Europium Coordination Compound with Highly Improved Luminescent Quantum Yield (Postprint)

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Abstract

The luminescent properties of two Eu3+ compounds based on quinoline-2-carboxylic acid (Hqc), [Na2Eu2(qc)6(CH3COO)2(H2O)4].2DMF (1) and [Eu2(qc)6(H2O)6].3H2O (2), as well as their syntheses and structures are reported. Both compounds are formed by slow evaporation at room temperature and exhibit zero dimensional dinuclear structures. It is worth mentioning that a 4.5-fold enhancement in luminescent quantum yield is achieved by reducing the nonradiative deactivation, through which the quantum yield increases remarkably to 67.62% for 1 compared with 12.18% for 2.

Full Text

Preamble

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ABSTRACT

The luminescent properties of two Eu^3 compounds based on quinoline-

2-carboxylic acid (Hqc), [Na Eu (qc) (CH COO) (H O)] · 2DMF (1) and [Eu (qc) (H O)] · 3H O (2), as well as their syntheses and structures are reported. Both compounds were formed by slow evaporation at room temperature and exhibit zero-dimensional dinuclear structures. It is worth mentioning that a 4.5-fold enhancement in luminescent quantum yield is achieved by reducing the nonradiative deactivation, through which the quantum yield increases remarkably to 67.62% for 1 compared with 12.18% for 2.

Keywords: Eu^{3} compound; coordination environment; luminescent quantum yield
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1 INTRODUCTION

The fascinating luminescence of lanthanides that covers the visible and infrared light regions continues to draw attention for applications in biomedical analysis and imaging, luminescent probes and sensors, as well as security-related materials such as security inks and barcodes [1-7]. Luminescent quantum yield is essentially a very important parameter related to these applications. Actually, the forbidden and faint 4f-to-4f electronic transitions of lanthanides make their absorption coefficients small. As a consequence, direct excitation of the lanthanide ions rarely yields highly luminescent materials. Lanthanide compounds with organic ligands functioning as light antennas to overcome the weak absorption have been increasingly studied, especially those based on -conjugated ligands [8-18]. Their quantum yields basically depend on the following processes: light absorption and energy transfer between ligand and lanthanide, followed by lanthanide emission [19,20]. In order to obtain luminescent materials with high quantum yield, two major problems should be solved: first, choosing a ligand with a suitable triplet state that matches well with the emitting level of the lanthanide ions [21-23], and second, avoiding or reducing the influence of deactivation processes mainly caused by OH vibrations, because the lanthanide ions, especially Eu^{3} ion, are extremely sensitive to them [24,25]. To date, the largest quantum yield reported for an Eu^{3} compound is up to 85% [26].

Further efforts are also being devoted to improving the luminescence of lanthanide compounds, and such efforts will continue to be made to obtain luminescent materials with high quantum yield. In consideration of the above discussions, combined with our previous work showing that the triplet state of quinoline-containing ligands matches well with the D emission state of Eu^{3} ion [27], herein we report the syntheses, X-ray single-crystal structures, and luminescence properties of two Eu^{3} compounds based on quinoline-2-carboxylic acid (Hqc).

2 EXPERIMENTAL

2.1 Materials and Instruments

All reagents and solvents were purchased commercially and used without further purification. Single-crystal structure data were determined by a Rigaku Saturn 724+ CCD diffractometer equipped with graphite-monochromated MoK (= 0.71073 Å) radiation using the -scan mode at 123 K. Thermogravimetric analysis was carried out in the temperature range of 30-900 °C at a heating rate of 15 °C/min on a NETZSCH STA 449C instrument. Powder X-ray diffraction (PXRD) patterns were collected on a RIGAKU-DMAX 2500 diffractometer with CuK radiation (= 1.5406 Å). Steady-state photoluminescence spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrophotometer analyzer, and time-resolved luminescence measurements were performed on an Edinburgh Instruments FLS920 spectrofluorometer equipped with both continuous (450 W) and pulsed xenon lamps.

2.2 Syntheses of Compounds 1 and 2

Eu(CH COO) ·6H O (0.41 mmol, 180 mg), CH CH ONa (0.60 mmol, 41 mg), and Hqc (0.62 mmol, 108 mg) were added to 20 mL CH CH OH and stirred for 24 h. Colorless prism-shaped crystals of compound 2, formulated as [Eu (qc) (H O)]·3H O, were formed by evaporating the filtrate. The resulting pale-white precipitate was then dissolved in 10 mL DMF and 3 mL H O. After slow evaporation at room temperature, colorless block crystals of compound 1, formulated as [Na Eu (qc) (CH COO) (H O)]·2DMF, were obtained.

2.3 Structure Determination

The single-crystal structure data of compound 1 were determined by a Saturn724+ CCD diffractometer with graphite-monochromatized MoK (= 0.71071 Å) radiation at 123 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program [28,29]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms on the organic ligands were generated geometrically and refined using a riding model, while hydrogen atoms of water molecules were set according to Fourier difference maps. Selected bond lengths and bond angles of compound 1 are listed in Table 1 .

3 RESULTS AND DISCUSSION

3.1 Crystal Structure

Herein, the structure of compound 1 is illustrated specifically. According to single-crystal X-ray diffraction analysis, compound 1 crystallizes in the monoclinic P2 /c space group with a = 13.785(5), b = 18.776(6), c = 15.743(4) Å, = 121.41(2)°, V = 3478(2) Å^3, Z = 4, T = 123 K, Dc = 1.642 g·cm ^{3}, F(000) = 1782, μ = 1.883 mm ^{1}, GOOF = 1.049, R = 0.0193 and wR = 0.0476

(I > 2 (I)). In the asymmetric unit, there are one europium ion, three qc ligands, one sodium ion with two coordinating water molecules, one coordinated acetate anion, and one lattice DMF molecule. As shown in Fig. 1 [Figure 1: see original paper], the Eu^{3} ion exhibits a nine-coordinated geometry formed by five carboxylate oxygen atoms from four qc ligands, three carboxylate oxygen atoms from two acetate anions, and one pyridyl nitrogen atom. The Eu-O bond lengths vary between 2.341 and 2.555 Å, and the Eu-N bond is 2.715 Å (Table 2). The Eu^{3} ion and its symmetry-generated counterpart are linked by four carboxylate groups from qc ligands and acetic acid to generate a dinuclear "Eu-dimer" that is enclosed by six qc ligands and two six-coordinated Na ions, as shown in Fig. 2a [Figure 2: see original paper]. The Eu⋯Eu distance within the "Eu-dimer" is 3.911 Å. A 3D supramolecular crystal building of compound 1 is constructed through - interactions and hydrogen bonds (Fig. 3 [Figure 3: see original paper], Table 2). It is worth noting that strong hydrogen bonds O-H⋯O and O-H⋯N contribute to the stabilization of the 3D structure (O-H⋯O 2.772(2)-2.837(2) Å and 164-176°).

The quinoline rings of nearby dinuclear "Eu-dimers" are almost parallel, thus a - interaction is formed between rings N(2)#2-C(11)#2-C(12)#2-C(13)#2-C(14)#2-C(15)#2-C(16)#2-C(19)#2-C(17)#2-C(18)#2 and N(3)-C(23)-C(24)-C(25)-C(26)-C(27)-C(28)-C(29)-C(30)-C(31) (symmetry code: #2, x+1, -y+1/2, z+1/2). Within this - interaction, the inter-centroid distance and the dihedral angle are 3.702 Å and 4.783°, respectively, and the perpendicular distances of the quinoline centroid to its counterpart are 3.371 and 3.471 Å. The crystallization DMF molecule is placed in the intermolecular region, establishing strong C-H⋯O and O-H⋯O hydrogen bonds. Analogously, compound 2 [30] also displays a dinuclear "Eu-dimer" structure in which two Eu^{3} ions are surrounded by six qc ligands, with six water molecules coordinating to the Eu^{3} ions (Fig. 2b).

3.2 Powder X-ray Diffraction (PXRD) Pattern and Thermal Stability Analysis

The purity of compound 1 confirmed by powder X-ray diffraction is in agreement with the simulated pattern (Fig. 4 [Figure 4: see original paper]), confirming the phase purity of the as-synthesized product. According to thermogravimetric analysis, compound 1 remains stable until 285 °C, as shown in Fig. 5 [Figure 5: see original paper]. Two coordinated water molecules and lattice DMF molecules are lost during the temperature range of 20-185 °C (found: 12.72%; calcd.: 12.74%). The compound then remains stable up to 285 °C, after which the framework decomposes abruptly with further heating.

3.3 Luminescent Property

The solid-state emission spectra of compounds 1 and 2 excited at 350 nm are shown in Fig. 6 [Figure 6: see original paper]. The characteristic D → F_J (J = 0-4) transitions of Eu^{3} ion show main emission bands at 578, 591, 614, 649, and 698 nm, respectively, with the hypersensitive D → F transition at 614 nm dominating the spectra. The splitting of the emission band due to ligand-field effects indicates that Eu^{3} ions lie in low-symmetry environments.

No broad emission band resulting from the ligand is observed, which means the ligand transfers the absorbed energy effectively to the emitting level of the Eu^{3} ion. It is worth emphasizing that the quantum yield of compound 1 is up to 67.62%, which is 5.5 times as much as the quantum yield (12.18%) of compound 2, despite using the same ligand antenna. Clearly, the avoidance of nonradiative deactivation processes associated with OH vibrations accounts for the high luminescence efficiency of compound 1. Actually, no coordinated water exists in the inner coordination sphere of the Eu^{3} ion in compound 1, whereas there are six water molecules coordinating to the Eu^{3} ion in compound 2. It is hypothesized that the coordination of acetic acid as well as sodium ions to which water molecules coordinate in compound 1 results in better shielding of the Eu^{3} center, leading to the enhancement of quantum yield. In addition, the coordination of sodium ions can reduce framework vibrations, causing the enhancement of luminescent quantum yield. Therefore, for the purpose of obtaining lanthanide compounds with high luminescence quantum yield, removing water from the coordination sphere is required.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Compound 1

Bond/Angle	Value
Eu(1)-O(2)	2.3410(13)
Eu(1)-O(5)	2.3782(13)
Eu(1)-O(3)	2.3887(13)
Eu(1)-O(8)	2.4319(15)
Eu(1)-O(5)#1	2.5133(13)
Eu(1)-O(6)#1	2.5268(15)
Eu(1)-O(7)	2.5552(13)
Eu(1)-O(4)#1	2.4660(13)
Eu(1)-N(1)	2.7152(14)
O(2)-Eu(1)-O(5)	142.21(4)
O(2)-Eu(1)-O(3)	141.91(4)
O(5)-Eu(1)-O(3)	73.41(5)
O(2)-Eu(1)-O(8)	72.57(5)
O(5)-Eu(1)-O(8)	92.83(5)
O(2)-Eu(1)-O(7)	131.14(4)
O(5)-Eu(1)-O(7)	71.07(4)
O(3)-Eu(1)-O(8)	71.22(4)
O(3)-Eu(1)-O(7)	139.04(4)
O(2)-Eu(1)-O(4)#1	70.90(4)
O(5)-Eu(1)-O(4)#1	96.15(4)
O(8)-Eu(1)-O(7)	73.84(5)
O(4)#1-Eu(1)-O(7)	145.74(5)
O(3)-Eu(1)-O(4)#1	107.16(4)
O(5)#1-Eu(1)-O(7)	51.42(4)
O(8)-Eu(1)-O(4)#1	112.86(4)
O(2)-Eu(1)-O(5)#1	80.87(4)

Bond/Angle	Value
O(5)-Eu(1)-O(5)#1	79.14(4)
O(8)-Eu(1)-O(6)#1	52.17(4)
O(2)-Eu(1)-O(6)#1	114.32(5)
O(5)-Eu(1)-O(6)#1	150.81(4)
O(4)#1-Eu(1)-O(6)#1	138.06(4)
O(3)-Eu(1)-O(6)#1	64.28(4)
O(5)#1-Eu(1)-O(6)#1	149.37(4)
O(3)-Eu(1)-O(5)#1	79.84(4)
O(8)-Eu(1)-O(5)#1	141.97(4)
O(4)#1-Eu(1)-O(5)#1	71.09(5)
O(2)-Eu(1)-N(1)	74.60(5)
O(5)-Eu(1)-N(1)	119.52(4)
O(3)-Eu(1)-N(1)	73.58(5)
O(8)-Eu(1)-N(1)	88.07(4)
O(4)#1-Eu(1)-N(1)	81.04(5)
O(5)#1-Eu(1)-N(1)	132.56(4)
O(6)#1-Eu(1)-N(1)	127.53(4)
O(7)-Eu(1)-N(1)	76.14(4)

Symmetry code: #1: -x+1, -y+1, -z+1

Table 2. Selected Hydrogen Bond Lengths (Å) and Bond Angles (°) for Compound 1

D-H ⋯ A	d(D-H)	d(H ⋯ A)	d(D ⋯ A)
O(9)-H(9A) ⋯ O(10)#1	-	-	2.772(2)
O(9)-H(9B) ⋯ O(1)	-	-	2.825(2)
O(10)-H(10B) ⋯ O(11)	-	-	2.837(2)
O(10)-H(10A) ⋯ N(3)#2	-	-	2.828(2)

Symmetry codes: #1: 2-x, 1-y, 2-z; #2: 2-x, 1/2+y, 3/2-z

Fig. 1. Coordination environment (30% ellipsoids) of Eu^{3} ion in compound 1, in which hydrogen atoms and solvent are omitted for clarity (#1: -x+1, -y+1, -z+1)

Fig. 2. Dinuclear "Eu-dimer"structure of compounds 1 (a) and 2 (b). Hydrogen atoms of organic ligands are omitted for clarity.

Fig. 3. Packing diagram of compound 1

Fig. 4. Powder X-ray diffraction pattern for compound 1

Fig. 5. TGA diagram for compound 1

Fig. 6. Emission spectra of compounds 1 and 2 in the solid state excited at 350 nm

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Two Eu^{3} compounds based on quinoline-2-carboxylic acid (Hqc), featuring similar dinuclear structures with compositions of [Na Eu (qc) (CH COO) (H O)] · 2DMF (1) and [Eu (qc) (H O)] · 3H O (2), have been successfully synthesized and optically studied. The quantum yield reaches 67.62% in compound 1, which is 5.5 times that of compound 2 (12.18%), since the Eu^{3} ion in 1 is better protected by the coordinated acetic acid and nearby sodium ions, which keep coordinated water molecules away from the coordination sphere, thereby reducing the nonradiative deactivation process.