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Anion-responsive luminescent Eu³⁺ complexes with ring-like rigid quinoline–amide ligands

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Introduction

A lot of luminescent lanthanide complexes has been applied in biochemical sensors, naked-eye detection of inorganic anions and other chemical systems, because the organic ligand-sensitized complexes combine the outstanding optical properties of the lanthanide ions (microsecond to millisecond lifetimes, characteristic and narrow emission bands, and large Stokes shifts), effective intramolecular energy transfer to the central lanthanide ions (the so-called "antenna effect") of designed organic ligands and the regulated structures of complexes [1–4]. Because trivalent lanthanide ions have high coordination flexibility and lack of preferential geometries, the researchers' attention has been focused on the structure-property relationships of lanthanide complexes in the past decades [5-7]. According to the dynamic and unsaturated coordination features, various designed organic ligands and their luminescent lanthanide complexes which exhibited anion-responsive luminescence profiles had been synthesized [8–10].

In order to study the anion-responsive luminescence behavior of the europium complexes, two tetradentate ring-like rigid quinoline– amide ligands, 2-[2-(1,3-dioxolan-2-yl)quinolin-8-yloxy]-N-benzylacetamide (L^{I}) and 3-[2-(1,3-dioxolan-2-yl)quinolin-8-yloxy]-1,1diphenylpropan-2-one (L^{II}) (Scheme 1), in which the quinoline skeleton was the effective photoantenna [8,11] for excitation of the europium ions were designed. It is expected that the quinoline–amide

ABSTRACT

Two novel ring-like rigid quinoline–amide ligands, 2-[2-(1,3-dioxolan-2-yl)quinolin-8-yloxy]-N-benzylacetamide (L^{I}) and 3-[2-(1,3-dioxolan-2-yl)quinolin-8-yloxy]-1,1-diphenylpropan-2-one (L^{II}), were designed to assemble the anion-responsive luminescent europium complexes. Crystallographic studies of the EuL^I(NO₃)₃ and EuL^{II}(NO₃)₃ revealed that the tetradentate ligands L^{I} and L^{II} cooperatively coordinated with Eu³⁺ ion and some available sites around central europium ions for guest anions were reserved in the complexes. The luminescent properties of the Eu(III) nitrate complexes in acetonitrile solutions were investigated. And the lowest triplet state energy levels of the ligands are well placed to allow energy transfer to the resonance level of Eu(III). At the same time, the luminescence titration experiments and the Job's plot analysis demonstrated the formation of 1:1 complexes in the solutions. The luminescence intensities at 616 nm were enhanced by addition of NO₃⁻ or Cl⁻ anion to the mixed acetonitrile solutions of Eu(CF₃SO₃)₃ and the ligands.

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type ligands would coordinate chelated with the central lanthanide ions in equatorial plane and several available coordination sites in axial to interact with guest anions were reserved in the complex, thus the novel lanthanide complexes might exhibit anion-responsive luminescence profiles. As a part of our systematic studies, herein we report the assembly and anion-responsive luminescent properties of the Eu³⁺ complexes with the rigid quinoline–amide ligands L^I and L^{II}.

The synthetic route for the ligands 2-[2-(1,3-dioxolan-2-yl) quinolin-8-yloxy]-N-benzylacetamide (L¹) and 3-[2-(1,3-dioxolan-2yl)quinolin-8-yloxy]-1,1-diphenylpropan-2-one (L^{II}) is shown in Scheme 1. The 2-(1,3-dioxolan-2-yl)quinolin-8-ol (b) [12] was prepared through the acetalation reaction between 2-carbaldehvde-8-hydroxyquinoline (a) [13] and glycol. The ligands L^{I} and L^{II} [14] were synthesized via that the amide groups were introduced by the etherification reaction between the chloroacetamide type compounds and 2-(1,3-dioxolan-2-yl)quinolin-8-ol (b). The introduced oxygen atoms are expected to function as "hard" donors for lanthanide cations and form steady five-membered chelate rings. The europium complexes $EuL^{I}(NO_{3})_{3}$ and $EuL^{II}(NO_{3})_{3}$ were readily prepared by mixing stoichiometric amounts of ligands and Eu(NO₃)₃·6H₂O in mixed solvents of chloroform and ethyl acetate (v:v=1:1). The data of the elemental analysis indicate that the complexes conform to a 1:1 metal-to-ligand stoichiometry and the conductivity measurements for the complexes in acetonitrile solutions indicate that the complexes are non-electrolyte [15].

Slow diffusion of diethyl ether into the acetonitrile solutions of the europium complexes afforded colorless rhombic crystals. The single-crystal X-ray analysis of the complexes $EuL^{I}(NO_{3})_{3}$ and $EuL^{II}(NO_{3})_{3}$ reveal that they are isomorphous with the central Eu atom

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Scheme 1. The synthetic route for the ligands L^I and L^{II}.

coordinated with 10 donor atoms [16]. Six of them belong to three bidentate nitrate groups and the remaining four are from the tetradentate ligands (Figs. 1a and 2a). The coordination polyhedra around Eu³⁺ are both distorted bicapped square antiprisms (Figs. 1b and 2b). The ligands wrap around the metal ion with its oxygen atoms and nitrogen atoms and form a ring-like coordination structure together with the Eu atom. The four donor atoms of the ligands are not quite coplanar, their deviation from the mean plane being in the range 0.080–0.146 Å and 0.021–0.037 Å. The mean absolute deviations are 0.113 Å and 0.040 Å from the mean plane. The europium atoms lie out of the planes by 0.279 Å and 0.368 Å.

The excitation (left) and emission (right) spectra of the Eu(NO₃)₃ complexes with ligands L¹ and L¹¹ in acetonitrile solutions at room temperature are shown in Fig. 3). The excitation spectra, which are obtained by monitoring within the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu³⁺, both exhibit a broad excitation band (BEB) between 320 and 400 nm which

is ascribed to the $\pi-\pi^*$ electron transition of the ligands. Upon excitation at the maximum excited wavelength of the ligands' absorption band, the emission spectra of all samples reveal the characteristic emission bands of the Eu^{3+} ion at ~580 nm, ~590 nm and ~616 nm, indicating that the energy transfer from the ligands to central ion Eu^{3+} (antenna effect) seems comparatively efficient. The relative intensities ratio value $\eta({}^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1)$ of the EuL¹ (NO₃)₃ and EuL^{II}(NO₃)₃ are 3.1 and 3.6, respectively, indicating that the Eu^{3+} ions do not lie in centro-symmetric coordination sites, in agreement with the crystal structure analysis. The lifetimes of EuL¹ (NO₃)₃ and EuL^{II}(NO₃)₃ in CH₃CN solutions are 1.40 ms and 1.44 ms, respectively, fitted from the luminescence decay curves by single exponential process.

In order to acquire the lowest triplet excited state T_1 of the ligands L^1 and L^{II} , the phosphorescence spectra of the Gd³⁺ complexes were measured at 77 K in mixed solvents of methanol and ethanol



Fig. 1. The coordination sphere (a) and coordination polyhedron (b) of Eul¹(NO₃)₃ (purple: Eu ion; blue: N atom; red: oxygen atom). The key bond distances and angles (Å and °): Eu (1)–O(1) 2.352(3), Eu(1)–O(2) 2.639(3), Eu(1)–O(3) 2.469(3), Eu(1)–N(2) 2.598(3), Eu(1)–O(5) 2.459(3), Eu(1)–O(6) 2.462(3), Eu(1)–O(8) 2.481(3), Eu(1)–O(9) 2.553(3), Eu (1)–O(11) 2.475(4), Eu (1)–O(12) 2.452(4), and O(1)–Eu (1)–O(2) 61.27(9), N(2)–Eu (1)–O(2) 60.49(9), O(3)–Eu (1)–N(2) 62.15(10), O(5)–Eu (1)–O(6) 50.35(12), O(8)–Eu (1)–O (9) 49.54(10), O(12)–Eu (1)–O(11) 50.10(14).



Fig. 2. The coordination sphere (a) and coordination polyhedron (b) of EuL^{II}(NO₃)₃ (purple: Eu ion; blue: N atom; red: oxygen atom). The key bond distances and angles (Å and °): Eu (1)–O(1) 2.378(2), Eu(1)–O(2) 2.6073(19), Eu(1)–O(3) 2.460(2), Eu(1)–N(2) 2.567(2), Eu(1)–O(5) 2.466(2), Eu(1)–O(7) 2.486(2), Eu(1)–O(8) 2.505(2), Eu(1)–O(10) 2.532(2), Eu(1)–O(11) 2.521(2), Eu(1)–O(13) 2.491(2), and O(1)–Eu(1)–O(2) 61.52(6), N(2)–Eu(1)–O(2) 61.70(7), O(3)–Eu(1)–N(2) 63.09(7), O(5)–Eu(1)–O(7) 51.39(8), O(8)–Eu(1)–O (10) 49.73(8), O(13)–Eu(1)–O(11) 50.36(8).

(v:v=1:1). The triplet state energy levels T_1 of the ligands L^I and L^{II} , which were calculated from the shortest wavelength phosphores-



Fig. 3. Room temperature excitation (monitored within the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition) and emission (monitored at the maximum excited wavelength) spectra for EuL^{II}(NO₃)₃ (a) and EuL^{II}(NO₃)₃ (b) in CH₃CN solution ([complex] = 1×10^{-3} mol L⁻¹).

cence band, are 19,084 and 19,417 respectively. These energy levels are above the lowest excited resonance level 5D_0 of Eu $^{3+}$ (17,286 cm $^{-1}$), however, below the lowest excited resonance level 5D_4 of Tb $^{3+}$ (20,545 cm $^{-1}$). The results of the triplet state energy levels T₁ of the ligands L^I and L^{II} indicate that these ligands are suitable sensitizers for the europium ion.

To study the stoichiometries between the ligand L^{I} or L^{II} and Eu^{3+} , the luminescence titration experiments were also carried out using 10^{-4} mol L^{-1} ligand L^{I} or L^{II} in acetonitrile solution (Fig. 4). The emission peaks at ~592 and ~617 nm increased upon gradual addition of $Eu(NO_3)_3$ and remained constant after 1.0 equiv Eu $(NO_3)_3$ was added. A Job's plot analysis exhibited a maximum at 0.5 mol fraction of $Eu(NO_3)_3$ (inset of Fig. 4), indicating the formation of 1:1 complexes in the solutions.

Lanthanide luminescence behaviors are influenced by the change of the coordination environment around the lanthanide centre [17]. Considering the coordinatively unsaturated characters of the quinoline–amide type ligands, europium complexes with ligands L^I and L^{II} might exhibit anion-responsive luminescence profiles for particular anions, because the stoichiometry, geometry, and structure of the ternary "ligand–lanthanide–anion" complex are often alerted by the additional coordination from external anion [18].

When ligand L^I or L^{II} was mixed with an equimolar quantity of Eu(CF₃SO₃)₃ in CH₃CN solutions (0.5×10^{-4} mol L⁻¹), characteristic Eu³⁺ luminescence spectra were observed. The anion responsiveness studies of the lanthanide complexes are investigated and the relative luminescence intensities changes at 616 nm for L^{I} -Eu(CF₃SO₃)₃ and L^{II}-Eu(CF₃SO₃)₃ complexes upon addition of three equivalents tetrabutylammonium salt containing the F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, NO_3^- , $CH_3CO_2^-$, HSO_4^- or $H_2PO_4^-$ anions are summarized in Fig. 5. The Eu^{3+} complexes with ligands L^{I} or L^{II} exhibited the similar anionresponse luminescence behaviors which the luminescence increased upon addition of Cl^- or NO_3^- . Considering the descriptions of the single-crystal structures and complexation in CH₃CN solution, the ligands and Eu³⁺ ion might prefer the formation of 1:1 complexes, in which the ligands would occupy the coordination sites of the central Eu³⁺ ion in equatorial plane and the potential exchangeable coordination sites of the central Eu³⁺ ion in axial would be kept back. We deduce that based on the appropriate coordination capacity and radius of anions, Cl⁻ and NO₃⁻ might coordinate into the inner coordination sphere of central Eu³⁺ and prevent luminescence quenching by the water or solvent molecules.



Fig. 4. Luminescence spectra of L^I and L^{II} $(1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ in CH₃CN upon addition of different concentrations of Eu(NO₃)₃ (0, 2.0×10^{-5} , 4.0×10^{-5} , 6.0×10^{-5} , 8.0×10^{-5} , 1.0×10^{-4} , and 1.2×10^{-4} mol L⁻¹, respectively). The Job's plots for L^I and L^{II} vs. Eu³⁺.

The results of this work represent novel ligands design based on quinoline acted as effective photoantennae for excitation of the europium ion and pre-controlled structures of the complexes affected by the polydentate rigid ligands. Sensitized by the ring-like rigid quinoline–amide ligands, the Eu^{3+} complexes have shown the characteristic europium emission and selectivity for Cl⁻ and NO₃⁻.

Acknowledgements

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Appendix A. Supplementary material

CCDC 770381 and CCDC 770382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2010.04.020.

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none 1 а F CI. 457 Br CIO4 NO3 530 CH3CO2 HSO₄⁻ H₂PO₄ 100 300 400 500 200 **Relative Intensity** none b F CI 246 Br Ľ CIO4-NO₃ 343 CH3CO2 HSO4 H₂PO₄ 50 100 150 200 250 300 350 Ó **Relative Intensity**

Fig. 5. Anion-responsive profiles of luminescent quinoline–amide ligands– Eu^{3+} complexes [Eu(CF₃SO₃)₃]= 0.5×10^{-4} mol L⁻¹; [ligand]= 0.5×10^{-4} mol L⁻¹; a: excitation at 317 nm, slit widths 10/10 nm; b: excitation at 320 nm, slit widths 10/10 nm; [nBu₄NX]= 1.5×10^{-4} mol L⁻¹.

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- [12] A.R. Katritzky, W.Q. Fan, Q.L. Li, Tetrahedron Letters 28 (1987) 1195 2-(1,3-dioxolan-2-yl)quinolin-8-ol (b): white solid, yield 90%.¹H NMR (400 MHz, CDCl3, ppm): 8.209–8.188(d, 1H, *J*=8.4 Hz), 8.164(s, 1H), 7.673–7.652(d, 1H, *J*=8.4 Hz), 7.482–7.442(t, 1H, *J*=8.4 Hz), 7.341–7.318(dd, 1H, *J*=1.2 Hz, *J*=8.4 Hz), 7.202–7.181(dd, 1H, *J*=0.8 Hz, *J*=7.6 Hz), 5.990(s, 1H), 4.254–4.194(m, 2H), 4.170–4.110(m, 2H).
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- [14] Ligand L¹: white solid, yield 76%,¹H NMR (CDCl3, 400 MHz):8.868(s, 1H), 8.225-8.204(d, 1H, J = 8.4 Hz), 7.673-7.652 (d, 1H, J = 8.4 Hz), 7.539-7.506(t, 2H, J = 6.6 Hz), 7.295-7.219(m, 6H), 5.697(s, 1H), 4.854(s, 1H), 4.562-4.547(d, 2H, J = 6.0 Hz), 4.159-4.099(m, 2H), 4.053-3.993(m, 2H). IR (KBr pellet, cm-1) v: 3076 (m, Ar-H), 2924 (m, C-H), 1670 (s, C O), 1555 (m), 1475 (m), 1431 (m), 1379 (m), 1318 (m), 1256 (m), 1106 (s), 838 (m), 757 (m). Ligand L^{II}: white solid, yield 80%, ¹H NMR (CDCl3, 400 MHz): 8.178-8.156(d, 1H, J = 8.8 Hz), 7.668-7.647 (d, 1H, J = 8.4 Hz), 7.429-7.324(m, 10H), 7.058-7.046(d, 1H, J = 4.8 Hz), 6.001(s, 1H), 4.935(s, 1H), 4.245-4.185(m, 2H), 4.147-4.087(m, 2H). IR (KBr pellet, cm-1) v: 3057 (m, Ar-H), 2914 (m, C-H), 1685 (s, C O), 1597 (m), 1487 (m), 1428 (m), 1377 (m), 1319 (m), 1254 (m), 1108 (s), 840 (m), 764 (m), 701 (m).
- [15] Element analysis (%) for EuL¹(NO₃)₃ Calcd.: C 35.91, H 2.87, N 9.97; found: C 36.13, H 2.78, N 9.78. IR (KBr pellet, cm-1) v: 1651(s, C O), NO3-(C2v): 1479(s, v1), 1312(s. v4), 1034 (m, v2), 817(m, v5). Element analysis (%) for EuL^{II}(NO₃)₃ Calcd.: C 40.85, H 2.90, N 9.16; found: C 41.31, H 2.83, N 8.66. IR (KBr pellet, cm-1) v: 1634 (s, C O), NO3-(C2v): 1490 (s, v1), 1306 (s, v4), 1030 (m, v2), 816(m, v5).
- [16] Data for single crystal of the complexes was collected on a Bruker SMART CCD detector diffractometer using graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 298 ± 2 K. The structures were solved by direct methods and refined by full-matrix least squares techniques with anisotropic thermal factors for all nonhydrogen atoms. The hydrogen atoms were added geometrically and not refined. All calculations were performed using the program package SHELXTL

97. Crystal data for EuL¹(NO₃)₃: monoclinic, space group P21/n, Mr = 702.38, a = 8.88130(10) Å, b = 20.8024(3) Å, c = 14.0311(2)Å, $\beta = 96.2540(10)^{\circ}$ V = 2576.85(6) Å³, Z = 4, $D_{calcd} = 1.810$ g/cm³, GOF = 1.064, final $R_1 = 0.0293$, $wR_2 = 0.0599$. Crystal data for EuL¹¹(NO₃)₃: monoclinic, space group P21/c, Mr = 764.45, a = 8.9691(2) Å, b = 13.2371(3) Å, c = 23.9924(5) Å, $\beta = 96.7910$ (10)° V = 2828.51(11) Å³, Z = 4, $D_{calcd} = 1.795$ g/cm³, GOF = 0.967, final $R_1 = 0.0287$, $wR_2 = 0.0580$.

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