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### Synthesis and luminescence properties of salicylaldehyde

#### isonicotinoyl hydrazone derivatives and their europium complexes

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**Abstract:** Four novel salicylaldehyde isonicotinoyl hydrazone derivatives and their corresponding europium ion complexes were synthesized and characterized. Whilst the luminescence properties and the fluorescence quantum yields of the target complexes were investigated. The results indicated that the ligands favored energy transfers to the emitting energy level of europium ion, and four target europium complexes showed the characteristic luminescence of central europium ion. Besides the luminescence intensity of the complex with methoxy group, which possessed the highest fluorescence quantum yield (0.522), was stronger than that of other complexes. Furthermore, the electrochemical properties of the target complexes were further investigated by cyclic voltammetry, the results indicated that the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels and the oxidation potential of the complexes with electron donating group increased, however, that of the complexes with accepting electron group reduced.

Keywords: Acylhydrazone; Complex; Synthesis; Luminescence properties;

Electrochemical properties

#### 1. Introduction

Schiff base compounds, the aldehyde or ketone analogs in which the carbonyl group is replaced by an imine or azomethine group, are considered privileged ligands, because of their simple preparation in the condensation of amines with carbonyl compounds .Therefore, Schiff base ligands have gained paramount importance due to their versatility, such as catalytic property, biological activity, antibacterial, dyes, etc. [1-10].

The  $Eu^{3+}$  ion possesses several unique luminescence properties. However, it has a very small absorption coefficient. This shortfall is overcome by introducing an organic ligand to sensitize  $Eu^{3+}$  ion. The sensitizeng ligand transfers energy to the  $Eu^{3+}$  ion effectively, which can enhance luminescence of  $Eu^{3+}$  ion [11]. Therefore, it is significant to design and synthesis the ligand, whose triplet energy level matches better to the emitting level of the rare earth ions. This results are attributed to their excellent coordination nature to the  $Eu^{3+}$  ion.

Schiff bases ligands and their  $Eu^{3+}$  ion complexes have a variety of applications in biological, clinical, analytical and industrial fields [12]. Among these, heterocyclic Schiff base ligands and their  $Eu^{3+}$  ion complexes do have drawed significant interest.

To our konwledge, systsalicylaldehyde–acylhydrazones act as tetradentate ligand were reported only in the discrete trinuclear metal complexes of special compartmental ligands[13]. However, systsalicylaldehyde–acylhydrazones have been seldom reported in literature with their corresponding rare earth ions complexes due to their poor solubility, not to mention the luminescence properties of their rare earth complexes. On the other hand, the salicylaldehyde isonicotinoyl hydrazone (SIH) compounds possess good conjugated plane, rigid stucture and various coordination sites, and good biological activity[14-18], are theoretically suitably used as the organic ligand of the rare earth luminescent complexes. Aiming to enrich in the other application filed, SIH has been focused notably on a salicylaldehyde-derived chelator, which has been recently shown to possess very strong and concentration-dependent properties on the optics, sensors, medicine [19-22].

As described herein, we used isonicotinic acid, salicylaldehyde and aniline

derivatives as raw materials to synthesize four SIH derivatives with acetanilide as the end group. Their corresponding complexes with europium ions had also been prepared and characterized. Meanwhile, the luminescence and electrochemical properties of the title complexes were investigated, and the relationship between the structure of the ligand and the properties of complexes was also explored in detail. The synthetic route to salicylaldehyde isonicotinic acid hydrazon ( $L^{a-d}$ ) derivatives schiff bases as outlined was shown in **Scheme 1**.

#### 2. Experimental

#### 2.1 Materials and methods

The purity of  $Eu_2O_3$  was 99.99%. Europium nitrate was prepared according to the literature [23]. Isonicotinic acid and aniline derivatives were of chemical pure (CP) grade, dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) and other reagents were of AR grade and used without further purification.

spectra were registered in DMSO-d<sub>6</sub>/CDCl<sub>3</sub> at  $^{1}\mathrm{H}$ NMR Brucker spectrophotometer (400 MHz) with tetramethylsilane (TMS) as an internal standard. Mass spectra were evaluated with the MAT95XP Mass Spectrometer. Infrared radiation (IR) spectra (400 cm<sup>-1</sup>-4000 cm<sup>-1</sup>) were achieved in KBr discs by a PERKIN-ELMER Spectrum One. UV-visible (UV-vis) spectra (190-50 nm) were recorded by LabTech UV-2100 spectrophotometer, with DMSO as solvent and reference. Elemental analysis of the complexes was carried out on a Flash EA1112 elemental analyzer. Melting points of all compounds were established on a XT-4 binocular microscope apparatus and were uncorrected. The molar conductivity was recorded with DDS-12A digital display conductivity instrument. Thermal gravimetric analysis was carried out on a NETZSCH STA 409PC thermal gravimetric analyzer, with the empty crucible for comparison in air atmosphere, and the rate of temperature increase was 10/min. Cyclic voltammetry curve testing using three electrodes were glassy electrode, a platinum electrode and a saturated calomel electrode, ferrocene as external standard, nitrite solution was used as the supporting electrolyte and DMSO as the solvent, the test scanning speed was 100 mV  $\cdot$  s<sup>-1</sup> and the sensitivity was 1 mA.

The fluorescence spectra was measured by using powder samples on a Hitachi F-2700 fluorescence spectrophotometer at room temperature, the scanning speed was 1200 nm/min, and the voltage was set to 700 V. The europium ion was established by EDTA titration using xylenol orange as an indicator.

#### 2.2 General procedure for the synthesis of intermediates

# 2.2.1 General procedure for synthesis of N'-(2-hydroxybenzylidene) isonicotinohydrazide (2)

To the solution of isonicotinic acid (50 mmol, 6.15 g) in methanol (50 mL), acetyl chloride (5 mL) was gradually added and the reaction mixture was stirred in ice water bath. Then the reaction mixture was heated to the required temperature and refluxed for 24 h with stirring in the oil bath. Next, the mixture was suction filtrated, and filtrate was distilled under reduced pressure to obtain methyl isonicotinate.

Subsequently, the obtained product was added into a 150 mL three-neck flask, absolute alcohol (60 mL) was gradually added dropwise into it, and the mixture was heated to 85 °C. To this solution, the hydrazine hydrate (10 mL 80%) was added and refluxed for 6 h, and then the excess solvent was removed under reduced pressure, the residue was recrystallized from absolute alcohol to get white needle isonicotinoylhydrazide crystal (compound **1**).

To the solution of compound **1** (0.04 mol 5.88 g) in absolute alcohol (60 mL 95%), salicylaldehyde (0.04 mol 4.88 g) was added in a 150 mL three-neck flask, the mixture solution was refluxed for 8 h with stiring, the resulting mixture was separated by suction filtration, the residue was recrystallized with absolute alcohol three times to get yellow crystal and dried under vacuum for 24 h to get N'–(2–hydroxybenzylidene) isonicotinohydrazide (compound **2**).

N'–(2–hydroxybenzylidene) isonicotinohydrazide (7.72 g) Yield: 80%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm): 12.31 (s, 1H), 11.08 (s, 1H), 8.81 (dd, *J* = 4.4, 1.6 Hz, 2H), 8.69 (s, 1H), 7.85 (dd, *J* = 4.4, 1.6 Hz, 2H), 7.62 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.44–7.14 (m, 1H), 7.07–6.89 (m, 2H). MS (EI) [MS = mass spectrometry; EI = electron ioniozation] m/z (%): 241 (M, 27), 123 (100), 106 (97), 91 (10),78 (74), 51 (55).

#### 2.2.2 Synthesis of 2-chloro-N-phenylacetamide derivatives (3<sup>a</sup>-3<sup>d</sup>)

The synthesis procedures of compound  $3^{b}-3^{d}$  were similar to that of compound  $3^{a}$ , thus we take the synthesis method of compound  $3^{a}$  for example. Aniline (0.066 mol, 6.15 g) was dissolved into acetic acid (40–50 mL) in a 100 mL single-neck flask, then the chloroacetyl chloride (0.074 mol, 8.36 g) was added dropwise with stirring for 30 min in the ice bath, the resulting mixture was reacted for another one hour at room temperture. Subsequently, the mixture was poured into saturated sodium acetate (150 mL) solution to form milky white precipitate. Finally, this precipitate was suction filtrated, washed three times with distilled water and recrystallized from the mixed solution of absolute alcohol and water (1/2, v/v). The product was dried under vacuum for 24 h to obtained compound  $3^{a}$ .

2-chloro-N-phenylacetamide (3<sup>a</sup>) A white needle solid. yield: 68%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ/ppm: 10.29 (s, 1H, NH), 7.77–7.47 (m, 2H, ArH), 7.40–7.22 (m, 2H, ArH), 7.18–6.95 (m, 1H, ArH), 4.25 (s, 2H, CH<sub>2</sub>); MS (EI) m/z (%): 172 (M+3, 3), 171 (M+2, 25), 169 (M, 80), 121 (3), 120 (40), 106 (7), 94 (10), 93 (100), 77 (22), 65 (28).

2-chloro-N-(4-chlorophenyl)acetamide (3<sup>b</sup>) A white needle solid. yield: 94%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ/ppm: 7.67–7.57 (m, 2H, ArH), 7.46–7.34 (m, 2H, ArH), 4.26 (s, 2H, CH<sub>2</sub>); MS (EI) m/z (%): 207 (M+3, 5),205 (M+1, 33), 203 (M–1, 52), 156 (4), 154 (13), 129 (32), 127 (100), 126 (15), 111 (5), 99 (14), 77 (5), 63 (7).

2-chloro-N-p-tolyacetamide (3<sup>c</sup>) A white flake solid yield: 78%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ/ppm: 10.21 (s, 1H, NH), 7.42–7.46 (m, 2H, ArH), 7.16–7.18 (m, 2H, ArH), 4.22 (s, 2H, CH<sub>2</sub>), 2.21 (s, 3H, CH<sub>3</sub>); MS (EI) m/z (%): 186 (M+3, 3), 185 (M+2, 25), 183 (M, 75), 148 (4), 134 (27), 107 (100), 106 (76), 91 (16),77 (26), 51 (10).

2-chloro-N-(4-methoxyphenyl)acetamide (3<sup>d</sup>) A faint purple solid. yield: 53%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ/ppm: 10.18 (s, 1H, NH), 7.54–7.48 (m, 2H, ArH), 6.95–6.87 (m, 2H, ArH), 4.22 (s, 2H, CH<sub>2</sub>), 3.73 (s, 3H, CH<sub>3</sub>); MS (EI) m/z (%): 202 (M+3, 3), 201 (M+2,32), 199 (M, 100), 124 (29), 123 (72), 108 (72), 95 (13), 80 (6).

#### 2.2.3 Synthesis of salicylaldehyde isonicotinoyl hydrazone derivatives $(L^a - L^d)$

As the synthesis methods of compounds  $L^{a-d}$  were similar with each others, only the synthesis procedures of compound  $L^a$  was described as example. To the solution of compound 2 (3 mmol, 0.72 g) in 30 mL DMF, potassium carbonate (7.5 mmol, 1.04 g) and potassium iodide (3.3 mmol, 0.54 g) were added into a 150 mL three-neck flask, the reaction solution was heated to 80 °C and stirred for 1.5 h. Subsequently, cmpound  $3^a$  (3.3 mmol, 0.60 g) dissolved in 30 mL DMF was slowly added into the flask. The resulting solution was stirred for 20 h at 80 °C, and then cooled down at room temperature after the solvent DMF was removed under vacuum. The residue was gradually poured into 300 mL distilled water and stirred for 30 min. A fine brown precipitate was formed, filtrated, washed with water, and recrystalled from the mixed solution of absolute alcohol and chloroform (1/3, v/v) to obtain the compound  $L^a$ 

(E)-N'-(2-(2-0x0-2-(phenylamino)ethoxy)benzylidene)isonicotinohydrazide (L<sup>a</sup>) A brown powder. Yield: 74%. m.p. 196 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 11.07 (s, 1H, N=CH), 9.07 (d, *J* = 7.6 Hz, 1H, pyridine protons), 8.78 (d, *J* = 6.0 Hz, 1H, pyridine protons), 8.01 (s, 1H, NH), 7.71 (d, *J* = 7.7 Hz, 2H, pyridine protons), 7.69–7.32 (m, 6H, ArH), 7.29 (d, *J* = 8.2 Hz, 2H, ArH), 7.02(s, 1H, NH), 6.96 (d, *J* = 8.6 Hz, 1H, ArH), 4.66 (s, 2H, CH<sub>2</sub>); IR (KBr) v/cm<sup>-1</sup>: 3615, 3430, 3048, 2922, 2860, 1644, 1619, 1547,1492,1456, 1242; MS (EI) m/z (%): 392 (M+18, 2), 374 (M, 6), 328 (M–46, 8), 296 (25), 252 (100), 238 (12), 195 (25), 166 (77), 133 (52), 119 (31), 106 (87), 93 (74), 77 (93), 65 (51); Anal. Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub>: C, 67.37; H, 4.85; N, 14.96; O, 12.82. Found: C, 67.39; H, 4.82; N, 14.91.

(E)-N'-(2-(2-(4-chlorophenylamino)-2-oxoethoxy)benzylidene)isonicotinohydraz ide (L<sup>b</sup>) A brown powder. Yield: 89%. m.p. 215 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 11.10 (s, 1H, N=CH), 8.81 (s, 1H, pyridine protons), 8.70 (dd, *J* = 30.1, 9.5 Hz, 1H, pyridine protons), 8.19 (s, 1H, NH), 7.83 (t, *J* = 12.4 Hz, 2H, pyridine protons), 7.69–7.54 (m, 4H, ArH), 7.44 (d, *J* = 7.3 Hz, 1H, ArH), 7.22 (dd, *J* = 18.9, 8.5 Hz, 2H, ArH), 6.95 (dd, *J* = 15.5, 7.4 Hz, 1H, ArH), 6.80 (s, 1H, NH), 5.06 (d, *J* = 6.9 Hz, 2H, CH<sub>2</sub>); IR (KBr) v/cm<sup>-1</sup>: 3602, 3430, 3273, 3041, 2922, 2876, 1646, 1614, 1539, 1492, 1466, 1248; MS (EI) m/z (%): 409 (M+1, 2), 408 (M, 4), 374 (M-35, 6), 328

(M-35-46, 3), 296 (6), 254 (19), 240 (13), 226 (6), 195 (17), 164 (12), 149 (10), 133 (24), 120 (28), 106 (100), 93 (45), 77 (48), 65 (28); Anal. Calcd. for  $C_{21}H_{17}ClN_4O_3$ : C, 61.69; H, 4.19; Cl, 8.67; N, 13.70; O, 11.74. Found: C, 61.67; H, 4.22; Cl, 8.64; N, 13.73.

(E)-N'-(2-(2-(p-toluidino)-2-oxoethoxy)benzylidene)isonicotinohydrazide (L<sup>c</sup>) A dark brown powder. Yield: 76%. m.p. 218 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 11.16 (s, 1H, N=CH), 9.28 (s, 1H, pyridine protons), 8.39 (s, 1H, pyridine protons), 8.22 (s, 1H, NH), 7.56–7.51 (m, 2H, pyridine protons), 7.48–7.17 (m, 4H, ArH), 7.00–6.86 (m, 4H, ArH), 6.81 (s, 1H, NH), 4.88 (s, 2H, CH<sub>2</sub>), 2.29 (s, 3H, CH<sub>3</sub>); IR (KBr) v/cm<sup>-1</sup>: 3600, 3290, 3422, 3048, 2922, 2868, 1652, 1608, 1539, 1464, 1438, 1243; MS (EI) m/z (%): 389 (M+1, 2), 388 (M, 7), 374 (2), 328 (2), 296 (4), 266 (9), 254 (9), 240 (7), 226 (4), 195 (3), 162 (4), 149 (8), 133 (23), 120 (25), 106 (100), 91 (34), 78 (53), 65 (15); Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>: C, 68.03; H, 5.19; N, 14.42; O, 12.36. Found: C, 68.05; H, 5.21; N, 14.40.

(E)-N'-(2-(2-(4-methoxyphenylamino)-2-oxoethoxy)benzylidene)isonicotinohydr azide (L<sup>d</sup>) A dark brown powder. Yield: 56%. m.p. 229 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm: 11.06 (s, 1H, N=CH), 8.96 (m, 1H, pyridine protons), 8.77 (d, *J* = 5.2 Hz, 1H, pyridine protons), 8.33 (s, 1H, NH), 7.59–7.54 (m, 2H, pyridine protons), 7.45 (dd, *J* = 17.8, 8.3 Hz, 2H, ArH), 6.97–6.81 (m, 5H, ArH), 6.78 (d, *J* = 8.7 Hz, 1H, NH), 4.70 (d, *J* = 28.4 Hz, 2H, CH<sub>2</sub>), 2.91 (s, 3H, CH<sub>3</sub>); IR (KBr) v/cm<sup>-1</sup>: 3598, 3435, 3307, 3065, 2932, 2876, 1641, 1608, 1562, 1511, 1463, 1245; MS (EI) m/z (%): 422 (M+18, 2), 404 (M, 4), 374 (4), 328 (5), 296 (4), 266 (11), 254 (9), 240 (8), 226 (4), 195 (4), 162 (4), 149 (8), 133 (23), 120 (26), 106 (100), 91 (34), 78 (53), 65 (15); Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>O<sub>4</sub>: C, 65.34; H, 4.98; N, 13.85; O, 15.82. Found: C, 65.37; H, 4.50; N, 13.89.

#### 2.2.4 Preparation of the target europium complexes

To the solution of compound  $L^a$  (0.5 mmol, 0.19 g) dissolved in chloroform (30 mL), the solution of europium nitrate (5 mL, 0.1 M) in absolute alcohol was added dropwise into a 100 mL three-neck flask, the reaction solution was heated to 80 °C,

and stirred and refluxed for 4 h. Then a heavy white precipitate was formed, and filtrated, purified by washing thoroughly with chloroform several times, and dried for 6 h under vacuum to get the europium complex with ligand  $L^a$ . Other target complexes were prepared by the same method.

#### 3. Results and discussion

#### 3.1 Elemental analysis and molar conductivity of europium complexes

Analytical data for the newly synthesized europium complexes were listed in **Table 1**. Results of elemental analysis indicate that the composition of the four novel europium complexes are conformed to  $[EuL^{a-d}(NO_3)_2](NO_3) \cdot H_2O$ , ligands  $L^a-L^d$  were easily dissolved in DMSO, DMF, and slightly dissolved in chloroform, absolute alcohol, but hardly dissolved in ethylether, benzene and deionized water, while the synthesized europium complexes were only soluble in DMSO and DMF. The molar conductance values of the target complexes in acetone solution are in the range of  $106-112 \text{ S} \cdot \text{cm}^2/\text{mol}$ , which indicates that the synthesized europium complexes are conformed to a kind of 1:1 electrolytes [24].

#### 3.2 UV-vis spectral analysis

The UV-vis absorption spectra data of the free ligands  $L^a-L^d$  and their europium complexes were listed in **Table 2**, which were recorded in DMSO solution. Since the UV-vis spectra of four synthesized europium complexes are similar, only the UV-vis spectra of  $[EuL^{a,b}(NO_3)_2](NO_3)\cdot H_2O$  as well as their corresponding ligands  $L^{a,b}$  are selected, as shown in **Figs 1** and **2**, respectively.

It is apparently seen from **Figs. 1** and **2** that the UV-vis spectral shapes of the  $[EuL^{a}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  and  $[EuL^{b}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  are similar to that of the free ligand  $L^{a}$  and  $L^{b}$ , which suggests that the coordination of the europium ion does not have a significant influence on the  $\pi \rightarrow \pi^{*}$  state energy, and also reveals that the absorption of the complex is mainly attributed to the ligand. It can be seen from **Table 2** that absorb peaks appeared at 285 nm, 319 nm and 286 nm, 323 nm are assigned to the  $\pi \rightarrow \pi^{*}$  and  $n \rightarrow \pi^{*}$  transitions of  $L^{a}$  and  $L^{b}$ , respectively. Moreover, the transition absorption peaks of  $[EuL^{a}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  and  $[EuL^{b}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  compared

to the corresponding ligands  $L^a$  and  $L^b$  are red shifted, the reasons are that the introduction of  $Eu^{3+}$  ions enlarged the ligands'conjugated system, which prove that nitrogen atom of C=N group and the oxygen atom of C=O group of  $L^a$  and  $L^b$  are coordinated to the europium ion [25].

#### 3.3 Infrared radiation (IR) spectra analysis

The IR spectral data of the ligands  $L^a - L^d$  and their europium complexes were listed in **Table 3**. Since the IR spectra of four synthesized europium complexes display similar manners,only the IR spectra of  $[EuL^b(NO_3)_2](NO_3)$ ·H<sub>2</sub>O and  $[EuL^d(NO_3)_2](NO_3)$ ·H<sub>2</sub>O as well as their corresponding ligands  $L^b$  and  $L^d$  are selected, as shown in **Figs. 3** and **4**, respectively.

It is apparently seen from Table 3 and Figs. 3 and 4 that the free ligands  $L^b$  and  $L^d$ exhibit absorption bands at 1614 cm<sup>-1</sup> and 1608 cm<sup>-1</sup>, respectively, which are assigned to the v(C=N) stretching vibration of the benzene ring. While the absorption bands of their corresponding europium complexes are shifted subtlely by about 8  $cm^{-1}$ and 14 cm<sup>-1</sup> to a higher frequency compared to that of the free ligands  $L^{b}$  and  $L^{d}$ , respectively, which confirms that the nitrogen atom of the C=N group is coordinated to the europium ion successfully [25]. The absorption bands of ligands  $L^b$  and  $L^d$ located at 1646 cm<sup>-1</sup> and 1641 cm<sup>-1</sup>, respectively, which are attributed to the stretching vibration of the v(N-C=O) group. As for their corresponding europium complexes, the v(N-C=O) group stretching frequence are shifted to 1641  $\text{cm}^{-1}$  and 1635 cm<sup>-1</sup>, respectively. All these results suggest that the oxygen atom of N-C=O group is coordinated to the europium ion. The absorption bands of  $L^b$  and  $L^d$ appearing at 1240 cm<sup>-1</sup> and 1050 cm<sup>-1</sup>, respectively, attributing to the stretching vibration of the Ar-O-C group, but it does not shift obviously in the target europium complexes, indicating that the oxygen atom of Ar-O-C group is not coordinate to the europium ion. The above results reveal that the position of the characteristic IR absorption bands provides significant indications regarding bonding sites of the ligands when coordinating to the europium ion [26].

According to the data in Table 3, the characteristic frequencies of the

coordinating nitrate groups in  $[EuL^{b}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  are appeared approximately at 1479 cm<sup>-1</sup> (v<sub>1</sub>), 1388 cm<sup>-1</sup> (v<sub>4</sub>), 1094 cm<sup>-1</sup> (v<sub>2</sub>) and 835 cm<sup>-1</sup> (v<sub>3</sub>). In addition, the difference between the two strongest absorption bands of the nitrate groups (|v<sub>1</sub>-v<sub>4</sub>|) can be defined as  $\Delta v$ . It is generally believed that the  $\Delta v$  value is below 200 for the bidentate nitrate moiety, but above 200 for the monodentate nitrate moiety. While the  $\Delta v$  values of  $[EuL^{b}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  and  $[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  are about 91 cm<sup>-1</sup> and 104 cm<sup>-1</sup>, respectively, which indicates that the nitrate groups are coordinated to the europium ion as bidentate ligands [27]. Meanwhile, there are free nitrate groups in the target complexes, which are agreement with the results of the conductivity experiment, and also confirmed to the following thermal gravimetric analyses [27–30].

#### 3.4 Thermal analysis

To investigate thermal stability and details of thermal decomposition of the target europium complexes, thermal analysis was carried out and the thermogravimetric analysis data were summarized in **Table 4.** The four synthesized target complexes present similar thermal decomposition behavior, herein, only the TG-DSC curve of  $[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  were given as a representative example for illustration in detail, which are shown in **Fig. 5**.

The TG-DSC curve of [EuL<sup>c</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O were measured in the range of 20–800 °C. It can be observed from **Table 4** and **Fig. 5** that there is a little mass loss (observed value 2.40%) from 20 °C to 91 °C, that is due to the desorption of one crystal water molecular (calculated value 2.42%). Meanwhile, the weight loss at 287.1 °C and 630.7 °C was 8.35% and 16.72%, corresponding to the loss process of the external a molecules nitrate and internally two molecule nitrate of the target europium complexes, respectively, which is well corresponding with the calculated values(8.33% and 16.67%). The target europium complex presentes an exothermic peak at 475.9 °C and weight loss 51.79%, attributing to the decomposition of the free organic ligand. Further heated to 800 °C, the europium complex was completely decomposed, and the mass loss percentage is 24.58%, which is close to the calculated

values of 23.66%, corresponding to the formation of  $Eu_2O_3$ . The thermal analysis results demonstrate that the target europium complexes have high thermal stability. At the same time, the structures of the target europium complexes were further confirmed.

#### 3.5 Fluorescence properties analysis

The luminescence characteristics of the target europium complexes in the solid state were measured at room temperature under a drive voltage of 700 V, and excitation and emission slit widths were 5.0 nm. Under identical experimental conditions, the fluorescence spectra data of the synthesized europium complexes were summarized in Table 5. Since the observed fluorescence spectra of four target europium complexes are very similar, the fluorescence spectrum of [EuL<sup>d</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O is selected for illustration, and its excitation and emission spectrum are presented in Figs. 6 and 7, respectively.

It is shown in **Fig. 6** that the complex  $[\text{EuL}^{d}(\text{NO}_{3})_{2}](\text{NO}_{3})\cdot\text{H}_{2}\text{O}$  exhibits a broad band in the 320–390 nm region ( $\lambda_{\text{max}}$ =362). Therefore, the wavelength at 362 nm was used to measure the luminescence intensities of the four europium complexes. The characteristic emission spectrum (**Fig. 7**) of the target europium complex is consisted of three main bands at approximately 594 nm ( ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$ ), 620 nm ( ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$ ), 621 nm ( ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$ ). Additionally, we can see the intensity of the  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$  transition (electric dipole) is greater than that of the  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$  transition (magnetic dipole) and the former is about 3.41 times stronger than that of the latter, which suggests that europium does not lie in a centro-symmetric coordination site [25]. It can be noted that there is a narrow and sharp emission peak appearing at approximately 620 nm, which shows that the target europium complexes have good monochromaticity and the energy is efficiently transferred from the excited triplet state of the ligand to the vibrational state of the europium.

The relative luminescence intensity of europium complexes is linked to the efficiency of the intramolecular energy transfer between the triple levels of the ligand and the emitting level of the europium ion, which depends on the energy gap between

the two levels. Thus, it is easily seen from Table 5 that four synthesised europium complexes present the characteristic luminescence of europium, which indicates that the four ligands L<sup>a</sup>–L<sup>d</sup> are comparatively mild organic chelators for the absorption and transfer of energy to the europium ion. Meanwhile, the luminescence intensity of complex  $[EuL^{b}(NO_{3})_{2}](NO_{3}) \cdot H_{2}O$  is lower than that of other complexes, which is due to ligand L<sup>b</sup> having an electrophilic group (-Cl) causes the electron density of the benzene ring to decrease. At the same time, the introduction of the accepting electronic group easily results in fluorescence quenching. However, the luminescence intensity of  $[EuL^{d}(NO_{3})_{2}](NO_{3}) \cdot H_{2}O$  is better than that of other complexes. It appeares that the triplet levels of the ligand  $L^d$  are in an appropriate level of the central europium ion and cause an energy transfer from ligand to europium ion more easily. This stems from the fact that the ligand  $L^{d}$  has an activating group (-OCH<sub>3</sub>) that donates electrons to the benzene ring and enlarges the  $\pi$ -conjugated system of ligand L<sup>d</sup>. The above results further highlight that the nature of the substituted group has significant impact upon the fluorescence intensity of the target europium complexes.

#### 3.6 Fluorescence quantum yields analysis

The fluorescence quantum yields ( $\Phi_{fx}$ ) of the target europium complexes were determined by the reference method [28] using sulfuric acid solution (0.1 M) of quinine sulfate (1.0 µg/L) with a known quantum yield ( $\Phi_{fstd}$ =0.55) as standard reference at room temperature. The fluorescence quantum yields( $\Phi_{fx}$ ) were calculated using the following formula and summarized in **Table 6**.

$$\Phi_{fx} = \frac{n_x^2}{n_{std}^2} \times \frac{F_x}{F_{std}} \times \frac{A_{std}}{A_x} \times \Phi_{fstd}$$

Where,  $\Phi_{fx}$  is the fluorescence quantum yield of sample, subscripts *std* and *X* refer to the standard and the unkonwn, respectively. *n* represents the refractive indices ( $n_X=1.48$ ,  $n_{std}=1.337$ ). *F* is the area of fluorescence integral, and *A* is the absorbance at the excitation wavelength. The fluorescence spectral date of the target europium complexes were measured at room temperature in DMSO solution.

It can be seen from Table 6 that [EuL<sup>d</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O exhibits the highest quantum yield (0.522), resulting from the good p $-\pi$  conjugation, a rigid plane, and the triplet energy level of ligand L<sup>d</sup> methoxy-substituted group matches better to excite the state level of europium ion, thus the corresponding europium complex shows good light–emitting ability. By contrast,  $[EuL^{b}(NO_{3})_{2}](NO_{3}) \cdot H_{2}O$  shows the lowest quantum yield (0.308), which is attributed to the  $\pi \rightarrow \pi^*$  transition of the electron-accepting group (-Cl) substituent belongs to forbidden transition, the excited state molecules are seldom obtained. According to intramolecular charge-transfer theory [31], introduction of the para-chlorine substituent can prohibit intramolecular charge-transfer and reduce both benzene ring electron density and the conjugation of the whole molecular system; this is the reason for the lower fluorescence quantum yield of  $[EuL^{b}(NO_{3})_{2}](NO_{3}) \cdot H_{2}O$ . The above results reveal that the para-position substituent on the benzene ring has significant effect on the fluorescence quantum yields of the target europium complexes. In other words, the electron-donating group can increase the fluorescence quantum yield of the target europium complexes and electron-accepting group can decrease the fluorescence quantum yield, which is consistent with fluorescence data of the target europium complexes.

#### 3.7 Electrochemical properties analysis

Cyclic voltammetry (CV) experiments were conducted to detect the electrochemical properties of the synthesized target europium complexes. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the target europium complexes were estimated according to the electrochemical performance and the UV-vis absorption spectra [32]. The HOMO and LUMO data for the target europium complexes were obtained using equation  $E_{HOMO}=4.74+eE_{OX}$ ,  $E_{LUMO}=E_{HOMO}-Eg$ ,  $Eg=1240/\lambda_{onset}(eV)$  [24] ( $E_{OX}$  is the oxidation potential of the europium complexes;  $\lambda_{onset}$  is the maximum UV-vis absorption spectra peak starting value). Four cyclic voltammetrics were depicted in **Fig. 8** and their electrochemical data were presented in **Table 7**.

It can be seen from **Table 7** that the oxidation potential of four target europium complexes occurs in the potential range +0.656 V to +0.764 V. The Eg of four target europium complexes is between 4.715 eV and 4.751 eV. Compared with that of the complex [EuL<sup>a</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O, the oxidation potential and HOMO energy levels of the complexes [EuL<sup>c,d</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O are raise, in contrast, that of the complex [EuL<sup>b</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O drop; these phenomena are ascribed to the fact of the ligands L<sup>c,d</sup> owning electron–donating groups (–CH<sub>3</sub>, –OCH<sub>3</sub>, respectively) and ligand L<sup>b</sup> owning electron–accepting groups (–Cl). The results demonstrate that the introduction of electron–donating groups can increase both benzene ring electron density and the oxidation potential of the synthesised europium complexes, while the introduction of electron–accepting groups can reduce it. In other words, the nature of the substituent group can affect the HOMO energy levels of the target europium complexes.

#### 4. Conclusions

Four novel salicylaldehyde isonicotinoyl hydrazone derivatives and their corresponding europium complexes were prepared successfully. Fluorescence properties and fluorescence quantum yields of the target europium complexes were investigated, the results showed that the ligands  $L^a - L^d$  were an efficient sensitizer for europium luminescence, four target complexes exhibited characteristic fluorescence emissions of europium ion. The fluorescence intensity of the synthesized europium complex methoxy-substituted group was stronger than that of other complexes and presented the highest fluorescence quantum yield (0.522). The substituents' nature had pronounced effect upon the electrochemical properties of the target europium complexes. Moreover, the test results of cyclic voltammograms of the target europium complexes showed that the introduction of the electron-accepting groups tended to decrease the oxidation potential and HOMO energy levels of the target europium complexes, however, introduction of the electron-donating groups could increase the corresponding complexes oxidation potential and HOMO energy levels. In addition, the thermal analysis provided information about the high thermal stability for the target europium complexes. These results demonstrated that the synthesized target

europium complexes possessed good application prospects and theoretical research value.

5. Abbreviations	5
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UV-vis	Ultraviolet visible;
IR	infrared spectra
CV	cyclic voltammetric
НОМО	highest occupied molecular orbital;
LUMO	lowest unoccupied molecular orbital.
DMF	dimethyl formamide

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### **Tables Captions**

 Table 1 Elemental analysis and molar conductance data of the target europium

 complexes

Table 2 The UV-vis data of the target europium complexes and corresponding ligands

Table 3 The IR data of the target europium complexes and corresponding ligands

Table 4 The thermogravimetric data of the target europium complexes

Table 5 The fluorescence spectral data of the target europium complexes

Table 6 The fluorescence quantum yields of the target europium complexes

Table 7 The  $E_{HOMO}$ ,  $E_{LUMO}$  and Eg of the target europium complexes

### **Figures/Scheme Captions**

Scheme 1. Synthesis route for salicylaldehyde isonicotinoyl hydrazon derivatives
Fig. 1 UV-vis spectra of [EuL<sup>a</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O (a) and L<sup>a</sup> (b)
Fig. 2 UV-vis spectra of [EuL<sup>b</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)·H<sub>2</sub>O (a) and L<sup>b</sup> (b)

**Fig. 3** The IR spectra of  $[EuL^{b}(NO_{3})_{2}](NO_{3})$ ·H<sub>2</sub>O (a) and  $L^{b}$  (b) **Fig. 4** The IR spectra of  $[EuL^{d}(NO_{3})_{2}](NO_{3})$ ·H<sub>2</sub>O (a) and  $L^{d}$  (b)

Fig. 5 The TG-DSC curve of [EuL<sup>c</sup>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) H<sub>2</sub>O

**Fig. 6** The excitation spectrum of  $[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$ 

**Fig. 7** The emission spectrum of  $[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$ 

Fig. 8. The CV curves of the target europium complexes

### Figures



Scheme 1. Synthesis route for salicylaldehyde isonicotinoyl hydrazon derivatives



Fig. 1 UV-vis spectra of  $[EuL^a(NO_3)_2](NO_3)^{\cdot}H_2O\left(a\right)$  and  $L^a\left(b\right)$ 



Fig. 2 UV-vis spectra of  $[EuL^{b}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$  (a) and  $L^{b}$  (b)



Fig. 3 The IR spectra of  $[EuL^b(NO_3)_2](NO_3)$ ·H<sub>2</sub>O (a) and  $L^b$  (b)



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**Fig. 7** The emission spectrum of  $[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$ 



Fig. 8. The CV curves of the target europium complexes

### **Tables**

Table 1 Elemental analysis and molar conductance data of the target europium complexes

Complete	mea	$\Lambda_{\rm m}({\rm acetone})$			
Complex	С	Н	Ν	Eu	$(S.cm^2.mol^{-1})$
$[EuL^{a}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	34.48 (34.53)	2.79 (2.76)	14.39 (13.42)	20.85 (20.81)	106
$[EuL^{b}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	33.01 (32.98)	2.54 (2.50)	12.76 (12.82)	19.89 (19.87)	119
$[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	35.52 (35.50)	2.96 (2.98)	13.14 (13.17)	20.45 (20.41)	114
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	34.72 (34.75)	2.94 (2.92)	12.86 (12.89)	19.94 (19.98)	122

Complex	$\lambda_{max}$ (nm)	Ligand	$\lambda_{max}(nm)$
$[EuL^{a}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	288, 324	L <sup>a</sup>	285, 319
$[EuL^b(NO_3)_2](NO_3)\cdot H_2O$	288, 325	L <sup>b</sup>	286, 323
$[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	287, 324	L°	283, 322
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	286	$\mathbf{L}^{d}$	285

Table 2 The UV-vis data of the target europium complexes and corresponding ligands

Complex	$\nu_{NH}$	$\nu_{Ar-H}$	v <sub>Ar-C=C</sub>	$\nu_{C\!=\!N}$	$v_{N-C=0}$	$\nu_{C-O-C}$	$v_{NO3}^{-1}$
L <sup>a</sup>	3430	3048	1547, 1492	1619	1644	1242	
$[EuLa(NO_3)_2](NO_3) \cdot H_2O$	3442	3059	1551, 1497	1627	1638	1246	1474, 1383, 1039, 835
L <sup>b</sup>	3430	3041	1539, 1492	1614	1646	1248	
$[EuL^b(NO_3)_2](NO_3) \cdot H_2O$	3440	3053	1541, 1493	1622	1641	1247	1479, 1388, 1094, 835
L <sup>c</sup>	3422	3048	1539, 1464	1608	1652	1243	
$[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	3437	3062	1542, 1489	1624	1640	1246	1478, 1368, 1042, 835
$L^d$	3435	3065	1562, 1511	1608	1641	1245	
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	3444	3075	1564, 1508	1622	1635	1250	1486, 1382, 1036, 829

Table 3 The IR data of the target europium complexes and corresponding ligands

Complex	H <sub>2</sub> O (lost)(calcd)(%)	NO <sub>3</sub> (lost)(calcd)(%)	Ligand (lost)(calcd)(%)	Metal reside (calcd)(%)
ľ	(lost) (%)	(lost) (%)	(lost) (%)	(lost) (%)
[EuL <sup>a</sup> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )·H <sub>2</sub> O	2.32 (2.47)	25.45 (25.48)	51.09 (51.23)	25.05 (24.11)
$[EuL^b(NO_3)_2](NO_3)\cdot H_2O$	2.28 (2.36)	24.17 (24.35)	53.35 (53.40)	24.62 (23.07)
$[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	2.40 (2.42)	25.07 (25.00)	51.79 (52.15)	24.58 (23.66)
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	2.26 (2.37)	24.19 (24.47)	53.24 (53.16)	24.08 (23.16)

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2](Nu.5.) (1)2](NO.3)·H2O 2.5(2.37) -



Complex	) /2000	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$		${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	
Complex	$\lambda_{ex}/\Pi\Pi$	$\lambda_{em}/nm$	I/a.u.	$\lambda_{em}/nm$	I/a.u.
$[EuLa(NO_3)_2](NO_3) \cdot H_2O$	362	594.5	376.7	620.5	1259
$[EuLb(NO_3)_2](NO_3) \cdot H_2O$	362	594.5	118.2	620.5	514.6
$[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	362	594.5	725.8	620	2216
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	362	595	831.5	621	2841
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A CCC					

Table 5 The fluorescence spectral data of the target europium complexes

Complexes	λ/nm	I/a u F <sub>w</sub>	Fu	Fluorescent quantum
complexes	N <sub>ex</sub> /IIII	1/ a.u.	1 X	yield( $\Phi_{fx}$ )
[EuL <sup>a</sup> (NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )·H <sub>2</sub> O	321	1588	73656.348	0.410
$[EuLb(NO_3)_2](NO_3) \cdot H_2O$	319	1106	54112.490	0.308
$[EuLc(NO_3)_2](NO_3) \cdot H_2O$	319	1697	86966.502	0.495
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	318	1725	90160.937	0.522

Table 6 The fluorescence quantum yields of the target europium complexes

Complex	$\lambda_{onset}(nm)$	Eox (V)	E <sub>HOMO</sub> (eV)	Eg (eV)	E <sub>LUMO</sub> (eV)
$[EuLa(NO_3)_2](NO_3) \cdot H_2O$	261	0.704	5.444	4.751	0.693
$[EuLb(NO_3)_2](NO_3) \cdot H_2O$	263	0.656	5.396	4.715	0.681
$[EuL^{c}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	262	0.761	5.501	4.733	0.768
$[EuL^{d}(NO_{3})_{2}](NO_{3})\cdot H_{2}O$	262	0.764	5.504	4.733	0.771

Table 7 The  $E_{HOMO}$ ,  $E_{LUMO}$  and Eg of the target europium complexes

## **Graphical Abstract**



### **Graphical Abstract (synopsis)**

Four novel salicylaldehyde isonicotinoyl hydrazone derivatives and their corresponding europium complexes were synthesized and characterized. The results indicated that all the complexes exhibited characteristic emissions of europium ion. The relationship between the structure of ligands and luminescence intensity of the europium complexes have been discussed.

### Highlights

- Four novel europium complexes have been prepared and characterized.
- All the europium complexes exhibited characteristic emissions of europium ion.
- The luminescence intensity of the synthesised target complexes have been discussed.
- The europium complexes possessed relatively good fluorescence quantum yields.
- The electrochemical properties of the target complexes have been estimated.

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