构型中。相邻 La³⁺离子通过双齿桥联或螯合桥联的 4-乙基苯甲酸根联结成一维链状结构。存在于分子内的氢键使一维链状结构更加稳定。由于相邻一维链的苯环间存在弱的 $\pi\cdots\pi$ 堆积作用, 使分子沿着 *a* 轴堆积形成二维层状结构。同时, 标题配合物固体具有光致发光特性, 蓝光区的较强发射归于配体的 $\pi\rightarrow\pi^*$ 电子跃迁。

关键词: 镧配合物; 4-乙基苯甲酸; 一维链; 晶体结构; 荧光

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Synthesis, Crystal Structure and Properties Study of 1D Chain-Like Lanthanum 4-ethylbenzoate Complex [La(EBA)₃(EBAH)(H₂O)]_n

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Abstract: The coordination polymer [La(EBA)₃(EBAH)(H₂O)]_n (EBA=4-ethylbenzoate, EBAH=4-ethylbenzoic acid) was synthesized by hydrothermal method in the presence of melamine and characterized by X-ray single crystal structural analysis, IR spectrum, UV spectrum, fluorescence spectrum, and thermogravimetric analysis. The complex crystallizes in triclinic crystal system and $P\bar{1}$ space group with the cell dimensions: *a*=0.953 19(3) nm, *b*=1.403 78(5) nm, *c*=1.498 47(5) nm, α =65.024(2)°, β =74.942(2)°, γ =74.734(2)°. The complex has 1D chain-like structure. La³⁺ ion is nine-coordinated by four oxygen atoms from four bridging-bidentate 4-EBA ligands, three oxygen atoms from two chelating-bridging 4-EBA ligands, one oxygen atom from one neutral 4-EBAH ligand and one from the coordinated water molecule in a distorted tricapped trigonal-prismatic geometry. The adjacent La³⁺ ions are linked by the carboxylate groups of 4-EBA ligands in the bridging-bidentate or chelating-bridging coordination mode, resulting in an infinite chain structure. The hydrogen bonds involving the water molecules, carboxylate groups and carboxyl H atoms are formed within the one-dimensional polymer. Viewed along *a* axis, two kinds of weak $\pi\cdots\pi$ interactions between the benzene rings of the neighboring chains connect the paralleling 1D chain into 2D layer structure. The luminescent property in solid state of complex was also studied and discussed. The intense blue fluorescence emission of the complex is attributed to the $\pi\rightarrow\pi^*$ electron transition of the ligands. CCDC: 764123.

Key words: lanthanum complex; 4-ethylbenzoic acid; 1D chain-like; crystal structure; fluorescence

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0 Introduction

There has been considerable interest in coordination polymers based on metal centers and multifunctional bridging ligands due to their fascinating structures and promising applications in practical areas such as catalysis, magnetism, non-linear optics, sensors and separation^[1-2]. To the best of our knowledge, carboxylate coordinates metal in various ways, for example, in the mode of monodentate, bidentate chelating, bidentate bridging or chelating-bridging. Lanthanide ions, because of the high and variety coordination numbers, their carboxylate complexes display a variety of amusing structures^[3-4].

As rigid ligands, benzoic acid and its derivatives have been widely used because they can bridge the center ions and form the π - π stacking to increase the stability of the structure. Different substituents or different positions of the substituents on the benzene ring result in various structures of the lanthanide complexes. For example, many lanthanide complexes with benzoic acid or its derivatives containing phen or 2,2'-bipy formed the dimeric unit with coordination number of eight or nine^[5-7]. However, lanthanide complexes with only monoacid ligand were usually obtained in the form of coordination polymer and this kind of complexes has higher thermal stability and strong fluorescence properties^[8-9]. With the aim of preparing stable functional polymer, we used 4-ethylbenzoic acid (4-EBAH) as ligand in the presence of melamine, and obtained a new one-dimensional polymeric $[\text{La}(\text{EBA})_3(\text{EBAH})(\text{H}_2\text{O})]_n$ prepared by hydrothermal method. The crystal structure, luminescent properties and thermal stability of the complex are reported in this paper.

1 Experimental

1.1 Reagents and general methods

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 4-ethylbenzoic acid (4-EBAH), melamine, DMF and DMSO are analytically pure grade and used as received. Elemental (C and H) analysis was performed on a Perkin-Elmer 2400LS analyzer. Infrared spectra were collected with a FTIR Thermo Nicolet Impact 410 spectrometer with KBr pellets in the 4 000 ~400 cm^{-1} regions. The UV-Vis spectra were

measured in DMF solvent ($1 \text{ mmol} \cdot \text{L}^{-1}$) by a UV-260 spectrophotometer. Excitation and luminescent spectra for the powdered solid samples were recorded at room temperature on a Hitachi F-4500 fluorescence spectrofluorometer (the pass width is 5.0 nm). Thermogravimetric analysis was conducted on a Perkin Elmer TG-7 with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ from 30 to $700 \text{ }^\circ\text{C}$ in air.

1.2 Synthesis of $[\text{La}(\text{EBA})_3(\text{EBAH})(\text{H}_2\text{O})]_n$

A mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.52 mmol), 4-EBAH (0.84 mmol) and melamine (0.4 mmol) was added to 10 mL distilled water, and pH of the resultant mixture was 5.5~6.5. The reaction mixture was transferred to the 25 mL stainless Teflon-lined autoclave and heated at 423 K under autogenous pressure for 7 d. After cooled to room temperature, the colorless prism crystals were separated from the mixture, washed with cold deionized water and dried at 350 K for 10 h in air. The yield was about 58 % based on La_2O_3 . The obtained complex is hardly soluble in water, methanol, anhydrous ethanol and acetonitrile, but facilely soluble in DMF and DMSO. Anal. Calcd. for $\text{C}_{36}\text{H}_{39}\text{O}_9\text{La}(\%)$: C 57.30, H 5.21; found(%): C 57.04, H 5.46.

1.3 X-ray crystal structure determination

A colorless prismatic crystal with dimensions of 0.35 mm×0.32 mm×0.23 mm was put on Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatized $\text{Mo K}\alpha$ radiation ($\lambda=0.071\ 073 \text{ nm}$) by using φ - ω scan mode at 296(2) K. Total of 22 559 reflections were collected in the range of $1.63^\circ \leq \theta \leq 27.43^\circ$, of which 7 733 were independent with $R_{\text{int}}=0.050$, and 6 206 with $I>\sigma(I)$ were considered as observed. Semi-empirical absorption correction was applied to the intensity data using the SADABS program^[10]. The structure was solved by direct methods and refined by full-matrix least-square on F^2 using the SHELXTL-97 program^[11]. All non-hydrogen atoms were refined anisotropically. All H atoms bounded to C atoms were generated geometrically and refined isotropically using the riding mode. The hydrogen atoms of water molecule and the carboxylic H atom were located in a difference Fourier map. The ethyl group C8-C9 was treated as disordered over two sites, with refined occupancies 0.714(7) and

0.286(7). A summary of crystal data and details of the structure refinements are listed in Table 1. CCDC: 764123.

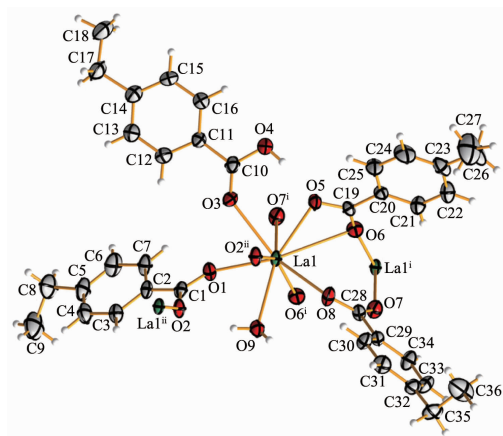
Table 1 Crystal data and structure refinement for the title complex

| | | | |
|---------------------|---|---|------------------|
| Empirical formula | $\text{C}_{36}\text{H}_{30}\text{O}_9\text{La}$ | V / nm^3 | 1.727 91(10) |
| Formula weight | 754.58 | $D / (\text{g} \cdot \text{m}^{-3})$ | 1.450 |
| Temperature / K | 296(2) | μ / mm^{-1} | 1.288 |
| Wavelength / nm | 0.071 073 | $F(000)$ | 768 |
| Crystal system | Triclinic | Crystal size / mm | 0.35×0.32×0.23 |
| Space group | $P\bar{1}$ | θ range for data collection / ($^\circ$) | 1.63 to 27.43 |
| a / nm | 0.953 19(3) | Reflections collected | 22 559 |
| b / nm | 1.403 78(5) | Independent reflections (R_{int}) | 7 733 (0.050) |
| c / nm | 1.498 47(5) | Observed reflections [$I > 2\sigma(I)$] | 6206 |
| $\alpha / (^\circ)$ | 65.024(2) | Final GooF | 1.014 |
| $\beta / (^\circ)$ | 74.942(2) | R_1, wR_2 [$I > 2\sigma(I)$] | 0.038 2, 0.070 9 |
| $\gamma / (^\circ)$ | 74.734(2) | R_1, wR_2 (all data) | 0.054 8, 0.077 2 |
| Z | 2 | Largest different peak and hole / ($\text{e} \cdot \text{nm}^{-3}$) | 676, -737 |

2 Results and discussion

2.1 Crystal structure of $[\text{La}(\text{EBA})_3(\text{EBAH})(\text{H}_2\text{O})]_n$

The representative structure of the complex including the atomic numbering scheme is described in Fig.1. The prominent characteristic is the 1D chain, in which the center La^{3+} ions act as nodes and are connected through 4-EBA ligands. Carboxyls (O1-C1-O2 and O7-C28-O8) adopt bidentate-bridging coordination fashion, namely, the two oxygen atoms coordinate to two different La^{3+} ions. Carboxyl (O5-C19-O6) adopts the chelating-bridging coordination mode, in which O5 and O6 coordinate to one La^{3+} ion by chelating fashion and O6 simultaneously bridges with another La^{3+} ion. While

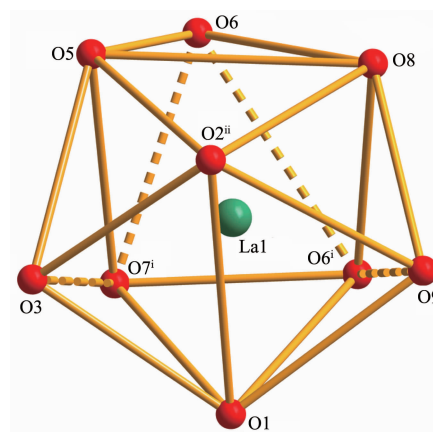


Symmetry codes used to generate equivalent atoms: ⁱ 1-x, -y, 1-z; ⁱⁱ 2-x, -y, 1-z

Fig.1 Molecular structure of the complex

the carboxyl (O3-C10-O4) adopts the monodentate mode in form of neutral 4-EBAH.

Each $\text{La}(\text{III})$ ion is coordinated with nine oxygen atoms, in which four oxygen atoms from four bridging-bidentate 4-EBA ligands, three oxygen atoms from two chelating-bridging 4-EBA ligands, one oxygen atom from one neutral 4-EBAH ligand and one from the coordinated water molecule. So each La^{3+} ion lies in a distorted tricapped trigonal-prismatic coordination environment (Fig.2). Atoms O2ⁱⁱ, O8 and O5 construct the upper plane of the distorted trigonal prism and atoms O1, O6ⁱ and O7ⁱ form the below one, with the dihedral angle of 5.744° between them. The O9, O3 and O6 atoms are at the vertices of each square pyramid.



Symmetry codes: ⁱ 1-x, -y, 1-z; ⁱⁱ 2-x, -y, 1-z

Fig.2 Coordination polyhedron of the title complex

And the mean distance from the upper and lower plane is 0.322 8 nm.

The adjacent La^{III} ions are linked by the carboxylate groups of 4-EBA ligands in the bridging-bidentate or chelating-bridging coordination mode, resulting in an infinite chain structure along the b axis. The distance between two adjacent La^{3+} ions is 0.426 05(3) nm for $\text{La1}^{\text{i}} \cdots \text{La1}$ and 0.545 10(3) nm for $\text{La1} \cdots \text{La1}^{\text{ii}}$. And the angle of $\text{La1}^{\text{i}} \cdots \text{La1} \cdots \text{La1}^{\text{ii}}$ is $157.753(6)^\circ$. The bond lengths of La1-O , except for La1-O6 , range from 0.244 7(2) to 0.267 2(2) nm, with a mean value of 0.252 2 nm, which are rational as literatures reported^[12-13]. Whereas, the rather long La1-O6 distance of 0.298 9(2) nm oversteps the average length of La-O bond^[12-13]. And the bond angles of O-La1-O (carboxyl) range from $45.65(7)^\circ$ to $154.20(7)^\circ$.

As shown in Table 3, the coordinating water, carboxylate oxygen atoms of 4-EBA ligands and carboxylic H atom of 4-EBAH ligand are involved in $\text{O-H} \cdots \text{O}$ hydrogen-bonding interactions ($\text{O9-H9B} \cdots \text{O2}$, $\text{O4-H4A} \cdots \text{O5}$). Furthermore, these hydrogen

bonds are all intramolecular, i.e. stabilize the one-dimensional chain structure of the polymer, as indicated in Fig.3. Additionally, at the same side of 1D chain, the benzene rings of 4-EBA ligands or 4-EBAH ligand parallel each other and the shortest vertical distance of the corresponding adjacent benzene rings are 0.560 8, 0.680 3, 0.578 1 and 0.431 4 nm for the

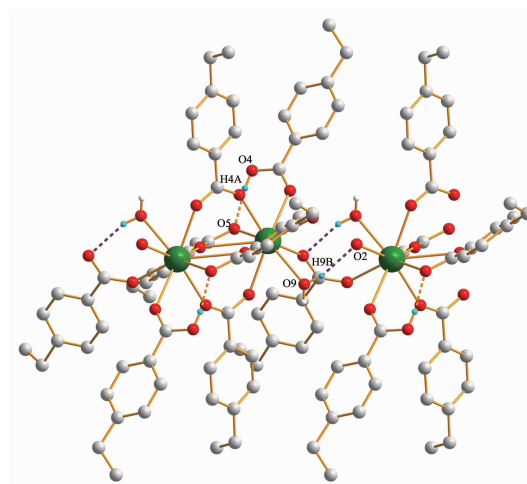


Fig.3 Intramolecular hydrogen bonds of extended chain-like structure along the b axis

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for the complex

| | | | | | |
|--|------------|---------------------------------------|------------|---------------------------------------|------------|
| La1-O7^{i} | 0.244 7(2) | La1-O8 | 0.247 9(2) | La1-O9 | 0.262 4(2) |
| La1-O1 | 0.245 2(2) | La1-O5 | 0.258 1(2) | La1-O3 | 0.267 2(2) |
| $\text{La1-O2}^{\text{ii}}$ | 0.245 7(2) | La1-O6^{i} | 0.246 6(2) | La1-O6 | 0.298 9(2) |
| $\text{O7}^{\text{i}}\text{-La1-O1}$ | 85.28(8) | $\text{O6}^{\text{i}}\text{-La1-O8}$ | 79.01(8) | $\text{O6}^{\text{i}}\text{-La1-O9}$ | 75.51(8) |
| $\text{O7}^{\text{i}}\text{-La1-O2}^{\text{ii}}$ | 138.38(8) | $\text{O7}^{\text{i}}\text{-La1-O5}$ | 78.88(8) | O8-La1-O9 | 65.78(8) |
| $\text{O1-La1-O2}^{\text{ii}}$ | 88.76(7) | O1-La1-O5 | 137.54(8) | O5-La1-O9 | 141.11(8) |
| $\text{O7}^{\text{i}}\text{-La1-O6}^{\text{i}}$ | 72.12(8) | $\text{O2}^{\text{ii}}\text{-La1-O5}$ | 78.20(7) | $\text{O7}^{\text{i}}\text{-La1-O3}$ | 70.76(8) |
| $\text{O1-La1-O6}^{\text{i}}$ | 88.38(8) | $\text{O6}^{\text{i}}\text{-La1-O5}$ | 122.55(7) | O1-La1-O3 | 67.79(8) |
| $\text{O2}^{\text{ii}}\text{-La1-O6}^{\text{i}}$ | 148.91(8) | O8-La1-O5 | 83.20(8) | $\text{O2}^{\text{ii}}\text{-La1-O3}$ | 68.89(8) |
| $\text{O7}^{\text{i}}\text{-La1-O8}$ | 129.47(8) | $\text{O7}^{\text{i}}\text{-La1-O9}$ | 138.97(8) | $\text{O6}^{\text{i}}\text{-La1-O3}$ | 137.01(8) |
| O1-La1-O8 | 134.89(8) | O1-La1-O9 | 69.16(8) | O8-La1-O3 | 142.87(8) |
| $\text{O2}^{\text{ii}}\text{-La1-O8}$ | 81.26(8) | $\text{O2}^{\text{ii}}\text{-La1-O9}$ | 74.56(8) | O5-La1-O3 | 69.82(7) |
| O9-La1-O3 | 122.91(7) | O8-La1-O6 | 63.95(7) | $\text{O6}^{\text{i}}\text{-La1-O6}$ | 77.73(7) |
| $\text{O7}^{\text{i}}\text{-La1-O6}$ | 69.86(7) | O5-La1-O6 | 45.65(7) | $\text{O2}^{\text{ii}}\text{-La1-O6}$ | 114.27(7) |
| O1-La1-O6 | 154.20(7) | O9-La1-O6 | 126.32(7) | O3-La1-O6 | 108.39(7) |

Symmetry codes used to generate equivalent atoms: ⁱ 1-x, -y, 1-z; ⁱⁱ 2-x, -y, 1-z.

Table 3 Hydrogen bond lengths and angles

| D-H \cdots A | D-H / nm | H \cdots A / nm | D \cdots A / nm | $\angle \text{DHA} / (^\circ)$ |
|----------------|----------|-------------------|-------------------|--------------------------------|
| O4-H4A-O5 | 0.082 | 0.184 | 0.265 2(3) | 170.8 |
| O9-H9B-O2 | 0.082 | 0.204 | 0.282 9(3) | 160.7 |

C2-C4-C6, C11-C13-C15, C20-C22-C24 and C29-C31-C33, respectively. Therefore, there is no obvious $\pi \cdots \pi$ packing effect within the one-dimensional polymer although the benzene rings parallel highly each other.

To some extent, the structure of the title complex is similar to that of complex $[\text{Eu}(\text{2-IBA})_3 \cdot \text{H}_2\text{O}]_n$ (2-IBA = 2-iodobenzoate)^[14]. The latter complex is also 1D polymer chain structure, in which Eu^{3+} ions are connected through two carboxyl groups of two 2-IBA ligands via the bridging-chelating-bridging tetradentate coordination mode. In the structure of 1D chain polymer $[\text{Eu}(\text{2,4-DCIBA})_3 \cdot (\text{CH}_3\text{CH}_2\text{OH})_2]_n$ (2, 4-DCIBA = 2, 4-dichlorobenzoate)^[15], each Eu^{3+} ion is eight-coordinated with four oxygen atoms of four bidentate-bridging 2,4-DCIBA anions, two oxygen atoms of one bidentate-chelating 2,4-DCIBA anion and two atoms of two ethanol molecules. Unlike the title complex, in the 1D polymeric chain of $[\text{Tb}(\text{3-IBA})_3(\text{H}_2\text{O})_2 \cdot 0.5(4,4'\text{-bipy})]_n$ (3-IBA = 3-iodobenzoate; 4,4'-bipy = 4,4'-bipyridine), each Tb^{3+} ion is connected through four bidentate bridging 3-IBA ligands and lies in a distorted square-antiprism geometry. The 4, 4'-bipy molecule in the crystal lattice does not coordinate to Tb^{3+} ion^[16]. In the dinuclear complex of $\{\text{La}[\text{o-C}_6\text{H}_4(\text{NO}_2)(\text{CO}_2)]_3 \cdot (\text{DMF})_2\}_2$ (*o*-nitro-benzoic acid), two La(III) ions are bridged by four *o*-nitro-benzoic acid ligands with their carboxyls and occupy the nine coordination sites, in which two carboxyl groups adopt bidentate-bridging coordination mode and the other two take monodentate-bridging mode^[17]. Obviously, the distinct difference from the final structures of these coordination complexes may be caused by the different ligands, for example, the different substituent groups or the different position locating in the benzene rings.

In addition, each unit cell is packed by six 1D polymeric chains along *a* axis. These 1D chains parallel each other with the shortest distance between the adjacent La^{3+} of 1.474 63(6) nm and 1.498 47(6) nm. Moreover, there are two kinds of inter-molecular $\pi \cdots \pi$ interactions between the benzene rings of neighboring polymeric chains. As shown in Fig.4, the benzene ring (C11, C12, C13, C14, C15, C16) and the adjacent A ring are parallel with $d_{\text{C-C}}=0.377\ 35\ \text{nm}$, $d_{\text{P-P}}=0.306\ 32$

nm, $\theta=0.233^\circ$, in which C_g is the ring centroid, $d_{\text{C-C}}$ is the centroid-centroid distance, $d_{\text{P-P}}$ is the vertical distance, and θ is the dihedral angle of two neighboring π -planes^[18]. Similarly, the benzene ring (C20, C21, C22, C23, C24, C25) and the neighboring B ring are also parallel highly with $d_{\text{C-C}}=0.394\ 12\ \text{nm}$, $d_{\text{P-P}}=0.356\ 02\ \text{nm}$, $\theta=0^\circ$. The weak $\pi \cdots \pi$ stacking interactions assemble the neighboring 1D chains into the two-dimensional layer structure paralleling to *bc* plane for the title complex.

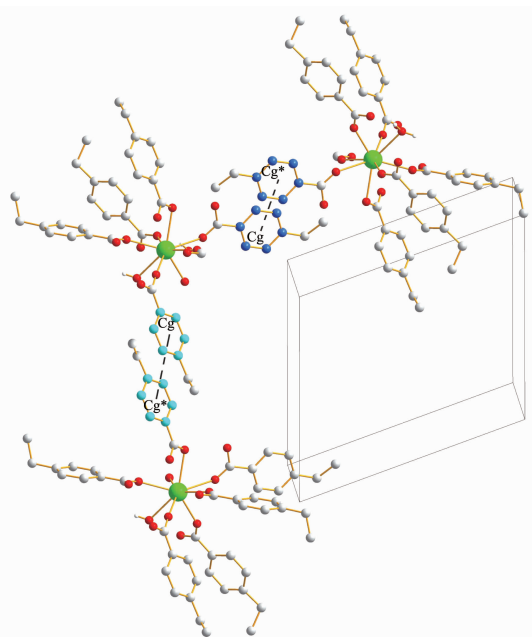


Fig.4 Arrangement of the $\pi \cdots \pi$ stacking interactions paralleling to *bc* plane of the title compound

2.2 IR and UV spectrum of the title complex

The IR spectrum of the complex was determined in the range of $4\ 000\sim 400\ \text{cm}^{-1}$ as KBr pellets. Compared with the 4-EBAH ligand, the IR spectral intensity of the complex around $1\ 710\ \text{cm}^{-1}$ is significantly weakened, which is observed for the $-\text{COOH}$ ^[19]. It demonstrates that there are several different coordinating fashions of the carboxylate groups in the complex, including the deprotonated anions and the neutral molecule. Another feature of the IR data of the complexes is the separation between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, which have often been used to discuss the coordination mode of carboxylate group in the carboxylate complexes. Two strong peaks at $1\ 532$ and $1\ 383\ \text{cm}^{-1}$ could be assigned to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching vibration of carboxyl

in 4-EBA ligand. The $\Delta\nu[\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-)]$ of 149 cm^{-1} suggests that the coordination of the carboxylate groups is most probably of the bridging type^[20], which is also supported by the results from single-crystal X-ray diffraction data. Peaks observed at $2\,985\sim 2\,846\text{ cm}^{-1}$ are in good agreement with C-H vibrations, and the wide absorption peak at about $3\,405\text{ cm}^{-1}$ is assigned to the vibrations of water molecules. The weak band at 435 cm^{-1} may be assigned to the vibrations of La-O bond^[21].

The UV spectra of the free ligand and the complex were recorded in DMF solvent with the concentration of $1\text{ mmol}\cdot\text{L}^{-1}$. Both of the spectra have one strong absorption peak at 272 nm attributing to $\pi\rightarrow\pi^*$ transition, however, the intensities are different. The absorption intensity of the complex ($\varepsilon=1.51\times 10^3$) is evidently stronger than that of free 4-EBAH ligand ($\varepsilon=0.72\times 10^3$), which is attributed to the coordination between the ligands and the center La^{3+} ions. Owing to the formation of complex, the degree of conjugation and intensities of UV absorption obviously increased.

2.3 Luminescent properties

The solid state fluorescence spectrum of the complex was measured at room temperature. The excitation spectrum was recorded in the range of $250\sim 400\text{ nm}$, setting 449 nm as the emission wavelength, in which there is a strong peak at 335 nm . In contrast to the weak luminescence of the free ligand, the complex exhibits one strong band centered at 449 nm excited at 335 nm in the solid state (Fig.5). Since there are no 4f electrons and the energy level of excited states below the triplet levels of the ligand for La(III) ions, the energy

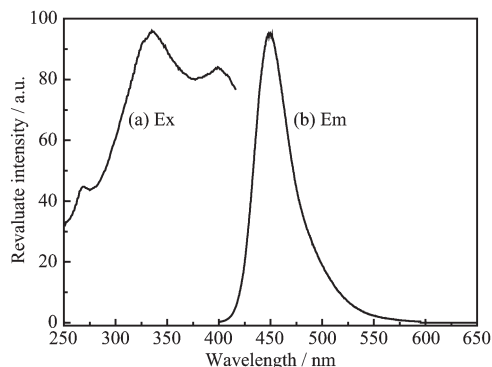


Fig.5 Excitation (a) and emission (b) spectra of the complex in the solid state

absorbed by the 4-EBA ligand cannot transfer to La(III) ions. The absorbed energy can only relax through its own energy levels. The intense blue fluorescence emission of the complex is attributed to the enhanced $\pi\rightarrow\pi^*$ electron transition of the ligand. Therefore, the complex emits the ligand-centered fluorescence.

2.4 Thermogravimetric analysis

The TG-DSC analysis was performed in air atmosphere with a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}$ in the temperature range from 30 to $700\text{ }^\circ\text{C}$. The results indicate that the complex involve two steps of weight losses. The first weight loss of 2.26% from 30 to $246\text{ }^\circ\text{C}$ corresponds to the coordinated water molecule (calculated 2.39%). The next mass reduction of 74.79% occurs in the range $246\sim 625\text{ }^\circ\text{C}$ and shows two apparent exothermic peaks, corresponding to the removal of organic ligands. The weight of the residue is 22.95% . Supposing La_2O_3 as final residue, calculated residue weight of the complex is 21.59% , which is in coincidence with experimental value. Results indicate that the complex is degraded to oxide, completely.

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