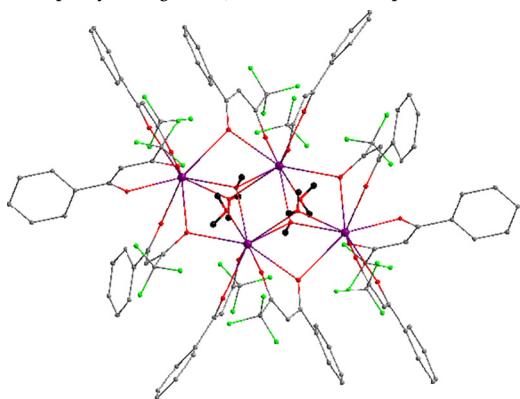


Short communication

Luminescence homoleptic cyclic tetranuclear $[\text{Ln}_4(\text{BTFA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$ complexes (Ln = Eu or Tb)Kaimeng Zhang^{a,1}, Xingmei Zhang^{b,1}, Jin Zhou^a, Guorui Fu^a, Yani He^a, Baoning Li^a, Xingqiang Lü^{a,*}^a School of Chemical Engineering, Shaanxi Key Laboratory of Degradable Medical Material, Northwest University, Xi'an 710069, Shaanxi, China^b School of Chemistry and Chemical Engineering, Xi'an University, Xi'an 710065, Shaanxi, China

GRAPHICAL ABSTRACT

For Eu^{3+} - or Tb^{3+} -centered luminescent tetranuclear complex $[\text{Ln}_4(\text{BTFA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$ (Ln = Eu, **2** or Tb, **3**) with the η^2 -Mode I and the $\mu(\text{O})$ - η^2 -bridging Mode II bonding of the $(\text{BTFA})^-$ ligands, two $\mu_3\text{-OH}^-$ anions, two μ_1 -coordinating H_2O and two μ_2 -bridging H_2O molecules surrounded from the four Ln^{3+} ions, color-purity red-light ($\Phi_{\text{Eu}}^{\text{L}} = 20.1\%$) for complex **2** while few near-white-light ($\Phi_{\text{em}} = 6.4\%$) for complex **3** are exhibited, respectively.



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ABSTRACT

Through self-assembly of the typical β -diketonate ligand **HBTF**A (**HBTF**A = 4,4,4-trifluoro-1-phenyl-1,3-butanedione) with $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ in the presence of Et_3N , the six-tenth in the η^2 -Mode I and the four-tenth in the $\mu(\text{O})$ - η^2 -bridging Mode II of the ten BTFA^- ligands, together with the involvement of two $\mu_3\text{-OH}^-$ anions, two μ_1 -coordinating H_2O and two μ_2 -bridging H_2O molecules, endow the formation of homoleptic cyclic tetranuclear complexes $[\text{Ln}_4(\text{BTFA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$ (Ln = La, **1**; Eu, **2**; Tb, **3** or Gd, **4**), respectively. Moreover, attributing to effective ligand-to- Ln^{3+} transfer energy, color-purity red-light ($\Phi_{\text{Eu}}^{\text{L}} = 20.1\%$) for complex **2** while few near-white-light ($\Phi_{\text{em}} = 6.4\%$) for complex **3** are exhibited, respectively, despite the $(\mu_3\text{-OH})^-$ - and H_2O -induced OH-oscillators surrounded from the four Ln^{3+} ions.

In contrast to mononuclear structure of either *tris*- β -diketonate- Ln^{3+} -complexes [**1**] or *tetrakis*- β -diketonate- Ln^{3+} -complexes [**2**] with

three or four enolic β -diketonate ligands in a typical O[•]O-chelating mode (η^2 -Mode-I, Scheme 1), self-assembly of the homoleptically

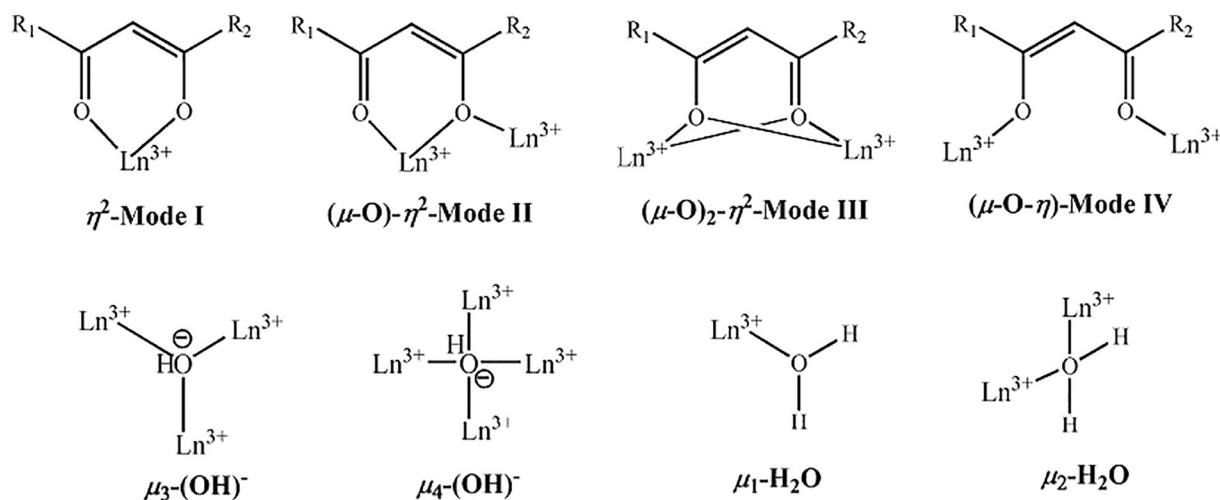
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Scheme 1. The bonding modes of the β -diketonate ligand, the $(\text{OH})^-$ anion and the coordinated H_2O molecule in polynuclear Ln^{3+} - β -diketone complexes.

polynuclear Ln^{3+} - β -diketone-complex with a predetermined structure is much challenging. From the viewpoint of synthetic strategies, Ln^{3+} -hydrolysis [3] or organic-base-deprotonation [4] gives hydrophilic hydroxo ($(\text{OH})^-$) and/or oxo ($(\text{O})^{2-}$) bridging to Ln^{3+} ions for a cluster core, from which, the ligation of several β -diketonate ligands with η^2 -Mode-I-included multiple bonding modes ($(\mu\text{-O})$ - η^2 -Mode-II, $(\mu\text{-O})_2$ - η^2 -Mode-III and $(\mu\text{-O-}\eta)$ -Mode-IV also in Scheme 1) in the outer-cluster periphery is favorable for the formation of a Ln^{3+} - β -diketone-hydroxo/oxo complex species. As to its finite-sized polynuclear complex, the structural diversity is highly dependent with the complicated effects of high and variable coordination number of the Ln^{3+} ion, steric hindrance of the β -diketone-type ligand as well as specific self-assembling reaction condition (pH, solvent or stoichiometry etc). Nonetheless, in consideration of the significant spin-orbit coupling between multiple Ln^{3+} ions within, concerted efforts have been devoted to homoleptically polynuclear Ln^{3+} - β -diketone complexes with desirable optical [5] and magnetic properties [6].

As a matter of fact, higher-nuclearity up to nonanuclear ($[\text{Ln}_9(\text{acac})_{16}(\text{OH})_9(\text{O})]$ [7] or $[\text{Y}_{9-x}\text{Ln}_x(\text{acac})_{16}(\text{OH})_9(\text{O})]$ [8] with η^2 -Mode-I for the coordinated acac^- ligands, $(\mu_3\text{-OH})_8$ and $(\mu_4\text{-OH})$ for nine $(\text{OH})^-$ anions and one $(\mu_4\text{-O})^{2-}$ anion; also shown in Scheme 1) or tetradecanuclear [9] cluster ($[\text{Ln}_{14}(\text{acac})_{24}(\text{OH})_{18}]$ with η^2 -Mode-I for the sixteen and $(\mu\text{-O})$ - η^2 -Mode-II for the eight of the twenty-four coordinated $(\text{acac})^-$ ligands, $(\mu_3\text{-OH})_{16}$ and $(\mu_4\text{-OH})_2$ for eighteen $(\text{OH})^-$ anions), is exclusively limited from the smallest hindrance β -diketone ligand Hacac (acetylacetonate). In contrast, the involvement of solvents in the inner-cluster core restrains the core's further aggregation with the decreased tetranuclear clusters ($[\text{Ln}_4(\text{acac})_8(\text{OCH}_3)_2(\text{CH}_3\text{OH})_2(\mu_3\text{-OH})_2]$) [10]. The rigid β -diketone ligand HDBM (dibenzoylacetonate) is commonly facilitated to exhibit tetranuclear [11] ($[\text{Ln}_4(\text{DBM})_{10}(\text{OH})_2]$ with η^2 -Mode-I for the four and $(\mu\text{-O})$ - η^2 -Mode-II for the six of the ten coordinated $(\text{DBM})^-$ ligands, $(\mu_3\text{-OH})_2$ for the two $(\text{OH})^-$ anions) to pentanuclear [12,13] ($[\text{Ln}_5(\text{DBM})_{10}(\text{OH})_5]$) with η^2 -Mode-I for the six and $(\mu\text{-O})$ - η^2 -Mode-II for the two and $(\mu\text{-O})_2$ - η^2 -Mode-III for the two of the ten coordinated $(\text{DBM})^-$ ligands, $(\mu_3\text{-OH})_4$ and $(\mu_4\text{-OH})$ for the five $(\text{OH})^-$ anions) Ln^{3+} -DBM-hydroxo complexes, where their nuclearity change is strictly relied on the relative ionic radius (lanthanide contraction) [14,15]. Actually, in accompany with the few tetranuclear [16] to octanuclear [17] and to nonanuclear [4] examples of Ln^{3+} - β -diketone-hydroxo/oxo complexes based on other typical β -diketone ligands (hfpd-H (1,1,1,5,5,5-hexafluoropentane-2,4-dione), Hthd (2,2,6,6-tetramethylheptane-3,5-dione) and HBA (benzoylacetonate)) with modest hindrance effects, to the best of our knowledge, the construction of β -diketone ligand **HBTFa**'s Ln^{3+} -clusters was also not reported. Herein, we report the series of new complexes $[\text{Ln}_4(\text{BTfA})_{10}(\mu_3$ -

$\text{OH})_2(\text{H}_2\text{O})_4]$ ($\text{Ln} = \text{La}$, **1**; Eu , **2**; Tb , **3** or Gd , **4**), where the incorporation (also in Scheme 1) of the η^2 -Mode I and the $(\mu\text{-O})$ - η^2 -bridging Mode II for the **BTfA** $^-$ ligands, two μ_3 - $(\text{OH})^-$ anions, two μ_1 -coordinating H_2O and two μ_2 -bridging H_2O molecules, contributes to the formation of their same homoleptic cyclic tetranuclear framework. Moreover, in consideration of the $^3\pi\text{-}\pi^*$ level ($\sim 20,800\text{ cm}^{-1}$) of **HBTFa** higher than the $^5\text{D}_0$ resonance level ($17,286\text{ cm}^{-1}$) of Eu^{3+} ion and the $^5\text{D}_4$ resonance level ($20,545\text{ cm}^{-1}$) of Tb^{3+} ion, effective sensitization of Eu^{3+} - or Tb^{3+} -centered characteristic luminescence is also discussed.

Through the treatment of the typical β -diketone ligand **HBTFa** with access Et_3N , the enolic β -diketonate ligand **BTfA** $^-$ was further self-assembled with $\text{LnCl}_3\cdot 6\text{H}_2\text{O}$ ($\text{Ln} = \text{La}$, Eu , Tb or Gd) at a stipulated molar ratio of 5:2 in a CHCl_3 -MeOH solution, resulting in the formation of complexes $[\text{Ln}_4(\text{BTfA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$ ($\text{Ln} = \text{La}$, **1**; Eu , **2**; Tb , **3** or Gd , **4**) soluble in common solvents except water, respectively. The four complexes **1–4** were well-characterized by EA, FT-IR, ^1H NMR and ESI-MS (in Supporting information (SI)). Molecular structure of $[\text{La}_4(\text{BTfA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]\cdot 4(\text{H}_2\text{O})\cdot (\text{CHCl}_3)$ (**1-4**· $(\text{H}_2\text{O})\cdot (\text{CHCl}_3)$), as the representative of complexes **1–4**, was obtained by single-crystal X-ray diffraction analysis with crystallographic data in Tables 1–2S (SI). Complex **1-4**· $(\text{H}_2\text{O})\cdot (\text{CHCl}_3)$ crystallizes in the triclinic space group P-1, and the structural unit is composed of one neutral molecule $[\text{La}_4(\text{BTfA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$, four solvates H_2O and one solvate CHCl_3 . As shown in Fig. 1a, for the host part $[\text{La}_4(\text{BTfA})_{10}(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4]$ lying about an inversion center, two equivalent $[\text{La}_2(\text{BTfA})_5(\mu_3\text{-OH})(\text{H}_2\text{O})_2]$ moieties are bridged by two O- β -diketonate atoms (O10 and O10a) of two **BTfA** $^-$ ligands and two O atoms (O5 and O5a) of two coordinated μ_3 - $(\text{OH})^-$ (also in Scheme 1) anions, leading to the formation of a homoleptic cyclic tetranuclear framework. In each of the two equivalent $[\text{La}_2(\text{BTfA})_5(\mu_3\text{-OH})(\text{H}_2\text{O})_2]$ moieties, two La^{3+} ($\text{La}1$ and $\text{La}2$) ions with the same nine-coordinate while different coordination environments (Fig. 1b) also link by one O- β -diketonate atom (O4) of one **BTfA** $^-$ ligand, one O- μ_3 - $(\text{OH})^-$ atom (O5) and one O atom (O2w) of one μ_2 -bridging H_2O molecule (also in Scheme 1). For the surrounding of $\text{La}1$ ion, besides two O atoms (O1 and O2) from one bidentate chelating (η^2 -Mode I, in Scheme 1) **BTfA** $^-$ ligand and three O atoms (O3, O4 and O10a) from two different tri-bridging $(\mu\text{-O})$ - η^2 -Mode II, in Scheme 1) **BTfA** $^-$ ligands, it saturates its coordination environment with two O- μ_3 - $(\text{OH})^-$ atoms (O5 and O5a), one O atom (O2w) of one μ_2 -bridging H_2O molecule and one O atom (O1w) of one μ_1 -coordinating H_2O molecule (Scheme 1). In contrast, four **BTfA** $^-$ ligands with two in the η^2 -Mode I and the other two in the $(\mu\text{-O})$ - η^2 -Mode II, provide seven O atoms binding to the $\text{La}2$ ion, while the rest are occupied by one O- μ_3 - $(\text{OH})^-$ atoms (O5) and one O atom (O2w) of the

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