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Synthesis and luminescence properties of 1,3,4-oxadiazole acetamide derivatives and their rare earth complexes

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ABSTRACT

A series of 1,3,4-oxadiazole acetamide derivatives have been designed and synthesized, and their complexes with Eu(III) and Tb(III) were also prepared. The luminescence properties of the target complexes were investigated, and the results indicated that all target complexes showed the characteristic luminescence of the central ions. The relative fluorescence intensities of the complexes with Eu(III) are higher than that of the complexes with Tb(III). The fluorescence quantum yields of the target complexes were calculated by the reference method, and the results showed that the complexes substituted by electron-donating group possess higher fluorescence quantum yields, compared with that of the complex without substituent, while the complexes substituted by electron-withdrawing group possess lower fluorescence quantum yields. The electrochemical properties of the target complexes were investigated by cyclic voltammetry, the HOMO energy levels of the target complexes substituted by electron-donating group are higher than that of the target complexes substituted by electron-withdrawing group.

1. Introduction

Because of the unique properties, the complexes of rare-earth elements with 1,3,4-oxadiazole and some of derivatives have drawn great attention among scholars. Along with in-depth studies, their application value has also attracted great attention in fluorescent materials, luminescent probes in bio-medical assays and emitters in electroluminescent (EL) devices [1]. In recent years, the design and synthesis of rare earth functional coordination compounds has been one of the researching hot points in the coordination chemistry field [2,3]. The luminescence intensities of rare earth complexes is relationship to the absorption efficiency of ligands, which is dependent on the ligand molecule with expanded π-conjugated system to shift the excitation band of its rare earth complex to visible region. But if expanded π-conjugated system is too small, it will not absorb ultraviolet-light, if is too big, it will not sensitize the rare earth ion to emit characteristic emission [4,5]. In this regard, much attention has been focused on the selecting of ligands with different structure [6]. In general, the architectures of such supramolecule net-works are built-up using multidentate organic ligands containing O- and/or N-donors [7]. In this paper, we choose 1,3,4-oxadiazole acetamide derivatives as chelating ligand, which has a rigid framework and can construct stable supramolecule structures via C—H···O or C—H···N hydrogen bonds and π–π stacks, their corresponding rare earth complexes which possess good stability, fine luminescent monochromaticity and strong fluorescence intensities [8,9]. Based on the above considerations, four novel 1,3,4-oxadiazole acetamide derivatives were designed and synthesized, and their corresponding Tb(III) and Eu(III) complexes were also prepared. The relationship between the structure of ligands and the fluorescence intensities of their rare earth complexes would be studied, meanwhile, the electrochemical properties and fluorescence quantum yields of the target rare earth complexes were discussed in detail. The synthesis route for the 1,3,4-oxadiazole acetamide derivatives ($\mathbf{L^{1-4}}$) is shown in Scheme 1.

2. Experimental

2.1. Materials and methods

Tb_2O_3 (purity 99.99%) and Eu_2O_3 (purity 99.99%) were purchased from commercial suppliers. $Eu(NO_3)_3$ (0.1 mol L^{-1}) and $Tb(NO_3)_3$ (0.1 mol L^{-1}) ethanol solution was prepared according to the literature [10].

Abbreviations: NMR, nuclear magnetic resonance; UV spectra, ultraviolet spectra; IR, infrared spectra; CV, cyclic voltammetric; EDTA, ethylenediaminetetraacetic acid; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

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^{1}H NMR spectra was recorded in DMSO-d_6/$CDCl_3$ on Brucker spectrophotometer (400 MHz) with TMS as an internal standard. Mass spectra were measured with the MAT95XP Mass Spectrometer. IR spectra (400–4000 cm^{-1}) were obtained in KBr discs by a PERKIN–ELMER Spectrum One. UV spectra (190–450 nm) were recorded by LabTech UV-2100 spectrophotometer, with DMSO as solvent and reference. Elemental analysis of the complexes was carried out on a VarioEL 111 CHNS analyzer. Melting points of all compounds were determined on an X-4 binocular microscope. Thermal gravimetric analysis were carried out on a NETZSCH STA 409PC thermal gravimetric analyzer. 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 dimethyl sulfoxide as the solvent, the test scanning speed was 100 mV s^{-1} and the sensitivity was 1 mA. The fluorescence spectra were measured by using powder samples on a Hitachi F-2700 Fluorescence Spectrophotometer at room temperature.

2.2. General procedure for synthesis of the intermediates

2.2.1. Synthesis of the compound *A*

The polyphosphate (15 mmol, 5.07 g) was added into a 150 mL three-neck flask and maintained the temperature at 50 °C for some time, and then a solution of hydrazine hydrate (80%, 6.5 mL) and salicylic acid (10 mmol, 1.38 g) was added with stirring. The reaction mixture was heated to 130 °C and refluxed for 7 h with stirring in the oil bath. After completion of the reaction, the resulting mixture was poured into the 500 mL cold water and standed over night with stirring. Then filtered and washed with water, evaporated to obtained the crude product, the compound **A** was obtained by recrystallization from the absolute ethanol. Yield, 76% [11].

2.2.2. Synthesis of the compound B^{1-4}

As the synthesis methods of the compounds $\mathbf{B^{1-4}}$ were similar, only synthesis of the 2-chloro-N-phenylacetamide compound $\mathbf{B^1}$ was described. A solution of aniline (66 mmol, 6.14 g) in glacial acetic acid (50 mL) was added into a 100 mL single-neck flask and then the acetyl chloride (74 mmol, 8.36 g) was gradually dropwise added under stirring in the ice water bath. The resulting reaction mixture was stirred for 1 h at room temperature and then poured into 300 mL saturated sodium acetate solution. Filtered off and washed several times with cold water. The compound $\mathbf{B^1}$ was obtained by recrystallization from the mixture of ethanol and water (1:1) and dried in vacuum for 12 h.

2-chloro-N-phenylacetamide (B^1). White crystals, yield (81%). ^{1}H NMR (400 MHz, DMSO) 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_2); 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-*p*-tolylacetamide (B^2). White crystals, yield (75%). ^{1}H NMR (400 MHz, DMSO-d_6) 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_2), 2.21 (s, 3H, CH_3); 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 (B^3). White crystals, yield (87%). ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: ^{1}H NMR (400 MHz, DMSO) δ/ppm: 10.43 (s, 1H, NH), 7.67–7.57 (m, 2H, ArH), 7.46–7.34 (m, 2H, ArH), 4.26 (s, 2H, CH_2); 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-(4-chlorophenyl)acetamide (B^4). Yellow crystals, yield (85%). ^{1}H NMR (400 MHz, DMSO) 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_2), 3.73 (s, 3H, CH_3); 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).

2.3. General procedure for synthesis of the target compound (L^{1-4})

As the synthesis methods of compounds $\mathbf{L^{1-4}}$ were similar, the synthesis of the target compound $\mathbf{L^1}$ was described as an example., the 2,2′-(1,3,4-oxadiazole-2,5-diyl)diphenol (2 mmol, 0.51 g) and anhydrous potassium carbonate (10 mmol, 1.38 g) were dissolved in a 100 mL single-necked flask with 50 mL DMF solution. The resulting mixture was refluxed at 80 °C for 1 h, the 2-chloro-N-phenylacetamide compound $\mathbf{B^1}$ (7 mmol, 1.18 g) and a little of KI were added and continued to reflux for 24 h. After completion of the reaction, the reaction mixture was cooled to room temperature, and then gradually poured into distilled water (500 mL) and stirred for 2 h. The resulting mixture was concentrated under reduced pressure and washed several times with distilled water until the pH value reached 7. The resulting product was further purified by recrystallization from the mixture of ethanol and chloroform (1:1), and dried in vacuum for 24 h. Thus the target compound $\mathbf{L^1}$ was obtained.

2,2′-(2,2′-(1,3,4-oxadiazole-2,5-diyl)bis(2,1-phenylene))bis(oxy)bis(N-phenylacetamide) (L^1). White powder, yield (84%). m.p. 265–266 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 10.55 (s, 2H, NH), 8.10 (dd, *J* = 7.8, J = 1.6 Hz, 2H, ArH), 7.73–7.68 (m, 4H, ArH), 7.65–7.59 (m, 2H, ArH), 7.26–7.22 (m, 2H, ArH), 7.13 (d, *J* = 8.2 Hz, 2H, ArH), 7.06 (dd, *J* = 10.8 Hz, *J* = 5.1 Hz, 4H, ArH), 6.86 (t, *J* = 7.4 Hz, 2H, ArH), 4.85 (s, 4H, CH_2); IR (KBr) v/cm^{-1}: 3306, 3020, 1759, 1692, 1601, 1255, 1165, 866; MS (EI) *m*/*z* (%): 522 (M + 2, 2), 520 (M, 4), 311 (100), 254 (78), 226 (18), 121 (47), 106 (24), 93 (51); Anal. Calcd. for $C_{30}H_{24}N_4O_5$: C, 69.22; H, 4.65; N, 10.76. Found: C, 69.21; H, 4.55; N, 10.56.

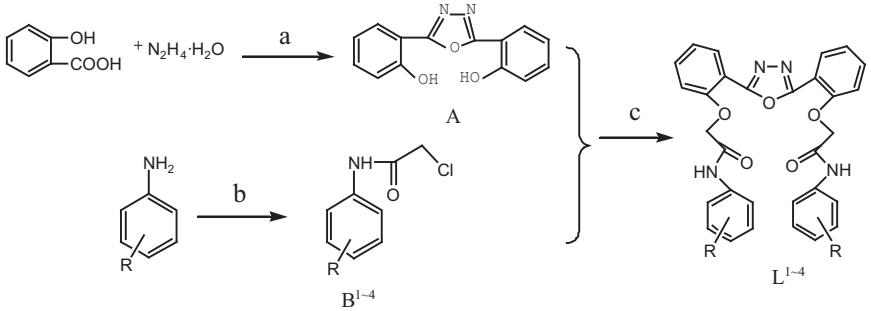
2,2′-(2,2′-(1,3,4-oxadiazole-2,5-diyl)bis(2,1-phenylene))bis(oxy)bis(N-p-tolylacetamide) (L^2). Yellow crystals, yield (71%). m.p. 259–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 10.45 (s, 2H, NH), 8.10 (dd, *J* = 7.8 Hz, *J* = 1.6 Hz, 2H, ArH), 7.64–7.59 (m, 2H, ArH), 7.53 (d, *J* = 8.4 Hz, 4H, ArH), 7.23 (d, *J* = 7.8 Hz, 2H, ArH), 7.12 (d, *J* = 8.3 Hz, 2H, ArH), 6.81 (d, *J* = 8.2 Hz, 4H, ArH), 4.82 (s, 4H, CH_2), 2.12 (s, 6H, CH_3); IR (KBr) v/cm^{-1}: 3325, 3132, 2151, 1680, 1600, 1268, 1166, 866; MS (EI) *m*/*z* (%): 550 (M + 2, 8), 549 (M + 1, 37), 548 (M, 100), 442 (97), 443 (26), 415 (61), 268 (72), 121 (44); Anal. Calcd. for $C_{32}H_{28}N_4O_5$: C, 70.06; H, 5.14; N, 10.21. Found: C, 70.04; H, 5.12; N, 10.11.

2,2′-(2,2′-(1,3,4-oxadiazole-2,5-diyl)bis(2,1-phenylene))bis(oxy)bis(N-(4-methoxyphenyl)acetamide) (L^3). White powder, yield (70%). m.p. 225–226 °C; 1H NMR (400 MHz, $CDCl_3$) δ/ppm: δ 10.45 (s, 2H, NH), 8.13–8.08 (m, 2H, ArH), 7.64–7.56 (m, 6H, ArH), 7.24 (d, *J* = 7.6 Hz, 2H, ArH), 7.13 (d, *J* = 8.3 Hz, 2H, ArH), 6.57 (d, *J* = 8.9 Hz, 4H, ArH), 4.83 (s, 4H, CH2), 3.66 (s, 6H, CH3O); IR (KBr) v/cm^{-1}: 3229, 3132, 1964, 1735, 1671, 1250, 1162, 964; MS (EI) *m*/*z* (%): 582 (M + 2, 3), 581 (M + 1, 12), 580 (M, 31), 458 (27), 300 (29), 283 (46), 136 (47), 123 (100), 121 (72), 108 (59); Anal. Calcd. for $C_{32}H_{28}N_4O_7$: C, 66.20; H, 4.86; N, 9.65; O 19.29. Found: C, 66.12; H, 4.62; N, 9.55.

2,2′-(2,2′-(1,3,4-oxadiazole-2,5-diyl)bis(2,1-phenylene))bis(oxy)bis(N-(4-chlorophenyl)acetamide) (L^4). Yellow crystals, yield (74%). m.p. 288–289 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 10.68 (s, 2H, NH), 8.14 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 2H, ArH), 7.67–7.63 (m, 2H, ArH), 7.56 (d, *J* = 8.8 Hz, 4H, ArH), 7.28 (d, *J* = 7.5 Hz, 2H, ArH), 7.13 (d, *J* = 8.3 Hz, 2H, ArH), 6.99–6.95 (m, 4H, ArH), 4.85 (s, 4H, CH_2); IR (KBr) v/cm^{-1}: 3223, 3040, 1879, 1691, 1604, 1267, 1164, 868; MS (EI) *m*/*z* (%): 592 (M + 4, 7), 591 (M + 3, 12), 590 (M + 2, 38), 589 (M + 1, 17), 588 (M, 56), 462 (97), 435 (86), 288 (60), 148 (57), 121 (100); Anal. Calcd. for $C_{30}H_{22}N_4O_5Cl_2$: C, 61.13; H, 3.76; N, 9.51. Found: C, 61.10; H, 3.56; N, 9.42.

2.4. Synthesis of the target rare earth complexes

The synthesis methods of the target rare earth complexes were similar, the synthesis of the europium complexes of compound $\mathbf{L^1}$ was described as an example. A mixture of compound $\mathbf{L^1}$ (0.40 mmol), chloroform (40 mL) was added into a 100 mL



B^1, R=4-H; B^2, R=4-CH_3; B^3, R=4-CH_3O; B^4, R=4-Cl

L^1, R=4-H; L^2, R=4-CH_3; L^3, R=4-CH_3O; L^4, R=4-Cl

(a) $H_6P_4O_{13}$, reflux, 7 h; (b) $ClCH_2COCl$, CH_3COOH, r.t., 1.5 h; (c) DMF, K_2CO_3, KI, reflux, 24 h

Scheme 1. The synthesis route for the ligands $\mathbf{L^{1-4}}$.