

## Metal-Controlled Assembly of Near-Infrared-Emitting Pentanuclear Lanthanide $\beta$ -Diketone Clusters

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Metal-controlled assembly results in a series of lanthanide clusters with the formula of  $\text{Ln}_5(\text{DBM})_{10}(\text{OH})_5 \cdot n(\text{solvent})$  (DBM = dibenzoylmethanido; Ln = Nd (1), Gd (2), Er (3), and Yb (4); solvent =  $\text{CH}_3\text{CN}$  or toluene). These pentanuclear clusters with square-pyramidal core structures have been characterized by X-ray diffraction analysis. Clusters 1, 3, and 4 show typical near-infrared (NIR) luminescence upon excitation at 350 nm, which represents the first examples of pentanuclear lanthanide clusters with sensitized NIR emission.

The design and synthesis of lanthanide clusters has attracted increasing attention as a result of the various symmetries and structural patterns that are possible to observe and fascinating properties, as well as potential applications as phosphors for fluorescent lighting, X-ray imaging, amplifiers for fiber-optic communication, luminescent tags for biological molecules, and contrast agents for magnetic resonance imaging.<sup>1–4</sup> Unfortunately, the chemistry of lanthanide clusters is not as well-developed as that of transition metals. While the general synthetic guidelines of high-symmetry coordination clusters have been achieved for transition metals, it is difficult to predict or control the structures of polynuclear assemblies based on lanthanide ions because there is a lack of strong stereochemical preferences, which leads to high and variable coordination numbers with geometries based principally on steric interactions between ligands.<sup>5–8</sup>

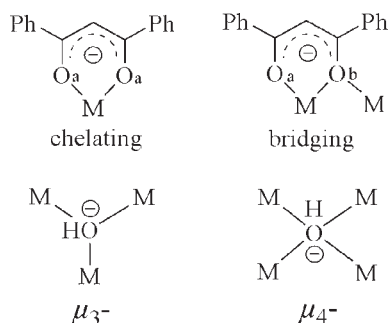
In general, the methodologies known to select for high-nuclearity clusters involve two synthetic pathways: one way is the controlled hydrolysis of air- and moisture-sensitive metal precursors, whereas the other is utilization of suitable ligands and coligands that coordinate to the metal centers, preventing infinite hydrolysis and thereby preventing the formation of highly insoluble and intractable materials.<sup>9,10</sup> Though these synthetic pathways have been extensively used to build high-nuclearity transition-metal clusters, the lanthanide counterparts still need to be explored in detail. The multinuclear clusters of lanthanides reported in the literature involve the use of flexible coordinating ligands like alkoxides, phenoxides, diketones, and more recently amino acids and *o*-nitrophenols.<sup>11–13</sup> We are especially interested in the near-infrared (NIR)-emitting lanthanide clusters with diketones, which have been recognized as efficient sensitizers for lanthanides.<sup>14</sup> The NIR-emitting lanthanides have been of particular interest in the past few years because of the numerous applications of NIR luminescence in telecommunications and medical imaging.<sup>14</sup> Despite the great potential of NIR lanthanide emission, lanthanide clusters with Nd, Er, and Yb have not been widely studied.<sup>15</sup> Furthermore, NIR-emitting lanthanide clusters that have been fully characterized photo-physically are even more rare.<sup>16</sup> Herein, a new method,

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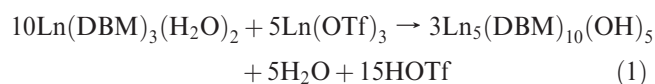
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Chart 1

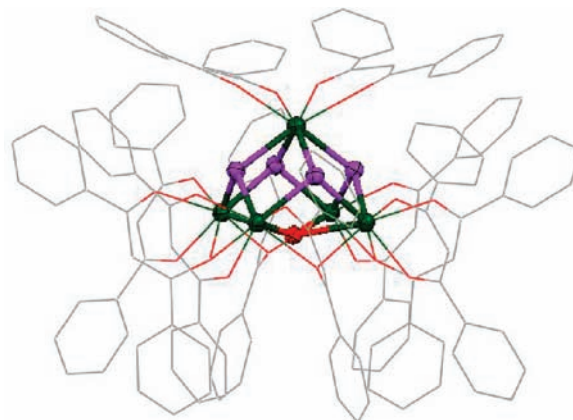


namely, metal-controlled assembly, is reported that can be used to prepare lanthanide  $\beta$ -diketone clusters in a rational way. In contrast to the one-pot synthesis of ligand-controlled hydrolysis, we first synthesize the lanthanide precursor  $\text{Ln}(\text{DBM})_3(\text{H}_2\text{O})_2$ , where  $\text{Ln} = \text{Nd}, \text{Gd}, \text{Er}, \text{and Yb}$  and  $\text{DBM} = \text{dibenzoylmethanido}$ , and then the coordinated water molecules are hydrolyzed under the control of additional  $\text{Ln}(\text{OTf})_3$  ( $\text{OTf} = \text{trifluoromethanesulfonate}$ ; reaction 1), which provides the pH adjustment and at the same time offers the metal source for cluster formation. Specifically, 2 equiv of  $\text{Ln}(\text{DBM})_3(\text{H}_2\text{O})_2$  were suspended in  $\text{CH}_3\text{CN}$  or toluene, and the addition of 1 equiv of  $\text{Ln}(\text{OTf})_3$  into the above suspension results a clear solution under mild heating. A series of pentanuclear lanthanide clusters with the composition  $\text{Ln}_5(\text{DBM})_{10}(\text{OH})_5 \cdot n(\text{solvent})$  (**1**,  $\text{Ln} = \text{Nd}$ ,  $n = 2$ , solvent = toluene; **2**,  $\text{Ln} = \text{Gd}$ ,  $n = 5$ , solvent =  $\text{CH}_3\text{CN}$ ; **3**,  $\text{Ln} = \text{Er}$ ,  $n = 2$ , solvent = toluene; **4**,  $\text{Ln} = \text{Yb}$ ,  $n = 2$ , solvent = toluene) were isolated in  $\sim 70\%$  yield. These complexes have been characterized by combustion analysis and single-crystal X-ray diffraction.

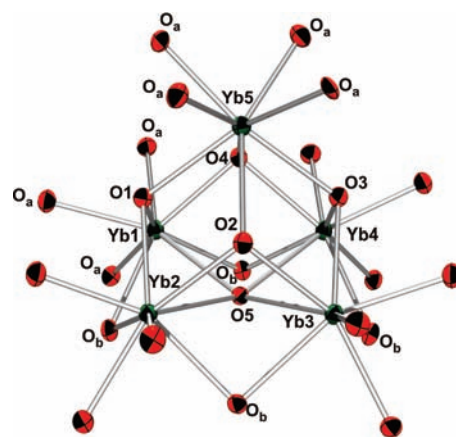


The lanthanide series can be divided into three groups according to mass and size: the lighter and larger La–Pm (group 1), the intermediate Sm–Dy (group 2), and the heavier but smaller Ho–Lu (group 3). Although the ions used in this study (i.e., lighter and bigger  $\text{Nd}^{3+}$ , intermediate  $\text{Gd}^{3+}$ , and heavier and smaller  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$ ) span the entire lanthanide series, the formation of isostructural clusters **1–4** represents a significant result and a departure from conventional thoughts regarding the structural parameters of lanthanide clusters being dominated by size and/or relative ionic charges. The photophysical studies of **1**, **3**, and **4** show sensitized NIR luminescence. As far as we know, these are the first examples of pentanuclear clusters with sensitized NIR emission.

Complex **4** is selected as a representative example of the isostructural crystal structures (Figure 1). Cluster **4** crystallizes in the tetragonal space group  $P4/n$ . The cluster **4** displays a highly regular square-based pyramidal arrangement of five  $\text{Yb}^{\text{III}}$  atoms. Each face of the square pyramid is capped by a  $\mu_3\text{-OH}^-$  group. Each Yb ion is coordinated to eight O atoms to form a local square-antiprism geometry around each metal center. A total of 10 peripheral ligands surrounding the cluster core show two different coordination modes. Six ligands are in terminal bidentate chelating modes and four are in bridging modes (Chart 1). Each Yb atom (e.g., Yb1) in



**Figure 1.** ORTEP diagram of **4** showing the selected atoms at the 30% probability level. H atoms and solvent molecules are omitted for clarity. Color code: green, Yb; red,  $\mu_4\text{-OH}^-$ ; purple,  $\mu_3\text{-OH}^-$ .

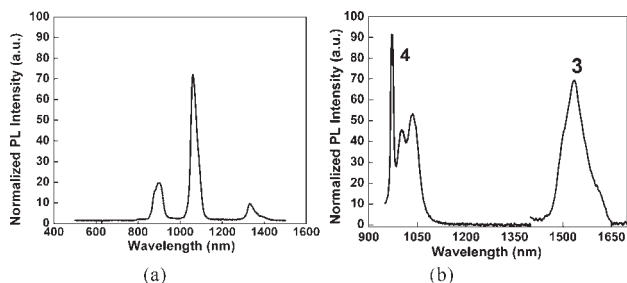


**Figure 2.** ORTEP diagram of **4** showing the labeling scheme of selected atoms at the 30% probability level. H atoms, toluene, and DBM ligands are omitted for clarity.

the square-pyramidal base is bound to two O atoms ( $\text{O}_a$ ) from a chelating DBM ligand, three (one  $\text{O}_a$  and two  $\text{O}_b$ ) from two bridging ligands, and two from  $\mu_3\text{-OH}^-$  ( $\text{O1}$  and  $\text{O4}$ ) as well as one from  $\mu_4\text{-OH}^-$  ( $\text{O5}$ ) (Figure 2). The apical Yb atom is linked to four O atoms ( $\text{O}_a$ ) from two chelating DBM ligands and four from  $\mu_3\text{-OH}^-$  ( $\text{O1}$ ,  $\text{O2}$ ,  $\text{O3}$ , and  $\text{O4}$ ). In the central  $\text{Yb}_5$  square pyramid, the Yb–Yb distances in the  $\text{Yb}_4$  base are shorter (ave = 3.4849 Å) than the distances to the pyramid apex Yb (ave = 3.7740 Å).

Even though the lanthanide elements are similar to each other in chemistry, finding the same structural motif in the whole lanthanide series is uncommon. The effect of the lanthanide contraction may play an important role in the formation of the structures of the complexes. Especially in lanthanide cluster chemistry, the formation of isostructural complexes across the whole lanthanide series is rather rare. A pentanuclear europium cluster with DBM has been reported by ligand-controlled hydrolysis.<sup>17</sup> However, the diketone clusters of other lanthanide elements were not reported. Our synthetic strategy reveals the consistent cluster formation behavior from Nd to Yb, providing easy and systematic access to the lanthanide hydroxo clusters by metal-controlled assembly.

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**Figure 3.** (a) Emission spectrum of cluster **1** in DCM at room temperature. (b) Emission spectra of clusters **3** and **4** in DCM at room temperature.

Absorption spectra of complexes **1–4** in acetonitrile were measured at room temperature. The UV–vis absorption behavior of these clusters is not significantly changed compared to that of the free DBM ligand. The UV absorption spectra show one principle  $\pi-\pi^*$  absorption peak at 350 nm, which is assigned as absorption of the DBM ligand. The molar absorption coefficients of **1–4** at 350 nm are  $1.33 \times 10^5$ ,  $1.67 \times 10^5$ ,  $1.82 \times 10^5$ , and  $1.71 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>, respectively, showing the strong absorptivity of these complexes. The increased molar absorption coefficients of the complexes compared to that of the Ln(DBM)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> precursor (ca.  $6.9 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) also indicate the effect of lanthanide cluster formation.

At room temperature in a DCM solution, the emission spectrum of complex **1** (Figure 3a), when excited at 350 nm, shows the exclusive NIR emission bands characteristic of Nd<sup>3+</sup>, with the three lines at 896, 1061, and 1332 nm corresponding to transitions from <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>J/2</sub> (*J* = 9, 11, and 13, respectively). The excitation spectrum of complex **1**, monitored at an emission wavelength of 1061 nm, closely matched the absorption spectrum of the DBM ligand. This indicates that, upon photoexcitation of the DBM ligand, the excitation energy was mainly absorbed by the DBM ligand and then transferred to the Nd<sup>3+</sup> ion. Time-resolved experiments were also performed by excitation of a DCM solution of **1** and monitoring of the decay of the emission of the strongest emission band at 1061 nm, resulting in an excited-state lifetime of 8.29 μs. An estimated quantum yield of **1** may be calculated by a comparison of the luminescence lifetime of **1** with the natural lifetime of Nd<sup>3+</sup>. By using  $\Phi = \tau/\tau_0$ , a value of 3.07% for the quantum yield of **1** is calculated, given a value  $\tau_0$  for the natural lifetime of Nd<sup>3+</sup> = 270 μs.<sup>18</sup> The Er<sup>3+</sup> cluster (**3**) also shows a strong NIR emission band at 1535 nm (Figure 3b), which originates from the 4f–4f electronic transition of the first excited state (<sup>4</sup>I<sub>13/2</sub>) to the ground state (<sup>4</sup>I<sub>15/2</sub>) of the partially filled 4f shell.

The luminescence of the ytterbium cluster **4** is characterized by an emission band at 972 nm (Figure 3b), which is

assigned to the <sup>2</sup>F<sub>5/2</sub> → <sup>2</sup>F<sub>7/2</sub> transition. Note that the Yb<sup>3+</sup> emission in **4** is not a single sharp transition, but rather it appears as a series of bands with two other broad bands centered at 1002 and 1035 nm. A similar splitting had been reported previously and is attributed to the crystal-field or Stark splitting.<sup>19</sup> The absolute quantum yield of **4** had been measured upon ligand excitation (350 nm) by using [Yb(tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>] as a reference.<sup>20</sup> The quantum yield of **4** is 0.61%, which is consistent with other published data, for instance, 1.8% for a bimetallic helicate in D<sub>2</sub>O,<sup>21</sup> 0.5% for a terphenyl-based complex in dimethyl sulfoxide,<sup>22</sup> or 0.31% for a complex with 4,4-difluoro-8-(2′:2′′;6′′:2′′′-terpyridin-4′′-yl)-1,3,5,7-tetramethyl-2,6-diethylbora-3a,4a-diaza-*s*-indacene in DCM.<sup>23</sup> The emission lifetime of **4** was determined to be  $\tau = 9.95$  μs, which, to the best of our knowledge, is the longest for ytterbium clusters reported to date.<sup>14</sup> The quantum yield of **4** estimated from the luminescence lifetime is 0.50%. The quantum efficiency increase agrees well with the corresponding lengthening of the emission lifetime, as seen in other lanthanide complexes.<sup>24</sup> The high quantum yields and long lifetimes may be due to the stabilized cluster structure.

In summary, we have explored the metal-controlled synthesis of NIR-emitting lanthanide clusters. A series of pentanuclear clusters with square-pyramidal core structures have been characterized by X-ray diffraction analysis. The consistent formation of isostructural clusters through the whole lanthanide series bodes well for the further application of this method with other  $\beta$ -diketone ligands. Complexes **1**, **3**, and **4** emit strong NIR luminescence at room temperature upon excitation of the DBM ligand, which provides important information for the NIR emission studies of lanthanide clusters. Further efforts utilizing different diketone ligands and the general synthetic strategy reported herein are underway.

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**Supporting Information Available:** Experimental details for the synthesis and characterization of **1–4**, spectroscopic details, X-ray diffraction tables, and crystallographic data for **1–4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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