

Short communication

A novel europium coordination polymer based on mixed carboxylic acid ligands: Synthesis, structure and luminescence

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ABSTRACT

A novel europium complex, formulated as $\{[Eu_4(H_3Pimda)_4(Himba)_2 \cdot 4H_2O] \cdot 4H_2O\}_n$ (**1**) ($H_3Pimda = 2$ -propyl-1H-imidazole-4,5-dicarboxylic acid, and $Himba = 4$ -(1H-imidazole-1-yl) benzoic acid), has been obtained by the hydrothermal reaction. Single crystal X-ray diffraction analysis shows that complex **1** exhibits one-dimensional (1-D) ribbon-double chain composed of tetranuclear europium clusters, and these chains are further linked by Himba ligands into the 2-D corrugated layer arrays. Complex **1** exhibits efficiently sensitized red luminescence in visible region in *N,N*-dimethyl formamide (DMF) based on characterization emission of europium(III) ion. When $Cd(NO_3)_2$ is dropped in the DMF suspension of **1**, the luminescence intensity increases linearly, rapidly, which indicates it may be employed as a fluorescent ratiometric probe for detection pollutant Cd(II) anion. In addition, complex **1** is characterized by elemental analysis, IR spectra, thermogravimetric (TG) analysis and PXRD measurement.

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Lanthanide-organic frameworks, a special class of prospective function materials, have attracted wide interests in chemistry and materials fields, not only because of their extraordinary architectures that result from the high and variable coordination numbers of the metal centers [1–3], but also due to a wide range of applications such as displaying devices, gas storage and separation, catalysis, luminescence sensors, magnetism, and fluorescent probes [4–6]. Especially, lanthanide-organic frameworks have emerged as fundamental luminescent materials, which can provide unique luminescent properties such as high luminescent quantum yield, larger Stokes shifts, and long-lived emission which cover a spectral range from the ultraviolet to the visible, even the near-infrared (NIR) regions [2,7]. However, the luminescence intensity is often quenched by the non-radiative exchange of electronic energy of Ln(III) to the high vibration modes of O–H, C–H bondings [8]. To overcome this disadvantage, our strategy is to employ the mixed carboxylic acids which have strong coordination abilities as starting materials to substitute the coordination water molecules and to construct stable lanthanide metal clusters [9]. On the other hand, in order to avoid deactivation processes, the role of the carboxylic ligand is to shield lanthanide center against the solvent [10]. As the chromophores, conjugational imidazole carboxylic acid ligands can form stable complexes with lanthanide ions and absorbed

light then transfer energy efficiently to lanthanide(III) ions as a result of sensitizing luminescence, by overcoming the problem of the Laporte forbidden *f–f* transitions [7]. In this contribution, H_3Pimda was employed as a functional ligand for the following considerations: (i) It is a multidentate and semi-flexible ligand which has multi-proton and donor-acceptor sites. (ii) It possesses nitrogen atoms and oxygen atoms which can afford a variety of coordination modes, such as, monodentate bridging, chelating and bidentate bridging. (iii) It could be changed the coordination modes as in protonation or deprotonation form with the pH value modification, resulting in possible novel structures and properties. Some metal organic frameworks based on H_3Pimda or $Himba$ with transition metal ion have been reported [11–13]. It is well known that cadmium(II) is a toxic and carcinogenic heavy metal, which harms human health and causes serious environmental problems. There are some analytical methods for detecting and monitoring Cd(II) have been documented [14–17]. However, lanthanide-organic framework as a fluorescent probe to detect Cd(II) ion has not been reported so far. As a continuation of our previous investigations [2], a new lanthanide-organic complex that combines H_3Pimda with $Himba$ has been isolated successfully [18]. The structure, photo-luminescence, and thermal decomposition are also investigated.

Single-crystal X-ray diffraction study [19] reveals that title complex crystallizes in the orthorhombic system, space group of *P*–1. The asymmetric unit contains two Eu(III) ions, two H_3Pimda ligands, one $Himba$ ligand, two coordinated water molecules and two lattice water molecules, as illustrated in Fig. 1. There are two crystallographically independent Eu(III) ions (Eu1, Eu2) in this unit and both of the two

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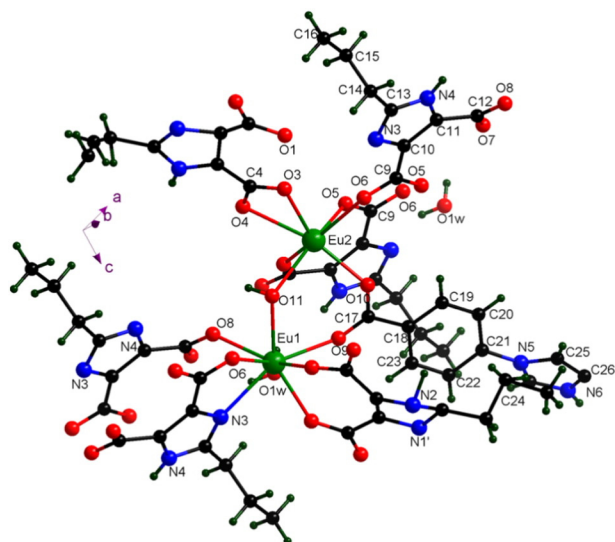


Fig. 1. The coordination environments of Eu(III) ions in the asymmetric unit of title complex with atomic numbering scheme in 1.

Eu(III) ions are eight-coordinated. The Eu1 is linked with seven oxygen atoms and one nitrogen atom completed the distorted tetragonal *anti*-prism geometry configuration, among which four oxygen atoms as well as one nitrogen atom from three H₃Pimda ligands, one oxygen atom from Himba ligand and other two oxygen atoms from water molecules. The coordination sphere around Eu2 ions is occupied by five oxygen atoms from three H₃Pimda ligands, one oxygen atom from Himba ligand and two oxygen atoms from two coordinated water molecules, which complete the distorted tetragonal *anti*-prism (as shown in Fig. 3(b)). Bond distance of Eu1—N is found to be 2.584(7) Å. The Eu(III)—O bond distances range from

2.329(6) Å to 2.627(7) Å. Bond angles of O—Eu(III)—O are in the range of 50.85(19)° and 152.56(17)° (see Table 2, in Supplementary Information for details). In H₃Pimda ligand, the protonation of carboxylic group and imidazole group adopt as $\mu_4-kO: kO, O': kO: kO, N'$ modes connecting four Eu(III) centers in bridging and cheating modes, as illustrated in Scheme 1(a). It is remarkable that two coordinated water molecules (O11, O11A (A: 1 - x, 1 - y, 1 - z)) are linked with three Eu(III) ions (Eu1A, Eu2A, Eu2), respectively, which leads to Eu2, O11, Eu2A and O11A forming a parallelogram array. In this parallelogram, the Eu2—O11 bond distances are 2.495 Å and 2.396 Å, and the bond angles of O11—Eu2—O11A and Eu2—O11—Eu2A are 69.28° and 110.72°, respectively. Meanwhile, oxygen atoms (O3, O10, O11, O11A) linked with Eu1, Eu2 and Eu2A, forming a vertical deficient cubane like array [21]. The adjacent crystallographic symmetry oxygen atoms connected three Eu(III) ions (Eu1A, Eu2, Eu2A) forming a vertical deficient cubane

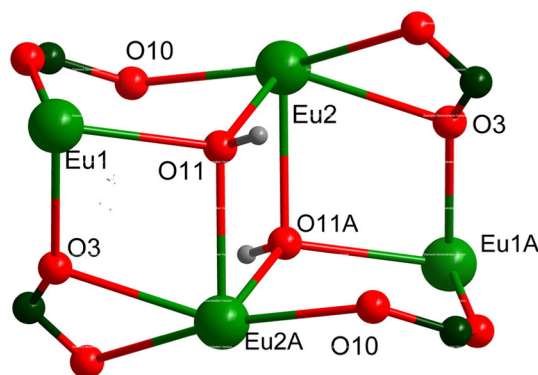
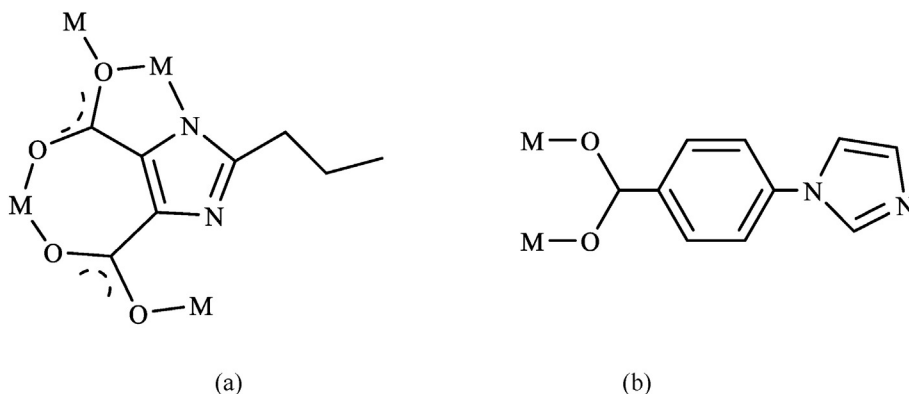


Fig. 2. Scheme displaying tetranuclear cluster linked by carboxylic group and coordinated waters.

like array. The two neighboring deficient cubanes share a common plane (composed of Eu2, O11, Eu2A, O11A) and form a tetranuclear {Eu₄} cluster (as described in Fig. 2). In this cluster, four adjacent Eu(III) ions form a parallelogram-core. Among which, adjacent Eu1 and Eu2 are linked by carboxylic bridging (O—C—O) from Himba ligand and oxygen atom from H₃Pimda ligand in cheating mode, resulting in the Eu1—Eu2 distance of only 3.817 Å and Eu1A—Eu2 distance is found to be 4.333 Å, as well as two complementary interior alternate angles Eu1—Eu2—Eu1A [121.23°] and Eu2—Eu1—Eu2A [58.77°], respectively. These tetranuclear {Eu₄} clusters are further connected by carboxylic group from Himba ligands into 1-D ribbon-double chain, as illustrated in Fig. 3(a). These chains are further linked by H₃Pimda ligands, propagating infinitely along the *ab* plane to produce a 2-D corrugated layer structure, as shown in Fig. 4. These grids are further connected by weak interaction to fabricate 3-D framework structure. After hypothetical removal of the guest and coordination water molecules, the total potential solvent accessible void was found to be 138.2 Å³ per cell volume for the 3-D non-interpenetrating framework (accounting for 8.6% of the total unit cell system, volume of 1614.4 Å³) [22].

In the IR spectrum of **1**, the weaker absorption peaks in the frequency region of 3100–3500 cm⁻¹ are attributed to O—H unsaturated stretching vibration of water molecules. The sharp bands in the ranges of 1601–1505 and 1462–1385 cm⁻¹ are attributed to asymmetric and symmetric stretching vibrations of carboxylic group, respectively [23].

To verify presence of water molecules of the title complex and evaluate its thermal stability, it was further investigated by thermo-gravimetric/differential thermal analysis (TG-DTA) under N₂ atmosphere with a heating rate of 10 °C min⁻¹ in the temperature range of 30–900 °C. As indicated in Fig. 5, the DTA curve reveals that the decomposition of complex **1** is a gradually exothermic process. The TG curve displays the initial weight loss of 7.11% (calculated: 7.39%) in the



Scheme 1. Coordination modes of H₃Pimda ligand and Himba ligand in complex **1**.

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