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Novel pyrazolone derivatives and corresponding europium(III) complexes: Synthesis and properties research

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ABSTRACT

A series of pyrazolone derivatives ligands L^{1-7} were successfully synthesized and validated by ¹H NMR and MS, corresponding europium complexes $[EuL^{1-7}(NO_3)_2]NO_3$:EtOAc were synthesized. Physico-chemistry properties of title complexes were determined by Elemental analysis, Molar conductance, UV absorption spectra, IR spectra and Thermogravimetric analysis. The title complexes exhibit characteristic red fluorescence of Eu^{3+} . The effect of various substituent groups in ligands on the of title Eu^{3+} complexes is ordered: $Cl > -Br > -OCH_3 > -F > -CH_3 > -H > -NO_2$, and $[EuL^6(NO_3)_2]NO_3$:EtOAc containing Cl possesses the strongest fluorescence intensity, so does fluorescence quantum yield. The electrochemical properties indicate that energy gap Eg and LUMO energy level are huge affected by substituent groups, and variation trends of LUMO energy level affected by diverse substituent groups are also different. The prepared title europium complexes have potential application prospects in the fields of photoelectric functional materials and life sciences.

1. Introduction

In recent years, due to unique structure and properties (larger Stokes shift and higher luminescence quantum efficiency), application of rare earth elements in luminescent materials has received widespread attention [1-6]. Rare earth complexes can emit characteristic fluorescence via rare earth ions combining with appropriate organic ligands [7-10]. Especially, fluorescent materials based on rare earth organic complexes present the advantages of high fluorescence intensity, pure color, low excitation energy and high fluorescence efficiency. Rare earth organic luminescent materials, which combine the advantages of inorganic luminescent materials and organic luminescent materials, can be used in the fields of life [6,11–13], industry [14–17] and other fields with excellent fluorescence performance. However, there are still some problems that need to be overcome, like poor thermal stability, lower luminescence intensity and inferior electron transport efficiency. Therefore, design and synthesis of novel rare earth complexes with excellent luminescence properties have always been the direction of research.

Luminescence intensity of rare earth complexes strongly depends on

light absorption efficiency of organic ligands and energy transfer efficiency between ligands and rare earth ions [4,18]. Therefore, design and synthesis of appropriate ligand is the key. In our early work, many rare earth organic ligands complexes are investigated [7,19]. Due to the presence of coordination active sites (such as carbonyl on pyrazole ring) [20], pyrazolone derivatives own outstanding coordination ability. However, corresponding rare earth complexes with excellent performance have been rarely reported.

In this work, synthesis and properties of novel pyrazolone derivatives ligands and corresponding rare earth complexes are studied. 1phenyl-3-methyl-5-pyrazolone and para-substituted phenols were used as raw material, a series of novel pyrazolone derivatives ligands were synthesized by reaction of intermediate 1-phenyl-3-methyl-4-chloroacetyl-5-pyrazolone and phenoxyacetic acid derivatives, and characterized by ¹H NMR and MS. The synthetic route was shown in Scheme 1. Europium was taken as the center ion, and corresponding europium (III) complexes were prepared. Their physico-chemistry properties were explored by molar conductance, elemental analysis, UV spectra, IR spectra and thermogravimetric analysis. Fluorescence and electrochemical properties were also investigated.

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R: H; CH₃; OCH₃; NO₂; F; Cl; Br

Scheme 1. Synthesis route of 1-phenyl-3-methyl-5-pyrazolone derivatives.

2. Experimental

2.1. Materials and methods

 $\rm Eu_2O_3$ (purity 99.99%), 1-phenyl-3-methyl-5-pyrazolone (chemical pure) and other reagents (analytical pure) were commercially available.

¹H NMR was measured by using an INOVA-400 high resolution nuclear magnetic resonance spectrometer with TMS as internal standard, and $CDCl_3$ or DMSO- d_6 as solvent. Mass spectra were recorded by the MAT95XP Mass Spectrometer. Elemental analysis was determined by Flash EA 1112 Elemental Analyzer. Melting points were obtained on XT-4 binocular microscopic melting point instrument. UV absorption spectra were recorded by LabTech UV-2100 UV-visible spectrophotometer. IR spectra $(4000 \text{ cm}^{-1}-400 \text{ cm}^{-1})$ were carried out on Shimadzu IRAffinity-1 infrared spectrometer. TG-DTA curves were measured by a DTG-60 thermogravimetric analyzer with a heating rate of 20 °C·min⁻¹ under static air atmosphere. Fluorescence spectra was measured by Hitachi F-2700 fluorescence spectrometer, both excitation and emission light slits were 5.0 nm. Cyclic voltammetry curve was tested by using three-electrodes (platinum electrode, a glassy carbon electrode and a saturated calomel electrode) system, with sodium nitrate (0.1 mol·L^{-1}) as the supporting electrolyte solution, DMSO as solvent, ferrocene as external standard, sensitivity was 0.1 mA-V^{-1} and scanning speed was $0.1 \text{ V} \cdot \text{s}^{-1}$.

2.2. Synthesis method

2.2.1. Synthesis of intermediates

Synthesis of 1-phenyl-3-methyl-4-chloroacetyl-5-pyrazolone (a), 30 mmol 1-phenyl-3-methyl-5-pyrazolone was dissolved in 50 mL 1,4-dioxane at 60 °C with constant stirring, and then 90 mmol Ca(OH)₂ was added. After 3 min, stop heating, and 3 mL chloroacetyl chloride was immediate dropwise added. After another 5 min, the mixture was refluxed at 90 °C for 1 h. When mixture was cooled to room temperature, 80 mL 2.0 mol·L⁻¹ HCl was added with slow stirred. Subsequently, the mixture is allowed to stand for another 12h, pale yellow precipitation was emerged. The precipitation was filtered and washed with dilute HCl and dried at 60 °C, crude product was formed, then recrystallized twice with the ethanol-water mixed solution to yield pale yellow needle crystals. Yield 60%. ¹H NMR (CDCl₃) δ /ppm: 7.79 (d, 2H, ArH), 7.47 (t, 2H, ArH), 7.33 (t, 1H, ArH), 4.45 (s, 2H, CH₂), 2.52 (s, 3H,CH₃); MS (EI) *m/z* (%): 252 (M+2, 13), 250 (M, 38), 216 (9), 214 (16), 201 (100), 186(5), 173 (4), 143 (4), 133 (3), 104(3), 92 (5), 91 (8), 77 (12), 51 (4).

Synthesis of phenoxyacetic acid derivative (b^{1-7}) , 55 mmol monochloroacetic acid was dissolved in 15 mL deionized water under the condition of ice water bath, then 30% NaOH solution was used to adjust pH 8–9, sodium chloroacetate solution was obtained. 45 mmol

NaOH was dissolved in mixed solvent of 15 mL deionized water and 5 mL ethanol at room temperature with constant stirring, 45 mmol phenol was subsequent slowly added. After stirring for another 20 min, sodium chloroacetate solution was added. Subsequently, the mixture was refluxed at 102 °C for 5 h. After the mixture was cooled to room temperature, pH was adjusted to 1-2 with 2.0 mol·L⁻¹ HCl, amounts of white precipitations were gained. The precipitations were filtered and washed 3 times with dilute hydrochloric acid, dried at 60 °C. White crude product was dispersed in 100 mL heated deionized water, pH was adjusted to 8.0 using saturated potassium carbonate solution, then mixture solution was filtered, and filtrate was collected. White precipitated was obtained by adjusting pH of filtrate to 1-2 with $2.0 \text{ mol} \cdot \text{L}^{-1}$ HCl. After cooled down to room temperature naturally, the mixture was filtered, washed with dilute hydrochloric acid, dried overnight in vacuum, then target product (b¹) was obtained. The synthetic procedures of phenoxyacetic acid derivative (\mathbf{b}^{2-7}) were similar to that of phenoxyacetic acid (b^1) .

Phenoxyacetic acid (b¹), white powder, yield 75%. ¹H NMR (400 MHz, CDCl₃) δ /ppm: 8.83 (dd, J = 5.0, 1.5 Hz, 2H), 8.03 (dd, J = 7.5, 1.5 Hz, 2H), 7.39 (dd, J = 7.5, 5.1 Hz, 2H). MS (EI) m/z (%): 153 (M+1, 8), 152 (M, 86), 108 (8), 107 (100), 94 (26), 79 (24), 77 (87), 65 (14).

P-methyl phenoxyacetic acid (b²), white powder, yield 74%. ¹H NMR (CDCl₃) δ /ppm: 7.11 (d, J = 8.4 Hz, 2H, ArH), 6.83 (d, J = 8.4 Hz, 2H, ArH), 4.66 (s, 2H, CH₂), 2.31 (s, 3H, CH₃); MS (EI) *m/z* (%): 167 (M+1, 10), 166 (M, 100), 121 (53), 107 (53), 91 (60), 77 (38), 65 (19).

P-methoxy phenoxyacetic acid (b³), white powder, yield 75%. ¹H NMR (CDCl₃) δ /ppm: 6.90–6.84 (m, 4H, ArH), 4.64 (s, 2H, CH₂), 3.78 (s, 3H, OCH₃); MS (EI) *m/z* (%): 183 (M+1, 6), 182 (M, 56), 123 (100), 109 (16), 95 (23), 77 (11).

P-Nitro phenoxyacetic acid (b⁴), white powder, yield 72%. ¹H NMR (CDCl₃) δ /ppm: 8.24 (d, J = 9.2 Hz, 2H, ArH), 7.00 (d, J = 9.2 Hz, 2H, ArH), 4.79 (s, 2H, CH₂); MS (EI) m/z (%): 198 (M+1, 9), 197 (M, 100), 182 (15), 167 (20), 152 (83), 139 (11), 123 (33), 109 (46), 92 (31), 76 (20).

P-fluoro phenoxyacetic acid (b⁵), white powder, yield 72%. ¹H NMR (CDCl₃) δ /ppm: 7.01 (d, J = 8.0 Hz, 2H, ArH), 6.88 (d, J = 10.6 Hz, 2H, ArH), 4.67 (s, 2H, CH₂); MS (EI) m/z (%): 171 (M+1, 8), 170 (M, 100), 125 (72), 112 (35), 95 (69), 75 (22).

P-chloro phenoxyacetic acid (b⁶), white powder, yield 77%. ¹H NMR (CDCl₃) δ /ppm: 7.28 (d, J = 8.4 Hz, 2H, ArH), 6.87 (d, J = 8.8 Hz, 2H, ArH), 4.68 (s, 2H, CH₂); MS (EI) m/z (%): 188 (M+2, 32), 186 (M, 100), 141 (64), 128 (44), 111 (42), 99 (20), 75 (23).

P-bromo phenoxyacetic acid (b⁷), white powder, yield 76%. ¹H NMR (CDCl₃) δ /ppm: 7.42 (d, 2H, ArH), 6.82 (d, *J* = 8.6 Hz, 2H, ArH), 4.67 (s, 2H, CH₂); MS (EI) *m*/*z* (%): 232 (M + 1, 100), 230 (M - 1, 96), 187 (45), 185 (47), 174 (29), 172 (28), 157 (34), 155 (30), 143 (16), 75

(13).

2.2.2. Synthesis of 1-phenyl-3-methyl-5-pyrazolone derivatives (L^{1-7})

5 mmol phenoxyacetic acid and 8 mmol anhydrous K_2CO_3 were dissolved in 20 mL DMF, refluxed at 80 °C for 1 h. Then 5 mmol 1phenyl-3-methyl-4-chloroacetyl-5-pyrazolone dissolved in 20 mL DMF and a little KI were added. The mixture was refluxed at 80 °C for another 10 h. After cooled to room temperature naturally, a certain amount of distilled water was blended under constant stirring. Subsequently, dilute HCl was added, and pale yellow precipitations were emerged, then filtered and washed with distilled water, dried at 60 °C, the crude product was obtained. Finally, crude product was recrystallized from absolute ethanol and dried in vacuum at 60 °C, target compound L^1 was collected. The synthetic procedures of 1-phenyl-3methyl-5-pyrazolone derivative (L^{2-7}) were similar to that of L^1 .

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl phenoxyacetate (L¹) Reddish-brown powder, yield 70%; m.p. 74–75 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.77 (d, J = 7.7 Hz, 2H, ArH), 7.47 (t, J = 7.9 Hz, 2H, ArH), 7.37–7.30 (m, 3H, ArH), 7.01 (dd, J = 14.9, 7.1 Hz, 3H, ArH), 5.21 (s, 2H, CH₂), 4.86 (s, 2H, CH₂), 2.48 (s, 3H, CH₃). MS (EI) m/z (%):368 (M+2, 3), 367 (M+1, 24), 366 (M, 100), 245 (37), 244 (50), 231 (19), 216 (6), 202 (12), 201 (94), 186(24), 152 (12), 107 (48), 92 (4), 79 (7), 77 (18). Anal. Calcd. for C₂₀H₁₆N₂O₅: C,65.7; H, 4.95; N, 7.65. Found: C, 66.34; H, 5.37; N, 7.87.

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl-4-methyl-phenoxyacetate (L^2) Dark red powder, yield 66%; m.p. 82–84 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.75 (d, J = 7.7 Hz, 2H, ArH), 7.45 (t, J = 7.3 Hz, 2H, ArH), 7.31 (d, J = 7.1 Hz, 1H, ArH), 7.11 (d, J = 7.8 Hz, 2H, ArH), 6.88 (d, J = 7.2 Hz, 2H, ArH), 5.19 (s, 2H, CH₂), 4.81 (s, 2H, CH₂), 2.46 (s, 3H, CH₃), 2.29 (d, J = 6.0 Hz,3H, CH₃). MS (EI) m/z (%):382 (M + 2, 4), 381 (M + 1, 24), 380 (M, 91), 359 (4), 358 (15), 341 (4), 274 (9), 246 (7), 245 (57), 244 (51), 231 (15), 216 (30), 201 (100), 79 (7), 187 (25), 174 (8), 166 (17), 122 (6), 121 (59), 93 (15), 91 (54), 77 (28), 65 (12). Anal. Calcd. for C₂₀H₂₀N₂O₅: C, 66.31; H, 5.30; N, 7.76. Found: C, 68.23; H, 5.61; N, 7.95.

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl-4-

methoxy-phenoxyacetate (L³) Reddish-brown powder, yield 69%; m.p. 84–86 °C; ¹H NMR (400 MHz, CDCl₃) δ/ppm: 7.77 (d, J = 7.6 Hz, 2H, ArH), 7.46 (t, J = 7.3 Hz, 2H), 7.35–7.30 (m, 1H, ArH), 6.94 (d, J = 9.0 Hz, 2H, ArH), 6.85 (d, J = 7.9 Hz, 2H, ArH), 5.20 (s, 2H, CH₂), 4.80 (s, 2H, CH₂), 3.77 (s, 3H, CH₃), 2.48 (s, 3H, CH₃). MS (EI) *m*/z (%):398 (M+2, 4), 397 (M+1, 24), 396 (M, 100), 358 (5), 273 (7), 245 (38), 244 (29), 231 (7), 216 (16), 201 (63), 187 (15), 182 (13), 174 (8), 137 (39), 123 (26), 109 (14), 91 (14), 77 (27), 65 (5). Anal. Calcd. for C₂₁H₂₀N₂O₆: C, 63.63; H, 5.09; N, 7.07. Found: C, 65.83; H, 5.76; N, 7.81.

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl-4-nitrophenoxyacetate (L⁴) Reddish-brown powder, yield 66%; m.p. 88–90 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 8.25 (d, J = 9.2 Hz, 2H, ArH), 7.75 (d, J = 7.9 Hz, 2H, ArH), 7.46 (t, J = 7.9 Hz, 2H, ArH), 7.33 (t, J = 6.4 Hz, 1H, ArH), 7.08 (d, J = 9.2 Hz, 2H, ArH), 5.23 (s, 2H, CH₂), 4.95 (s, 2H, CH₂), 2.48 (s, 3H, CH₃). MS (EI) m/z (%): 412 (M+1, 6), 411 (M, 26), 353 (5), 244 (6), 232 (19), 214 (21), 201 (100), 197 (20), 174 (16), 152 (22), 109 (14), 92 (17), 91 (30), 77 (43), 65 (15). Anal. Calcd. for C₂₀H₁₇N₃O₇: C, 58.39; H, 4.17; N, 10.21. Found: C, 62.34; H, 4.97; N,12.55.

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl-4-fluoroylphenoxyacetate (L^5) Reddish-brown powder, yield 68%; m.p. 76–77 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.75 (d, J = 7.9 Hz, 2H, ArH), 7.46 (t, J = 7.9 Hz, 2H, ArH), 7.32 (t, J = 7.4 Hz, 1H, ArH), 7.00 (d, J = 8.1 Hz, 2H, ArH), 6.95 (d, J = 4.3 Hz, 2H, ArH), 5.20 (s, 2H, CH₂), 4.81 (s, 2H, CH₂), 2.47 (s, 3H, CH₃). MS (EI) m/z (%):386 (M + 2, 4), 385 (M + 1, 22), 384 (M, 94), 358 (3), 245 (31), 244 (29), 231 (23), 216 (13), 201 (100), 187 (26), 170 (11), 125 (52), 97 (14), 95 (34), 91 (16), 77 (29), 67 (8). Anal. Calcd. for C₂₀H₁₇N₂O₅F: C, 62.50; H, 4.46; N, 7.29. Found: C, 61.08; H, 4.87; N, 7.08.

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl-4-chlorophenylacetate (L⁶) Reddish-brown powder, yield 68%; m.p. 78–80 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.75 (d, J = 8.0 Hz, 2H, ArH), 7.46 (t, J = 7.9 Hz, 2H, ArH), 7.36–7.27 (m, 2H, ArH), 6.92 (d, J = 9.0 Hz, 2H, ArH), 5.20 (s, 2H, CH₂), 4.82 (s, 2H, CH₂), 2.47 (s, 3H, CH₃). MS (EI) m/z (%): 402 (M+2, 26), 400 (M, 75), 358 (3), 245 (36), 244 (34), 231 (28), 216 (12), 201 (100), 186 (32), 174 (8), 143 (13), 141 (35), 113 (13), 111 (22), 91 (14), 77 (26), 65 (7). Anal. Calcd. for C₂₀H₁₉N₂O₅Cl: C, 59.93; H, 4.28; N, 6.99. Found: C, 61.63; H, 5.28; N, 7.17.

2-(1-phenyl-3-methyl-5-pyrazolone-4-yl)-2-oxoethyl-4-bromo phenylacetate (L⁷) Yellow powder, yield 67%; m.p. 84–86 °C; ¹H NMR (400 MHz, CDCl₃) δ /ppm: 7.77 (d, J = 7.9 Hz, 2H, ArH), 7.50–7.40 (m, 4H, ArH), 7.35–7.31 (m, 1H, ArH), 6.88 (d, J = 7.3 Hz, 2H, ArH), 5.20 (s, 2H, CH₂), 4.83 (s, 2H, CH₂), 2.48 (s, 3H, CH₃).MS (EI) m/z (%): 446 (M + 1, 35), 444 (M – 1, 36), 358 (2), 245 (27), 244 (26), 232 (27), 201 (100), 187 (42), 185 (33), 174 (23), 157 (22), 155 (17), 143 (8), 133 (6), 105 (9), 92 (12), 91 (23), 77 (39), 65 (12). Anal. Calcd. for C₂₀H₁₉N₂O₅Br: C, 53.95; H, 3.85; N, 6.29. Found: C, 52.60; H, 4.53; N, 7.12.

Since the two-dimensional (2D) and three-dimensional (3D) structure of the ligand L^{1-7} are similar, only the structure of compound L^1 was selected and shown in Fig. 1.

2.2.3. Preparation of title complexes

 Eu_2O_3 and a certain amount of deionized water were mixed at 60 °C under constant stirring, and then concentrated nitric acid was added. When Eu_2O_3 was completely dissolved, mixture solution was evaporated at 85 °C to remove remaining nitric acid till transparent solution was formed. Subsequently, ethyl acetate was added with stirring, then the $Eu(NO_3)_3$ in ethyl acetate (EtOAc) solution was obtained. 0.2 mmol pyrazolone derivative was dissolved in 20 mL of ethyl acetate at 60 °C, 1 mL above-prepared $Eu(NO_3)_3$ ethyl acetate solution was added, pH was adjusted to 6–7 using 1 mol·L⁻¹ sodium ethoxide solution. After refluxed for 5 h and cooled to room temperature, mixture was blend into petroleum ether, the precipitations were formed, then filtered,



Fig. 1. 2D(a) and 3D(b) structure of ligand L¹.

 Table 1

 Elemental analysis and molar conductance data of title europium complexes.

Complexes	Measured Value (Theoretical Value)/%				$\Lambda_{\rm m}$	
	С	Н	Ν	Eu	$(S \cdot cm^2 \cdot mol^{-1})$	
[EuL ¹ (NO ₃) ₂] NO ₃ ·EtOAc	36.11 (36.23)	3.42 (3.27)	9.01 (8.81)	18.98 (19.23)	73	
[EuL ² (NO ₃) ₂] NO ₃ ·EtOAc	37.41 (37.17)	3.66 (3.47)	8.87 (8.67)	18.79 (18.95)	78	
[EuL ³ (NO ₃) ₂] NO ₃ ·EtOAc	36.63 (36.45)	3.74 (3.40)	8.40 (8.51)	18.22 (18.58)	80	
[EuL ⁴ (NO ₃) ₂] NO ₃ ·EtOAc	34.59 (34.37)	3.24 (2.98)	9.73 (10.02)	18.07 (18.25)	69	
[EuL ⁵ (NO ₃) ₂] NO ₃ ·EtOAc	35.70 (35.42)	3.33 (3.08)	8.36 (8.61)	18.45 (18.81)	79	
[EuL ⁶ (NO ₃) ₂] NO ₃ ·EtOAc	34.99 (34.82)	3.22 (3.02)	8.19 (8.46)	18.09 (18.49)	86	
[EuL ⁷ (NO ₃) ₂] NO ₃ ·EtOAc	33.27 (33.03)	3.05 (2.87)	7.85 (8.03)	17.23 (17.53)	82	

washed with ethyl acetate, and dried at 60 $^\circ C$, finally title europium complex was formed.

3. Results and discussion

3.1. Composition and physical property of title europium complexes

Pyrazolone derivatives ligand (L^{1-7}) are easily dissolved in chloroform, DMF and DMSO, partially in ethanol, methanol, acetone, ethyl acetate and ether, hardly in cyclohexane and petroleum ether. The title europium complexes are easily dissolved in DMF and DMSO, partially in chloroform and acetone, hardly in ethanol, methanol, toluene, cyclohexane and anhydrous ether. Elemental analysis of title europium complexes were carried out, molar conductivity (dissolved in DMF with 10^{-3} mol·L⁻¹) was also determined, and the data are listed in Table 1.

From Table 1, it can be seen that the measured value of elemental contents are coincide well with theoretical values, the mole ratio of ligand (L^{1-7}) and europium ion is 1:1, so general formula of europium complexes is $[EuL^{1-7}(NO_3)_2]NO_3$ ·EtOAc. Meanwhile, the molar conductivity of the title europium complexes were in the range of 65–90 S cm²·mol⁻¹, indicated that title europium complexes are 1:1 electrolytes. It may be explained that two nitrates are coordinated with center europium ion in title europium complex, and a free nitrate ion is existed.

3.2. UV absorption spectra analysis

UV absorption spectra of ligand compound L^{1-7} and corresponding Eu^{3+} complexes (dissolved in DMSO with $5.0 \times 10^{-5} \, \text{mol} \cdot L^{-1}$) were determined, the characteristic absorption wavelength and molar absorption coeffcient (ϵ) are listed in Table 2.

From Table 2, max absorption peaks of ligands L^{1-7} are located between 268 and 271 nm, which belong to $\pi \rightarrow \pi^*$ transition of ligand L^{1-7} . Max absorption peaks of corresponding Eu³⁺ complexes all exhibit red shift, only degrees of red shift are different. Specially, a new absorption peak of L⁴ is emerged at 309 nm, which belongs to $n \rightarrow \pi^*$ transition of C=N conjugation of ligand L⁴, and corresponding complex [EuL⁴(NO₃)₂]NO₃:EtOAc also presents a absorption peak at 313 nm with 4 nm red shift.

Because UV absorption spectra of the title complexes are similar, only UV absorption spectra of L^4 and corresponding Eu^{3+} complex were selected, and shown in Fig. 2. UV characteristic absorption peaks of ligand are exhibited in UV absorption spectra of corresponding Eu^{3+} complex, suggesting that $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition energy in ligand are not influenced by the introduced Eu^{3+} , and f-f transition of Eu^{3+} is symmetry Laporte-forbidden owing to the nature of lanthanide[21]. Due to coordination of Eu^{3+} , the lone pair electrons of

Table 2

Characteristic absorption wavelength and ϵ of ligand and corresponding Eu^{3+} complexes.

-		
Compounds	λ (nm)	ϵ (1.0 × 10 ⁴ L·mol ⁻¹ ·cm ⁻¹)
L^1	271	0.96
[EuL ¹ (NO ₃) ₂]NO ₃ ·EtOAc	273	1.15
\mathbf{L}^2	269	1.00
[EuL ² (NO ₃) ₂]NO ₃ ·EtOAc	271	1.26
L^3	268	1.35
[EuL ³ (NO ₃) ₂]NO ₃ ·EtOAc	271	1.43
\mathbf{L}^{4}	271,309	1.02,0.74
[EuL ⁴ (NO ₃) ₂]NO ₃ ·EtOAc	276,313	1.26,0.78
L ⁵	271	1.24
[EuL ⁵ (NO ₃) ₂]NO ₃ ·EtOAc	274	1.38
L ⁶	271	1.40
[EuL ⁶ (NO ₃) ₂]NO ₃ ·EtOAc	272	1.52
L ⁷	270	1.49
[EuL ⁷ (NO ₃) ₂]NO ₃ ·EtOAc	274	1.55



Fig. 2. UV absorption spectra of [EuL⁴ (NO₃)₂]NO₃·EtOAc (a) and L⁴ (b).

oxygen atom in C=O group of ligand may be shifted, and introduced Eu³⁺ increase electron delocalization of the conjugated system, decrease corresponding electron transition energy, and improve the energy absorption and transition of complex, a red shift phenomenon of $\pi \rightarrow \pi^*$ absorption peak can be observed in Eu³⁺ complex. The molar absorption coeffcient ε of all ligands and complexes are $(0.9-1.6) \times 10^4$. Compared with ligand L¹⁻⁷, molar absorption coeffcient of $[\text{EuL}^{1-7}(\text{NO}_3)_2]\text{NO}_3$:EtOAc is changed. These results indicated that ligand L¹⁻⁷ was coordinated to Eu³⁺ successfully. Meanwhile, title Eu³⁺ complexes own good UV light absorption ability, and it is better for well fluorescence properties.

3.3. Infrared spectra analysis

IR spectra data of ligand L^{1-7} and corresponding complexes $[EuL^{1-7}(NO_3)_2]NO_3$:EtOAc are shown in Table 3. Because IR spectra of the title complexes are similar, only IR spectra of L^6 and corresponding Eu^{3+} complex $[EuL^2(NO_3)_2]NO_3$:EtOAc were selected and shown in Fig. 3.

From Table 3 and Fig. 3, it can be seen that L^6 exhibits three absorption peaks of benzene ring at 3043 cm^{-1} , 1454 cm^{-1} and 757 cm^{-1} . The absorption peaks at 1713 cm^{-1} and 1666 cm^{-1} are assigned to ν (C=O) of acyl group and ester group, respectively. The ν (C=N) of L^6 is located at 1593 cm^{-1} , characteristic absorption peak of ether bond ν (Ar-O-C) appeared at 1248 cm^{-1} and the ν (C-O-C) at 1173 cm^{-1} . The analysis results confirm the structure of ligand L^6 .

Table 3

IR data of ligand and corresponding complexes (cm^{-1}).

compounds	ν/О-Н	$\nu/C = O$	$\nu/C = N$	v/Ar-O-C	v/C-O-C	v/NO ₃ ⁻
L^1	-	1711,1665	1595	1250	1172	
[EuL1(NO3)2]NO3 EtOAc	3418	1695,1622	1593	1250	1176	1495,1360,1029,835,1385
L^2	-	1714,1669	1594	1250	1173	
[EuL ² (NO ₃) ₂]NO ₃ ·EtOAc	3419	1699,1622	1594	1254	1173	1496,1360,1029,835,1385
L^3	-	1719,1669	1594	1241	1184	
[EuL ³ (NO ₃) ₂]NO ₃ ·EtOAc	3419	1693,1631	1593	1242	1180	1496,1361,1029,835,1385
\mathbf{L}^4	-	1718,1665	1593	1236	1175	
[EuL4(NO3)2]NO3 EtOAc	3419	1702,1623	1594	1238	1175	1497,1363,1027,834,1385
L^5	-	1713,1668	1595	1252	1172	
[EuL ⁵ (NO ₃) ₂]NO ₃ ·EtOAc	3422	1689,1622	1595	1251	1173	1504,1357,1029,835,1385
Γ_{0}^{0}	-	1713,1666	1593	1248	1173	
[EuL ⁶ (NO ₃) ₂]NO ₃ ·EtOAc	3416	1700,1625	1594	1245	1173	1493,1358,1028,836,1385
L ⁷	-	1713,1669	1594	1234	1276	
[EuL ⁷ (NO ₃) ₂]NO ₃ ·EtOAc	3413	1700,1623	1594	1233	1275	1496,1340,1029,834,1385



Fig. 3. IR spectra of [EuL⁶(NO₃)₂]NO₃·EtOAc(a) and L⁶(b).

When ligand L^6 is combined with Eu^{3+} , complex $[EuL^2(NO_3)_2]$ NO₃:EtOAc exhibits a broad absorption peak at 3416 cm⁻¹, assigned to the ν (O-H) stretching vibration of enol-type hydroxyl group on the pyrazolone ring, it is indicated that the structure of pyrazolone ring may be affected. In addition, the ν (C=O) of acyl group and ester group in ligand L^6 are red shifted to 1700 cm⁻¹ and 1625 cm⁻¹, respectively, with 13 cm⁻¹ and 41 cm⁻¹ shift. It may be explained that when oxygen atom of C=O group coordinated to the Eu³⁺ ions, the electron on the C=O bonds moved toward europium ions and bond force constant was changed, so the vibration absorption peak of carbonyl group presents an obvious shift. It is also confirmed that the two oxygen atoms in C=O of the acyl group and ester group both are coordinated with Eu³⁺. Besides, the antisymmetric stretching vibration (ν_{as}) and symmetrical stretching vibration (ν_s) of NO₃⁻ are located at 1493 cm⁻¹ and 1358 cm⁻¹, the difference of vibration frequency $|\nu_{as}-\nu_s|$ is less than

Thermal analysis data of title Eu³⁺ complexes

200 cm⁻¹ (135 cm⁻¹), indicated that nitrate groups are coordinated to europium ions as bidentate ligands. The Eu³⁺ complexes own characteristic absorption peaks of nitrate groups with a strong absorption peak at 1385 cm⁻¹, implied that complexes own free nitrate groups. The ν (C=N), ν (Ar-O-C) and ν (C-O-C) in the pyrazolone ring is not changed significantly, suggested that C=N, Ar-O-C and C-O-C were not combined with Eu³⁺. The results confirm that ligand L⁶ was coordinated to Eu³⁺ successfully, which is consistent with the results of above analysis.

3.4. Thermal analysis

Thermal analysis is used to investigate thermal stability and decomposition process of title complexes, corresponding data are listed in Table 4. Because thermal behaviors of the title complexes are similar, only TG-DTA curve (Fig. 4) of $[EuL^3(NO_3)_2]NO_3$ ·EtOAc is selected for explanation.

From Table 4 and Fig. 4, [EuL³(NO₃)₂]NO₃·EtOAc presents 10.50% weight loss in the range of 60-180 °C with a small endothermic peak at 73 °C, which may be due to the loss of the ethyl acetate in complex, and this value is consistent with corresponding theoretical calculated weight loss of 10.70%. A major weight loss of 46.27% in the range of 210-420 °C with three exothermic peaks at 246 °C, 297 °Cand 380 °C, is assigned to the decomposition of ligand L³ (theoretical calculated content of 48.71%). Then a moderate weight loss of 7.41% among 420-520 °C with an exothermic peak at 448 °C, is attributed to decomposition of free nitrate ion (theoretical calculated content of 7.53%). Between 550 °C and 680 °C, 12.22% weight was lost with a exothermic peak at 630 °C, because of the decomposition of two coordination nitrates (theoretical calculated content of 15.07%). Beyond 680 °C, TG curve is basically horizontal, indicated that $[EuL^{3}(NO_{3})_{2}]$ NO3:EtOAc has been decomposed completely with 22.34% residual of Eu₂O₃ (theoretical value of 21.49%). The TG-DTA analysis results indicate that the title Eu³⁺ complexes own good thermal stability, and further validate the composition of title Eu³⁺ complexes, which are consistent with the above analysis results.

Complexes	Endothermic peak °C	Exothermic peak °C	Residual weight (theoretical value) °C
[EuL ¹ (NO ₃) ₂]NO ₃ ·EtOAc	65	246, 290, 378, 438	23.23 (22.25)
[EuL ² (NO ₃) ₂]NO ₃ ·EtOAc	75	259, 302, 385, 445	24.32 (21.92)
[EuL ³ (NO ₃) ₂]NO ₃ ·EtOAc	73	246, 297,380, 448	22.37 (21.49)
[EuL ⁴ (NO ₃) ₂]NO ₃ ·EtOAc	76	239, 293, 386, 444	22.73 (21.11)
[EuL ⁵ (NO ₃) ₂]NO ₃ ·EtOAc	75	240, 287, 375, 435	23.36 (21.76)
[EuL ⁶ (NO ₃) ₂]NO ₃ ·EtOAc	84	252, 366, 422, 620	23.46 (21.39)
[EuL ⁷ (NO ₃) ₂]NO ₃ ·EtOAc	80	254, 395, 448, 646	22.26 (20.29)



Fig. 4. TG-DTA curve of [EuL³(NO₃)₂]NO₃·EtOAc.

3.5. Possible structure of title europium complexes

According to above discussion, the title Eu^{3+} complexes own similar structure, their two-dimensional and three-dimensional structure are simulated and shown in Fig. 5.

3.6. Fluorescence properties

Fluorescence spectra of title europium complexes are measured, corresponding data are listed in Table 5. Because fluorescence spectra of the title complexes are similar, only spectra of $[EuL^6(NO_3)_2]$ NO₃·EtOAc was selected for illustration, shown in Fig. 6.

The fluorescence emission spectra of the title complexes [EuL¹⁻⁷(NO₃)₂]NO₃·EtOAc present the characteristic red fluorescence of central ion Eu^{3+} . Emission peaks at ~595 nm and ~620 nm, are assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (magnetic dipole transition) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (electric dipole transition), respectively. Emission peak at ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is sharp, corresponding peak width at half height is less than 10 nm, indicated that the title europium complexes own good monochromaticity [22]. Besides, the intensity at \sim 620 nm is strong, it may be because that the free ligand triplet energy level and Eu³⁺ resonance emission energy level are highly matched, accordingly, superior energy transfer efficiency is achieved between ligands and rare earth ions. Optimal excitation wavelength of [EuL⁶(NO₃)₂]NO₃·EtOAc is 357 nm. The fluorescence intensity ratio $\eta({}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1})$ is 3.65, indicated that Eu^{3+} is not located on the symmetric center of complexes [23]. Compared with [EuL¹(NO₃)₂]NO₃·EtOAc, fluorescence intensity of europium complex [EuL^{2,3}(NO₃)₂]NO₃·EtOAc, which contain electron-donating substituent (-CH₃ or -OCH₃), is significantly enhanced, this is because the electron cloud density of π bond system in ligand can be increased by introduction of electron donating groups, meanwhile, coordination capacity toward europium ion is also enhanced. On the other hand, the triplet energy level of $L^{2,3}$ is better

Table 5Fluorescence spectra data of the title complexes.

Complexes	λ _{ex} (nm)	I (a.u.)	$^5D_0 {\rightarrow} ^7F_1$		${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	
			λ _{em} (nm)	I (a.u.)	λ_{em} (nm)	I (a.u.)
[EuL ¹ (NO ₃) ₂] NO ₃ ·EtOAc	356	180	596	158	620	638
[EuL ² (NO ₃) ₂] NO ₃ ·EtOAc	356	256	594	174	619	788
[EuL ³ (NO ₃) ₂] NO ₂ ·EtOAc	356	624	595	484	620	1690
[EuL ⁴ (NO ₃) ₂] NO ₃ ·EtOAc	357	67	595	70	620	258
[EuL ⁵ (NO ₃) ₂] NO ₂ ·EtOAc	355	344	394	228	619	894
[EuL ⁶ (NO ₃) ₂] NO ₂ ·EtOAc	357	717	595	514	620	1876
[EuL ⁷ (NO ₃) ₂] NO ₃ ·EtOAc	356	678	595	548	620	1732



Fig. 6. Excitation spectra (a) and emission spectra (b) of $[{\rm EuL}^6({\rm NO}_3)_2]$ ${\rm NO}_3{:}{\rm EtOAc}.$

match to resonance emission energy level of Eu³⁺ with superior energy transfer efficiency. Therefore, complex [EuL^{2,3}(NO₃)₂]NO₃:EtOAc own stronger fluorescence intensity compared to [EuL¹(NO₃)₂]NO₃:EtOAc. Further, fluorescence intensity of [EuL³(NO₃)₂]NO₃:EtOAc is stronger than [EuL²(NO₃)₂]NO₃:EtOAc, it may be attributed to that -OCH₃ owns more powerful electron donating ability. [EuL⁴(NO₃)₂]NO₃:EtOAc, which contains electron-withdrawing groups (-NO₂), presents the smallest fluorescence intensity (258). It may be indicated that -NO₂ can reduce the electron cloud density of π bond system in ligand L⁴, weaken corresponding coordination ability, enlarge the variable between triplet energy level of L⁴ and resonance emission energy level of Eu³⁺. However, fluorescence intensity of [EuL⁵⁻⁷(NO₃)₂]NO₃:EtOAc, which



Fig. 5. Simulated schematic structure of [EuL¹⁻⁷(NO₃)₂]NO₃·EtOAc.

contains halogen groups, is stronger than $[EuL^{1}(NO_{3})_{2}]NO_{3}$:EtOAc. Halogen atoms own both conjugation effect and induced effect, and the conjugation effect may plays a dominate role, which enhance π bond of ligand L^{5-7} and molecular planarity, so coordination capacity of L^{5-7} is also improved. In addition, introduction of halogen accelerates energy level matching between ligand and center ion Eu^{3+} . So $[EuL^{5-7}(NO_{3})_{2}]NO_{3}$:EtOAc exhibit stronger fluorescence intensity. $[EuL^{6}(NO_{3})_{2}]NO_{3}$:EtOAc (which contains Cl atoms) exhibits the strongest fluorescence intensity. Due to heavy atom effect of halogen, fluorescence quenching may be caused, therefore, fluorescence intensity of $[EuL^{7}(NO_{3})_{2}]NO_{3}$:EtOAc is slightly weaken. It can be concluded that ligand L^{6} achieve more efficient energy transfer, and corresponding complex $[EuL^{6}(NO_{3})_{2}]NO_{3}$:EtOAc owns finest fluorescence property.

3.7. Fluorescence quantum yield

Fluorescence quantum yield is measured according to the proposed measure [24] and calculated by the following equation.

$$\Phi_{\mathrm{fx}} = \frac{n_{\mathrm{x}}^2}{n_{\mathrm{std}}^2} \cdot \frac{F_{\mathrm{x}}}{F_{\mathrm{std}}} \cdot \frac{A_{\mathrm{std}}}{A_{\mathrm{x}}} \cdot \Phi_{\mathrm{fstd}}$$

where Φ_{fx} represents fluorescence quantum yields, n_{std} (1.337) and n_x (1.480) are refractive index of the solution for sample and standard, solvent is DMSO, F is fluorescence integral area and A is UV absorbance, A_{std}/A_x is 1, Φ_{fstd} (0.55) is fluorescence quantum yield of the standard solution. The fluorescence quantum yields of the title complexes are listed in Table 6.

the order of hubrescence intensity. So it may be concluded that the complexes, which contain electron-donating substituent (like $-CH_3$ or $-OCH_3$) or halogen groups (like Cl), are benefit for the fluorescence property of complexes. The negative effect may be brought by introducing electron-withdrawing groups (like $-NO_2$) to ligand. Owing to the heavy atom effect of halogen groups, appropriate halogen should be adopted. In addition, the triplet energy level of ligand should well match to the resonance emission energy level of rare ions with superior energy transfer efficiency. In as-prepared complexes, $[Eu(NO_3)_2L^6]$ NO₃·EtOAc own the highest fluorescence quantum yield, namely the finest fluorescence property.

3.8. Electrochemical properties

Electrochemical properties of title complexes are investigated by means of a cyclic voltammetric technique in DMSO solution at electrochemical workstation. The HOMO energy level can be calculated according to equation $E_{HOMO} = -(4.74 \text{ eV} + E_{ox})$, E_{ox} represents the starting value of oxidation potential peak, ferrocene is used as external standard. LUMO energy level can be obtained by $E_{LUMO} = E_{HOMO} + E_{g}$, E_{g} is energy gap and calculated via $E_{g} = 1240/\lambda_{onset}$ (eV), λ_{onset} is

Table 6

Fluorescence quantum yield of title europium complex.

Complexes	λ_{ex} (nm)	I (a.u.)	Φ_{fx}
[EuL1(NO3)2]NO3·EtOAc	343	272	0.096
[EuL ² (NO ₃) ₂]NO ₃ ·EtOAc	346	328	0.136
[EuL ³ (NO ₃) ₂]NO ₃ ·EtOAc	342	416	0.184
[EuL ⁴ (NO ₃) ₂]NO ₃ ·EtOAc	339	116	0.064
[EuL ⁵ (NO ₃) ₂]NO ₃ ·EtOAc	345	336	0.144
[EuL ⁶ (NO ₃) ₂]NO ₃ ·EtOAc	347	448	0.208
[EuL ⁷ (NO ₃) ₂]NO ₃ ·EtOAc	348	364	0.160

maximum UV absorption peak [25–27]. The electrochemical data of complexes $[EuL^{1-7}(NO_3)_2]NO_3$ -EtOAc are listed in Table 7.

From Table 7, E_{ox} of complexes [EuL¹⁻⁷(NO₃)₂]NO₃·EtOAc are between 0.683 V and 0.696 V. Due to the effect of electron-donating groups (like -CH₃ and -OCH₃) in $L^{2,3}$, electron cloud density of $L^{2,3}$ are enhanced. When $L^{2,3}$ are coordinated to europium ions, corresponding oxidation potential Eox is increased, HOMO energy level is decreased, however, the LUMO energy level is increased. When electron-withdrawing substituent is introduced in L^4 , the E_{ox} of $[EuL^4(NO_3)_2]$ NO₃·EtOAc is lower than [EuL^{2,3}(NO₃)₂]NO₃·EtOAc, but bigger than [EuL¹(NO₃)₂]NO₃:EtOAc. HOMO energy level and LUMO energy level of [EuL⁴(NO₃)₂]NO₃:EtOAc are both decreased compared to [EuL¹(NO₃)₂]NO₃·EtOAc. It may be owing to the effect of electronwithdrawing substituent (-NO2), electron cloud density on benzene ring are weakened, and corresponding complex [EuL⁴(NO₃)₂]NO₃·EtOAc is hard to lose electrons, as a result, HOMO energy level and LUMO energy level are decreased. E_{ox} of [EuL⁶(NO₃)₂]NO₃·EtOAc is the smallest among [EuL^{5,6,7}(NO₃)₂]NO₃ EtOAc, which contain halogen group.

As is well known, fluorescence property of title complexes strongly depends on light absorption efficiency and energy transfer efficiency between ligands (L^{1-7}) and center ions (Eu^{3+}) . According to the aboveobtained results, the UV light absorption efficiencies of [EuL^{2,4,5}(NO₃)₂] NO₃ EtOAc are similar, however, the fluorescence property are greatly different due to the various substituent groups in ligands $L^{2,4,5}$. The complex [EuL⁶(NO₃)₂]NO₃ EtOAc owns excellent UV light absorption efficiencies among the title complexes, corresponding fluorescence property is finest, which validate that both light absorption efficiency and energy transfer efficiency are significant for fluorescence property of the title complexes, and it also can be deduced that the energy level of ligand L^6 best match with Eu^{3+} . Besides, it also can be seen that HUMO energy levels of the title europium complexes present negligible difference, corresponding energy gap E_g and LUMO energy level are significantly affected by substituent groups. From electrochemical results it can be concluded that electron-donating group can increase LUMO energy level, electron-withdrawing groups can reduce the LUMO energy level.

4. Conclusions

A series of novel pyrazolone derivatives were synthesized and characterized by ¹H NMR and MS. The corresponding europium (III) complexes were also prepared and characterized by elemental analysis, molar conductance, UV absorption spectra, IR spectra and thermogravimetric analysis. The general formula of europium complexes is $[EuL^{1-7}(NO_3)_2]NO_3$:EtOAc.

All the europium complexes exhibit characteristic red fluorescence of central ion Eu³⁺ with good thermal stability. The effect of various substituent groups in ligands on the of title complexes is ordered using fluorescence property as standard: Cl > -Br > -OCH₃ > -F > -CH₃ > -H > -NO₂, so [EuL⁶(NO₃)₂]NO₃·EtOAc possesses the strongest fluorescence intensity and fluorescence quantum yield Φ_{fx} due to excellent UV light absorption efficiency and energy transfer efficiency. Besides, electron-donating substituent groups can increase the LUMO energy level of title complexes, however, electron-withdrawing substituent groups reduce the LUMO energy level. Due to the double-edged effect of halogen groups, appropriate halogen should be adopted, in our work, [EuL⁶(NO₃)₂]NO₃·EtOAc owns the best performance.

The title europium complexes have widely application prospects in the fields of photoelectric functional materials and life sciences. As the superb coordination ability in pyrazolone derivatives, synthesis of various rare earth organic luminescent materials other than Eu can be achieved, and different colors of fluorescent material with excellent properties can be investigated. Wide material opportunities can also be provided for studying appropriate substituent group to exhibit optimal luminescent behaviors.

Electrochemical data of the title complexes.

Complexes	λ _{onset} (nm)	E _{ox} (V)	E _g (eV)	E _{HOMO} (eV)	E _{LUMO} (eV)
$[EuL^{1}(NO_{3})_{2}]NO_{3}EtOAc$ $[EuL^{2}(NO_{3})_{2}]NO_{3}EtOAc$ $[EuL^{3}(NO_{3})_{2}]NO_{3}EtOAc$ $[EuL^{4}(NO_{3})_{2}]NO_{3}EtOAc$ $[EuL^{5}(NO_{3})_{2}]NO_{3}EtOAc$ $[EuL^{5}(NO_{3})_{2}]NO_{3}EtOAc$	273 271 271 276 274 272	0.685 0.696 0.696 0.693 0.687 0.683	4.542 4.576 4.576 4.493 4.526 4.559	- 5.425 - 5.436 - 5.436 - 5.435 - 5.427 - 5.423	-0.883 -0.860 -0.860 -0.942 -0.901 -0.864
[EuL7(NO3)2]NO3EtOAc	274	0.685	4.526	- 5.425	-0.899

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References

- [1] Liang S, Shang M, Lian H, Li K, Zhang Y, Lin J. An efficient rare-earth free deep red emitting phosphor for improving the color rendering of white light-emitting diodes. J Mater Chem C 2017;5(11):2927–35. http://dx.doi.org/10.1039/C6TC05499D.
- [2] Zhong Y, Ma Z, Zhu S, Yue J, Zhang M, Antaris AL, et al. Boosting the down-shifting luminescence of rare-earth nanocrystals for biological imaging beyond 1500 nm. Nat Commun 2017;8(1):1–7. http://dx.doi.org/10.1038/s41467-017-00917-6.
- [3] Mahata P, Mondal SK, Singha DK, Majee P. Luminescent rare-earth-based MOFs as optical sensors. Dalton Trans 2017;46(2):301–28. http://dx.doi.org/10.1039/ C6DT03419E.
- [4] Einkauf JD, Clark JM, Paulive A, Tanner GP, De Lill DT. A general model of sensitized luminescence in lanthanide-based coordination polymers and metal-organic framework materials. Inorg Chem 2017;56(10):5544–52. http://dx.doi.org/10. 1021/acs.inorgchem.6b02838.
- [5] Zhu H, Chen X, Jin LM, Wang QJ, Wang F, Yu SF. Amplified spontaneous emission and lasing from lanthanide-doped up-conversion nanocrystals. ACS Nano 2013;7(12):11420–6. http://dx.doi.org/10.1021/nn405387t.
- [6] Liu Y, Ai K, Liu J, Yuan Q, He Y, Lu L. A high-performance ytterbium-based nanoparticulate contrast agent for in vivo X-ray computed tomography imaging. Angew Chem Int Ed 2012;51(6):1437–42. http://dx.doi.org/10.1002/anie. 201106686.
- [7] Zhang W, He W, Guo X, Chen Y, Wu L, Guo D. Synthesis and luminescence properties of 1,3,4-oxadiazole acetamide derivatives and their rare earth complexes. J Alloy Comp 2015;620(3):383–9. http://dx.doi.org/10.1016/j.jallcom.2014.09.153.
- [8] Li P, Yang D, Li H. Luminescence ethylenediamine sensor based on terbium complexes entrapment. Dyes Pigments 2016;132:306–9. http://dx.doi.org/10.1016/j. dyepig.2016.05.013.
- [9] Ghosh S, Abbas Z, Dasari S, Patra AK. Luminescent Eu³⁺ and Tb³⁺ complexes of 4aminophenyl terpyridine (ptpy): photophysical aspects, DNA and serum protein binding properties. J Lumin 2017;187:46–52. http://dx.doi.org/10.1016/j.jlumin. 2017.02.063.
- [10] Busschaert N, Caltagirone C, Van Rossom W, Gale PA. Applications of supramolecular anion recognition. Chem Rev 2015;115(15):8038–155. http://dx.doi.org/10. 1021/acs.chemrev.5b00099.

- [11] Nishioka T, Yuan J, Yamamoto Y, Sumitomo K, Wang Z, Hashino K, et al. New luminescent europium(III) chelates for DNA labeling. Inorg Chem 2006;45(10):4088–96. http://dx.doi.org/10.1021/ic051276g.
- [12] Schäferling M, Wolfbeis OS. Europium tetracycline as a luminescent probe for nucleoside phosphates and its application to the determination of kinase activity. Chem Eur J 2007;13(15):4342–9. http://dx.doi.org/10.1002/chem.200601509.
- [13] Fang L, Chen S, Fang T, Fang J, Lu C, Xu Z. Shape-memory polymer composites selectively triggered by near-infrared light of two certain wavelengths and their applications at macro-/microscale. Compos Sci Technol 2017;138:106–16. http:// dx.doi.org/10.1016/j.compscitech.2016.11.018.
- [14] Jinnai K, Kabe R, Adachi C. A near-infrared organic light-emitting diode based on an Yb(iii) complex synthesized by vacuum co-deposition. Chem Commun 2017;53(39):5457–60. http://dx.doi.org/10.1039/C7CC01580A.
- [15] Wei N, Zuo R-X, Zhang Y-Y, Han Z-B, Gu X-J. Robust high-connected rare-earth MOFs as efficient heterogeneous catalysts for CO₂ conversion. Chem Commun 2017;53(22):3224–7. http://dx.doi.org/10.1039/C7CC00363C.
- [16] Zhao B, Zhang H, Miao Y, Wang Z, Gao L, Wang H, et al. Low turn-on voltage and low roll-off rare earth europium complex-based organic light-emitting diodes with exciplex as the host. J Mater Chem C 2017;5(46):12182–8. http://dx.doi.org/10. 1039/C7TC03694A.
- [17] Jou J-H, Lin Y-X, Peng S-H, Li C-J, Yang Y-M, Chin C-L, et al. Highly efficient yellow organic light emitting diode with a novel wet- and dry-process feasible iridium complex emitter. Adv Funct Mater 2014;24(4):555–62. http://dx.doi.org/10.1002/ adfm.201302013.
- [18] Latva M, Takalo H, Mukkala V-M, Matachescu C, Rodríguez-Ubis J-C, Kankare J. Correlation between the lowest triplet state energy level of the ligand and lanthanide(III) luminescence quantum yield. J Lumin 1997;75(2):149–69. http://dx.doi. org/10.1016/S0022-2313(97)00113-0.
- [19] Shan W, Liu F, Liu J, Chen Y, Yang Z, Guo D. Synthesis and luminescence properties of salicylaldehyde isonicotinoyl hydrazone derivatives and their europium complexes. J Inorg Biochem 2015;150(4):100–7. http://dx.doi.org/10.1016/j. jinorgbio.2015.04.007.
- [20] Dai M, Xiao H, Ye C, Shu D, Shi L, Guo D. Synthesis and luminescence properties of terbium complexes based on 4-acyl pyrazolone derivatives. J Lumin 2017;188:223–9. http://dx.doi.org/10.1016/j.jlumin.2017.04.018.
- [21] Bünzli J-CG, Piguet C. Taking advantage of luminescent lanthanide ions. Chem Soc Rev 2005;34(12):1048. http://dx.doi.org/10.1039/b406082m.
- [22] Xu H, Sun Q, An Z, Wei Y, Liu X. Electroluminescence from europium(III) complexes. Coord Chem Rev 2015;293-294:228–49. http://dx.doi.org/10.1016/j.ccr. 2015.02.018.
- [23] Barbara PF, Rentzepis PM, Brus LE. Photochemical kinetics of salicylidenaniline. J Am Chem Soc 1980;102(8):2786–91. http://dx.doi.org/10.1021/ja00528a045.
- [24] Ci Y, Ji X. Determination of relative fluorescence quantum yields using a simplified method. Chin J Anal Chem 1986;14:616–8.
- [25] Ding B-D, Zhang J-M, Zhu W-Q, Zhen X-Y, Wu Y-Z, Jiang X-Y, et al. Fast and convenient determination of HOMO energy level of organic eletroluminescent material using electrochemistry method. Chem. Res. Appl 2002;14(6):712–4.
- [26] Wang D, Wang X, He Q, Zhou M, Rui W, Tao X, et al. Enhanced two-photon absorption of novel four-branched chromophore via vibronic coupling. Tetrahedron Lett 2008;49(41):5871–6. http://dx.doi.org/10.1016/j.tetlet.2008.07.116.
- [27] Bard A-J, Memming R, Miller B. Terminology in semiconductor electrochemistry and photoelectrochemical energy conversion. IUPAC 1991;63:569–96.