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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 $\mathbf{L^{1-7}}$ were successfully synthesized and validated by ^{1}H NMR and MS, corresponding europium complexes [Eu$L^{1-7}(NO_3)_2$]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 [Eu$L^6(NO_3)_2$]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. 1-phenyl-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 ^{1}H 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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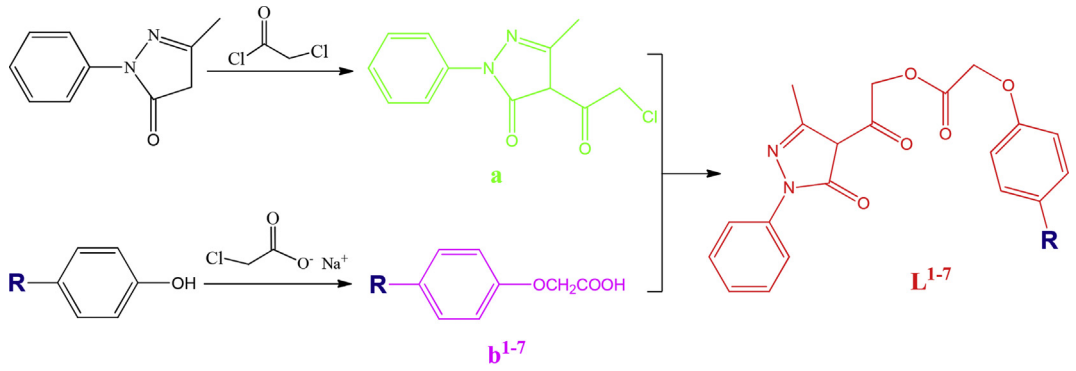

Scheme 1. Synthesis route of 1-phenyl-3-methyl-5-pyrazolone derivatives.

2. Experimental

2.1. Materials and methods

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 cm^{-1}-400 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 V·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 12 h, 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 ($CDCl_3$) δ/ppm: 7.79 (d, 2H, ArH), 7.47 (t, 2H, ArH), 7.33 (t, 1H, ArH), 4.45 (s, 2H, CH_2), 2.52 (s, 3H,CH_3); 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 mol·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 (b^1) was obtained. The synthetic procedures of phenoxyacetic acid derivative (b^{2-7}) were similar to that of phenoxyacetic acid (b^1).

Phenoxyacetic acid (b^1), white powder, yield 75%. ^1H NMR (400 MHz, $CDCl_3$) 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 (b^2), white powder, yield 74%. ^1H NMR ($CDCl_3$) δ/ppm: 7.11 (d, J = 8.4 Hz, 2H, ArH), 6.83 (d, J = 8.4 Hz, 2H, ArH), 4.66 (s, 2H, CH_2), 2.31 (s, 3H, CH_3); 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 (b^3), white powder, yield 75%. ^1H NMR ($CDCl_3$) δ/ppm: 6.90–6.84 (m, 4H, ArH), 4.64 (s, 2H, CH_2), 3.78 (s, 3H, OCH_3); MS (EI) *m/z* (%): 183 (M + 1, 6), 182 (M, 56), 123 (100), 109 (16), 95 (23), 77 (11).

P-Nitro phenoxyacetic acid (b^4), white powder, yield 72%. ^1H NMR ($CDCl_3$) δ/ppm: 8.24 (d, J = 9.2 Hz, 2H, ArH), 7.00 (d, J = 9.2 Hz, 2H, ArH), 4.79 (s, 2H, CH_2); 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 (b^5), white powder, yield 72%. ^1H NMR ($CDCl_3$) δ/ppm: 7.01 (d, J = 8.0 Hz, 2H, ArH), 6.88 (d, J = 10.6 Hz, 2H, ArH), 4.67 (s, 2H, CH_2); MS (EI) *m/z* (%): 171 (M + 1, 8), 170 (M, 100), 125 (72), 112 (35), 95 (69), 75 (22).

P-chloro phenoxyacetic acid (b^6), white powder, yield 77%. ^1H NMR ($CDCl_3$) δ/ppm: 7.28 (d, J = 8.4 Hz, 2H, ArH), 6.87 (d, J = 8.8 Hz, 2H, ArH), 4.68 (s, 2H, CH_2); 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 (b^7), white powder, yield 76%. ^1H NMR ($CDCl_3$) δ/ppm: 7.42 (d, 2H, ArH), 6.82 (d, J = 8.6 Hz, 2H, ArH), 4.67 (s, 2H, CH_2); 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