



Two cubane-type $\text{Ln}_4(\text{OH})_4$ compounds derived from tridentate ligand 8-hydroxyquinoline: Synthesis, structures, one/two-photon luminescence and magnetism

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ABSTRACT

Two novel tetranuclear compounds with general formula of $[\text{Ln}_4\text{L}_4(\mu_3\text{-OH})_4(\text{DMF})_x(\text{MeOH})_y]$ (compound **1**, $\text{Ln} = \text{Yb}$, $x = 3$, $y = 1$; compound **2**, $\text{Ln} = \text{Tb}$, $x = 4$, $y = 0$) were synthesized via simple hydrothermal reaction by using lanthanide nitrate and H_2L as reactants. The crystal structure of compounds **1** and **2** were in triclinic $P - 1$ monoclinic $P2/c$ space group, respectively, as evidenced by single crystal X-ray diffraction. Both of them show the coordination features, namely, a distorted tetranuclear lanthanide $\text{Ln}_4(\text{OH})_4$ cubane core consisting of four $\mu_3\text{-OH}^-$ bridges, while four H_2L ligands and four solvent molecules occupy the peripheral part of the cluster. Interestingly, compound **1** exhibits near infrared luminescence upon excitation at 530 nm because of Yb^{3+} ion. Furthermore, Compound **1** shows efficient two-photon upconversion property. Magnetic susceptibility measurements indicate that compounds **1** and **2** show an antiferromagnetic interaction between the adjacent Ln^{3+} ions.

1. Introduction

It is well known that lanthanide ions have sharp and intense emission bands due to their $f-f$ electronic transitions and long luminescent lifetime [1–3]. These properties make them to be promising candidate for biological imaging and bioanalytical applications [4–6], telecommunications [7], OLED/LED devices [8], and energy conversion [9]. Therefore, lanthanide-organic compounds are attracting increasing attention due to their special structures and potential applications as multifunctional materials (such as magnetic and luminescent materials) [10–16], which is a forefront topic in molecule-based materials.

However, lanthanide ions electronic transitions are forbidden by parity (Laporte) selection rules, leading to weak absorbance and low quantum yields [1–3]. One way to circumvent this problem is to surround the lanthanide ions with organic ligands can effectively absorb light and transfer to the metal centers (antenna effect) [17–20].

Carboxylate ligands can exhibit versatile coordination capability via distinct bonding with lanthanide ions. A class of particularly attractive organic linker is carboxylate anion derivative. Due to its rigidity in

structure, diversity in coordination geometry and capability to act as a multi-donor (O, N), many crystal structures assembled from carboxylate derivative and Ln^{3+} have been reported and their unique properties have been demonstrated [21,22]. Compounds containing cubane-like $\text{Ln}_4(\text{OH})_4$ building blocks of carboxylate derivative were also reported [23–25]. It is well known that 8-hydroxyquinoline derivatives are strong metal chelators capable of binding a variety of metal ions, yielding different geometries depending on the metal ions and their oxidation states [26]. However, 8-hydroxyquinoline derivatives containing modular distorted cubane-like $\text{Ln}_4(\text{OH})_4$ building blocks are relatively rare. One possible reason is that the lanthanide ions adopt high coordination numbers and versatile coordination behaviors, which make the coordination spheres of lanthanide cations more difficult to control [27]. Furthermore, it is very difficult to endow these target materials with specific properties. The high affinity of lanthanides for oxygen donor atoms makes the oxygen-containing ligands excellent candidates as bridging ligands for the preparation of stable architectures [28–32]. In addition, our recent results based on 2-substituted-8-hydroxyquinoline derivatives provides insight on how to rationally

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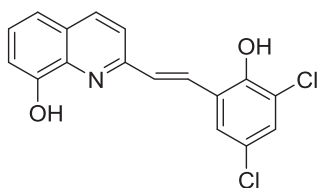
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Scheme 1. Representation of the ligand (*E*)-2-[2-(2-hydroxy-3,5-dichlorophenyl)ethenyl]-8-hydroxyquinoline (H_2L).

construct such photoluminescence materials using the ligands and Cd (II) or Zn(II) [33,34]. In this paper, the tridentate ligand H_2L (Scheme 1) was designed and synthesized, and two novel isostructural lanthanide-organic compounds **1** and **2** were obtained by using the tridentate ligand H_2L .

2. Experimental section

2.1. Materials and characterization methods

All of the chemicals are commercially available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-O CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400–4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. PXRD data were collected on a DMAX2500 diffractometer using Cu $K\alpha$ radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. The visible luminescent properties of compounds H_2L and **2** were carried out on a LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). The near-IR emission spectrum of compound **1** was recorded on an Edinburgh Analytical Instruments FLS920 equipped with a laser diode from the PicoQuant Company as the light source. The two-photon luminescence spectra of compound H_2L , **1** and **2** were captured by a compact spectrometer (QE65000, Ocean Optics) with a 920-nm fs laser (Mira900 Coherent). The room-temperature lifetime measurements were determined on a FSP920-combined time-resolved and steady-state fluorescence spectrometer (Edinburgh Instruments) equipped with a F900 microsecond flash lamp. All UV–vis absorption spectrum were recorded on a Lambda 20 UV–vis Spectrometer (Perkin Elmer, Inc., USA). 1H and ^{13}C NMR experiments were carried out on a MERCURY plus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Electropray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethanemethanol as mobile phase.

2.2. Synthesis of compounds H_2L , **1** and **2**

2.2.1. Synthesis of (*E*)-2-[2-(2-acetoxy-3,5-dichlorophenyl)ethenyl]-8-acetoxyquinoline (**A1**)

3,5-dichloro-salicylaldehyde (1.91 g, 10.0 mmol) was added to a solution of 8-hydroxyquinoline (1.59 g, 10.0 mmol) in acetic anhydride (10 mL). The mixture was heated under reflux for 15 h. After the mixture was cooled, it was subsequently poured into ice water (200 mL) and stirred overnight. The obtained solid was filtered and washed with DI water. The crude product was purified with column chromatography over silica gel using petroleum ether/EtOAc (4:1) as the eluent to give (*E*)-2-[2-(2-acetoxy-3,5-dichlorophenyl)ethenyl]-8-acetoxyquinoline as a purplish red solid (3.53 g, 85%); 1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, $J = 8.5$ Hz, 1 H), 7.69 (d, $J = 8.1$ Hz, 1 H), 7.63 (d, $J = 15.2$ Hz, 2 H), 7.55 (d, $J = 8.5$ Hz, 1 H), 7.50 (t, $J = 7.8$ Hz, 1 H), 7.44 (d, $J = 8.9$ Hz, 1 H), 7.41 (s, 1 H), 7.30 (d, $J = 16.1$ Hz, 1 H); ESI-MS m/z : 416.05 ($[M + H]^+$); elemental analysis: found C: 60.78, H: 3.56, N: 3.31 calculated for ($C_{21}H_{15}Cl_2NO_4$) C: 60.72, H: 3.61, N: 3.37 (%).

2.2.2. Synthesis of (*E*)-2-[2-(2-hydroxy-3,5-dichlorophenyl)ethenyl]-8-hydroxyquinoline (H_2L)

A solution of (*E*)-2-[2-(2-acetoxy-3,5-dichlorophenyl)ethenyl]-8-acetoxyquinoline (2.57 g, 6.2 mmol) in pyridine (60 mL) was refluxed for 30 min, after which 15 mL of water was added. The reaction mixture was refluxed for 24 h. After the mixture was cooled, more water (200 mL) was added to the mixture. The yellow solid obtained was filtered and washed with water, and dried in vacuo to give compound of H_2L (1.88 g, 91%). 1H NMR (400 MHz, DMSO) δ 10.12 (s, 1 H), 9.55 (s, 1 H), 8.32 (d, $J = 8.6$ Hz, 1 H), 8.21 (d, $J = 16.2$ Hz, 1 H), 7.76 (dd, $J = 9.1, 5.5$ Hz, 2 H), 7.60 (d, $J = 16.1$ Hz, 1 H), 7.51 (d, $J = 2.5$ Hz, 1 H), 7.45–7.34 (m, 3 H), 7.11 (dd, $J = 7.1, 1.6$ Hz, 1 H); ^{13}C NMR (101 MHz, DMSO) δ 153.65, 153.40, 150.54, 138.63, 137.10, 131.24, 129.00, 128.30, 128.15, 127.74, 125.96, 124.32, 123.27, 121.58, 118.11, 111.73, 39.98. ESI-MS m/z : 332 ($[M + H]^+$); elemental analysis: found C: 61.51, H: 3.35, N: 4.16 calculated for ($C_{17}H_{11}Cl_2NO_2$) C: 61.45, H: 3.31, N: 4.22 (%).

2.2.3. Synthesis of compound **1**

A mixture of $Yb(NO_3)_3 \cdot 5H_2O$ (2.6 mg, 0.02 mmol), H_2L (2.9 mg, 0.01 mmol), DMF (0.5 mL), and MeOH (1 mL) in a capped vial was heated at 80 °C for one day. Brown block like crystals of compound **1** suitable for single-crystal X-ray diffraction were collected. The solid was filtered, washed with MeOH, and dried in air. Yield: 4.55 mg (75%), m. p. > 400 °C; Elemental analysis: found: C, 40.51; H, 3.01; N, 4.12%. calculated for ($C_{81}H_{74}Cl_8N_7O_{18}Yb_4$): C, 40.36; H, 3.07; N, 4.07%. IR (KBr, ν/cm^{-1}): 3417.67(m), 3047.22(w), 2930.07(w), 1657.31(s), 1597.62(s), 1552.50(m), 1447.31(m), 1375.38(w), 1334.76(w), 1282.36(s), 1200.00(m), 1165.83(m), 1102.09(s), 964.28(m), 852.14(w), 831.94(w), 775.95(w), 747.95(s), 682.40(w), 490.47(w).

2.2.4. Synthesis of compound **2**

A mixture of $Tb(NO_3)_3$ (6.89 mg, 0.02 mmol), H_2L (2.9 mg, 0.01 mmol), $NH_3 \cdot H_2O$ (0.05 mL), DMF (0.5 mL), and MeOH (1 mL) was heated 80 °C in a capped vial for one day. Blue block-like crystals of compound **2** were filtered, washed with MeOH, and dried at room temperature. Yield: 4.63 mg (83%). m. p. > 400 °C, Elemental analysis: found: C, 41.55; H, 2.87; N, 4.90%. calculated for ($C_{80}H_{68}Cl_8N_8O_{16}Tb_4$): C, 41.45; H, 2.94; N, 4.84%. IR (KBr, ν/cm^{-1}): 3427.45(m), 2928.70(w), 1660.90(s), 1599.26(m), 1551.52(m), 1502.69(m), 1448.19(s), 1385.16(w), 1329.41(w), 1278.22(s), 1197.99(m), 1162.70(m), 1099.64(m), 967.36(w), 852.61(w), 830.35(w), 776.14(w), 747.46(w), 677.64(w), 486.93(w).

2.3. Crystal structure determinations

Single-crystal XRD data for compounds **1** and **2** were performed on a Bruker APEX area-detector X-ray diffractometer with Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Gottingen, Gottingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on F^2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Gottingen, Germany, 1997). The crystallographic figures have been generated using Diamond 3.1e software. Crystal data and details of the data collection are given in Table 1, whereas the selected bond distances and angles are presented in Table S1–2.

3. Results and discussion

3.1. Crystal structure description

Single-crystal X-ray diffraction studies reveal that compounds **1** and **2** both have an isostructural tetranuclear structure and crystallize in the

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