## ChemComm

## COMMUNICATION



Cite this: Chem. Commun., 2014, 50, 14728

Received 6th September 2014, Accepted 7th October 2014

DOI: 10.1039/c4cc07047j

www.rsc.org/chemcomm

## Reversible transformation between chiral and achiral Dy<sub>6</sub>Mo<sub>4</sub> clusters through a symmetric operation<sup>†</sup>

Yong Zheng, Yin-Yin Pan, Yan-Ping Ren, La-Sheng Long,\* Rong-Bin Huang and Lan-Sun Zheng

Three polynuclear lanthanide clusters:  $(NH_4)_2[Dy_6Mo_4O_{12}(rac-L^{3-})_4-(OOCCH_3)_8]\cdot4CH_3OH\cdot6H_2O$  (I),  $(Et_3NH)_2[Dy_6Mo_4O_{12}(rac-L^{3-})_4-(OOCCH_3)_8]\cdot18H_2O$  (II), and  $(Me_4N)_2[Dy_6Mo_4O_{12}(rac-L^{3-})_4(OOCCH_3)_8]\cdotCH_3OH\cdot14H_2O$  (III) (H\_3L = (E)-2-((2,3-dihydroxypropylimino)methyl)-phenol) were synthesized. Single-crystal analysis reveals that cluster I crystallized in the centrosymmetric space group  $(P4_2/n)$ , while clusters II and II crystallized in the chiral space group  $(P3_121)$  or  $P3_221$ ), and cluster I can be transformed into clusters II and III, when  $Et_3NH^+$  and  $Me_4N^+$ , respectively, are used to replace  $NH_4^+$ . Investigation on the solid-state vibrational circular dichroism (VCD) spectra shows that the clusters II and III are homochiral crystallization. Powder X-ray diffraction study demonstrates that the transformation between chiral and achiral clusters is reversible.

Chirality is ubiquitous in nature and plays a paramount role in the fields of biology,<sup>1</sup> medicine,<sup>2</sup> and materials science.<sup>3</sup> Although chirality can be obtained from chiral components through chiral transmission, the induction of chirality from achiral components coupled with spontaneous resolution is undoubtedly more attractive because it not only is related to the origin of homochirality in nature<sup>4</sup> but also significantly enriches chiral compounds; this enrichment, in turn, expands their potential applications in asymmetric catalysis,<sup>5</sup> enantioselective separation,<sup>6</sup> and noncentrosymmetric materials.7 In an effort to prepare chiral compounds from achiral components, chemists have developed several synthetic strategies, including the use of achiral components to construct helical compounds and generate chiral compounds,<sup>8</sup> the use of achiral multidentate ligands to prepare fan-type metal complexes and form chiral compounds,9 the use of flat twists of rigid achiral ligands to generate chiral compounds,<sup>10</sup> and the use of a symmetry breaker to induce the formation of chiral compounds.<sup>11</sup> Nevertheless, only 5–10% of racemates crystallize as conglomerates,<sup>12</sup> and this crystallization is stochastic.<sup>13</sup> Thus, the assembly of chiral compounds from achiral components remains a great challenge.<sup>14</sup>

Because of the broad applications of polynuclear lanthanide clusters in molecule-based magnetic materials,15 artificial nucleases for the hydrolytic cleavage of DNA and RNA,<sup>16</sup> contrast agents for magnetic resonance imaging,<sup>17</sup> and fixation media for atmospheric CO2,<sup>18</sup> research related to these clusters has been a topic of rapid growth in coordination and materials chemistry. Moreover, chiral polynuclear lanthanide clusters can promote magnetochiral dichroism or induce ferroelectric and piezoelectric properties, which make them highly desirable candidates for modern multifunctional materials.<sup>19</sup> However, chiral polynuclear lanthanide clusters constructed from achiral components remain rare.19d,e Here, we report the syntheses and crystal structures of three polynuclear lanthanide clusters: (NH<sub>4</sub>)<sub>2</sub>[Dy<sub>6</sub>Mo<sub>4</sub>O<sub>12</sub>(rac-L<sup>3-</sup>)<sub>4</sub>- $(OOCCH_3)_8$ ]·4CH<sub>3</sub>OH·6H<sub>2</sub>O (I),  $(Et_3NH)_2$ [Dy<sub>6</sub>Mo<sub>4</sub>O<sub>12</sub>(rac-L<sup>3-</sup>)<sub>4</sub>- $(OOCCH_3)_8$  18H<sub>2</sub>O (II), and  $(Me_4N)_2$   $[Dy_6Mo_4O_{12}(rac-L^{3-})_4 (OOCCH_3)_8$   $\cdot CH_3OH \cdot 14H_2O$  (III)  $(H_3L = (E) \cdot 2 \cdot ((2, 3 \cdot dihydroxy \cdot 1)))$ propylimino)methyl)-phenol, ESI,† Fig. S1). Single-crystal analysis reveals that cluster I, with  $S_4$  symmetry, can be transformed into chiral clusters II and III, with  $C_2$  symmetry, when Et<sub>3</sub>NH<sup>+</sup> and  $Me_4N^+$ , respectively, are used to replace  $NH_4^+$ . More significantly, the transformation between chiral and achiral clusters is reversible, demonstrating for the first time that a reversible transformation between chiral and achiral clusters can be realized through a symmetric operation of molecules with  $S_4$  symmetry.

Cluster I was prepared through the solvothermal reaction of racemic ligand *rac*-H<sub>3</sub>L, Dy(CH<sub>3</sub>COO)<sub>3</sub>·3H<sub>2</sub>O, (*n*-Bu<sub>4</sub>N)<sub>4</sub>Mo<sub>8</sub>O<sub>26</sub>, and NH<sub>3</sub>·H<sub>2</sub>O in MeOH. Single-crystal X-ray diffraction studies revealed that cluster I crystallizes in the centrosymmetric space group  $P4_2/n$  (no. 86). The asymmetric unit of cluster I contains only one-fourth of the anionic cluster [Dy<sub>6</sub>Mo<sub>4</sub>O<sub>12</sub>(*rac*-L<sup>3-</sup>)<sub>4</sub>-(OOCCH<sub>3</sub>)<sub>8</sub>]<sup>2-</sup> (1) in *S*<sub>4</sub> symmetry (Fig. 1a), half of the disordered counter cation NH<sub>4</sub><sup>+</sup>, and half of a water molecule, located in the same position as the counter-cation NH<sub>4</sub><sup>+</sup>; it also contains disordered guest methanol and water molecules. Structurally, anionic cluster

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State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: lslong@xmu.edu.cn; Fax: +86 592 218 3047 † Electronic supplementary information (ESI) available: Experimental section, syntheses, crystallographic data and characterization details of I-III, Fig. S1-S8. CCDC 967301-967305. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc07047j



Fig. 1 (a) Ball-and-stick plot showing the structure of the anionic cluster  $[Dy_6Mo_4O_{12}(rac-L^{3-})_4(OOCCH_3)_8]^{2-}$ . (b) Ball-and-stick plot showing the neutral polyoxometalate unit of  $Mo_4O_{12}$ . (c) Ball-and-stick structure of the  $Dy_6Mo_4O_{12}$  core.

1 can be viewed as six Dy atoms bridged by a neutral polyoxometalate Mo<sub>4</sub>O<sub>12</sub> unit (Fig. 1b), forming a cationic Dy<sub>6</sub>Mo<sub>4</sub>O<sub>12</sub> core (Fig. 1c). The Dy<sub>6</sub>Mo<sub>4</sub>O<sub>12</sub> core is further solidified by four rac-L<sup>3-</sup> ligands (Harris notation: 3.2211, ESI,<sup> $\dagger$ </sup> Fig. S2)<sup>20</sup> and eight acetate ligands in 2.11 and 2.21 modes. Four of the six Dy atoms (Dy1) are eight-coordinated by an NO2 donor from one  $L^{3-}$  (*R* or *S* configuration) ligand, one O<sub>alkoxy</sub> atom from another  $L^{3-}$  ligand, two  $\mu_3$ -O atoms from the Mo<sub>4</sub>O<sub>12</sub> unit, and two O<sub>acetate</sub> atoms in a trigonal dodecahedral coordination geometry; the remaining Dy atoms (Dy2) are eight-coordinated by two  $\mu_3$ -O atoms from the  $\mathrm{Mo}_4\mathrm{O}_{12}$  unit and six  $\mathrm{O}_{\mathrm{acetate}}$  atoms from two 2.11 acetates and two 2.21 acetates in the same coordination geometry as Dy1. Each Mo atom in the Mo<sub>4</sub>O<sub>12</sub> unit is chelated by two  $O_{alkoxy}$  atoms from a  $L^{3-}$  ligand and four oxo atoms and displays a distorted octahedral coordination geometry. Anionic cluster 1 in I is hydrogen bonded to four half-occupied  $NH_4^+$  cations (O<sub>acetate</sub>···H–N 3.012(1) Å), forming neutral cluster I in  $S_4$  symmetry (Fig. 2a). Neutral cluster I is further connected to neighboring clusters through hydrogen bonding of  $O_{acetate} \cdots H-N(O)-H \cdots O_{methoxyl}-H \cdots O_{acetate}$  and/or  $O_{acetate}$ ···H-N(O)-H···O<sub>water</sub>-H···O<sub>acetate</sub>, crystallizing as achiral solids. The Dy-O and Mo-O bond distances in I are 2.179(3)-2.534(3) and 1.692(3)-2.052(3) Å, respectively; these distances are similar to the corresponding values of 2.354(6)-2.391(6) and 1.688(5)-2.318(5) Å in the previously reported Dy<sup>III</sup>-Mo<sup>VI</sup> cluster.<sup>21</sup> The shortest intramolecular and intermolecular Dy...Dy separations in I are 3.848(1) and 8.084(1) Å, respectively.

Because both anionic cluster **1** and cluster **I** are in  $S_4$  symmetry (Fig. 1a and 2a), the symmetry of cluster **I** is expected to be broken when the disordered NH<sub>4</sub><sup>+</sup> cations are replaced by larger-volume ammonium cations. Therefore, Et<sub>3</sub>N and Me<sub>4</sub>N-OH were used to replace NH<sub>3</sub>·H<sub>2</sub>O to synthesize the cluster under conditions similar to those described for **I**. Single-crystal structure analysis revealed that both **II** and **III** crystallized in a chiral space group [either  $P3_121$  (no. 152) or  $P3_221$  (no. 154)]. Unlike cluster **I**, each asymmetric unit in clusters **II** and **III** consists of half the anionic cluster **1**, one counter cation (Et<sub>3</sub>NH<sup>+</sup> for **II** or Me<sub>4</sub>N<sup>+</sup> for **III**), together with disordered guest water/methanol molecules. As shown in Fig. 2b, each anionic cluster **1** in **II** is connected to



**Fig. 2** (a) Achiral neutral molecule of  $(NH_4)_2[Dy_6Mo_4O_{12}(rac-L^{3-})_4[OOCCH_3]_6]$  of **I**. (b) A pair of enantiomers in **II**. (c) A pair of enantiomers in **III**.<sup>22</sup> Purple atoms in **I** refer to disordered  $NH_4^+$  and  $H_2O$  molecules. Hydrogen atoms are omitted for clarity.

two  $E_{13}NH^+$  cations through hydrogen-bonding interactions *via* two  $O_{molybdate}$  atoms  $(O_{molybdate} \cdots H-N = 2.883(0) \text{ Å})$  as proton acceptors, whereas each anionic cluster **1** in **III** is connected to two  $Me_4N^+$  cations through static interactions. As a result, the symmetry of clusters **II** and **III** is reduced from  $S_4$  to  $C_2$  symmetry, and both clusters **II** and **III** crystallize as conglomerates. A pair of enantiomers was observed in different crystals (Fig. 2b).

The Dy–O and Mo–O bond distances are 2.200(7)-2.516(11)and 1.693(8)-2.051(7) Å for **II** and 2.179(16)-2.523(12) and 1.692(8)-2.048(9) Å for **III**; these distances are similar to those of 2.179(3)-2.534(3) and 1.692(3)-2.052(3) Å for **I**. The shortest intramolecular Dy···Dy separations in **II** and **III** are 3.852(1)and 3.866(1) Å, respectively, and these distances are comparable to that of 3.848(1) Å in **I**. The shortest intermolecular Dy···Dy separations of 7.360(1) Å for **II** and 7.259(1) Å for **III** are significantly shorter than that of 8.084(1) Å in **I**.

Interestingly, centrosymmetric crystals of I can be readily and reversibly transformed into chiral crystals of II and III by ion-exchange at room temperature. As shown in Fig. 3, when crystals of I were dipped into a 1.0 mol L<sup>-1</sup> methanol solution of Et<sub>3</sub>NHOAc for 24 hours, their powder X-ray diffraction (PXRD) pattern (I-ion exchange) was the same as that of II (II-as synthesized), indicating that cluster I was transformed into chiral cluster II. More significantly, this transformation was reversible. When crystals of II were dipped into a 1.0 mol L<sup>-1</sup> methanol solution of NH<sub>4</sub>OAc for 24 hours, their PXRD pattern (II-ion exchange) was the same as that of I (I-as synthesized).



Fig. 3 Simulated PXRD patterns for I and II, and experimental PXRD patterns for I and II synthesized and for I and II prepared through ion exchange.

Similarly, when crystals of **I** were dipped into a 1.0 mol  $L^{-1}$  methanol solution of Me<sub>4</sub>NOAc for 48 hours, their PXRD pattern was the same as that of **III**. And, when crystals of **III** were dipped into a 1.0 mol  $L^{-1}$  methanol solution of NH<sub>4</sub>OAc for 48 hours, their PXRD pattern was the same as that of **I** (ESI,† Fig. S3).

Although chiral compounds constructed from achiral components and crystallized as conglomerates have been previously observed,  $^{19d,23}$  no precedent exists for a reversible transformation between chiral and achiral solids to the best of our knowledge. Unambiguously, the reversible transformation between achiral and chiral clusters in the present work is closely related to the  $S_4$ symmetry of the anionic cluster **1** as well as to hydrogen bonding and/or static interactions between anionic cluster **1** and the counter cations; these hydrogen bonds and/or static interaction not only lead to the cations in clusters of **I**, **II**, and **III** being easily replaced through ion exchange, but also result in the symmetric change.

To further confirm the homochiral crystallization of II and III in a single crystal, the optical activity of the clusters was investigated through measuring their solid-state CD spectra (KCl pellet) based on a single crystal. However, no significant CD signal was observed in the visible and ultraviolet region. In contrast, solid-state vibrational circular dichroism (VCD) spectra based on a single crystal (KBr pellet) display distinct VCD signals in the range from 1750 to 1400 cm<sup>-1</sup>, indicating that the cluster crystallizes in homochirality in a single crystal. As shown in Fig. 4, the positive and negative values correspond to the III in P3121 and P3221 space group, respectively. Based on the IR spectra of III, the VCD couplets at about 1650 and 1630 cm<sup>-1</sup> are attributable to the asymmetric C=O stretching vibrations of the acetate ligand in III.<sup>24</sup> The VCD couplets at 1560, 1540, 1520, 1510 and 1490 cm<sup>-1</sup> are assigned to the antisymmetrical stretching of the C=N bond and skeleton vibrations of the aromatic rings in the ligand of  $L^{3-}$  in III,<sup>25</sup> while the VCD couplet at about 1450 cm<sup>-1</sup> is ascribed to the bending vibrations of the methylene ( $\delta CH_2$ ) or methyl ( $\delta CH_3$ ) groups in III.<sup>26</sup> It was mentioned that the distinct VCD signals observed in III indicate that VCD spectra are a remarkable complementarity that can be used as an advantage when a particular system is investigated by the selection of chiroptical procedures.



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Fig. 4 Solid-state VCD (top) and IR spectra (bottom) of III. The VCD spectra were measured through a KBr pellet, in which, the mass ratio of homochiral crystal to KBr is 1:50.

The direct-current (DC) magnetic properties of polycrystalline samples of I-III were measured at an applied magnetic field of 1000 Oe. The  $\chi_M T$  for I–III at 300 K were 89.9, 88.4, and 86.9  $\text{cm}^3 \text{ mol}^{-1}$  K (ESI,† Fig. S4), respectively; these values are close to the expected value of 85.0 cm<sup>3</sup> mol<sup>-1</sup> K for six noninteracting Dy(III) ions (S = 5/2, L = 5,  ${}^{6}H_{15/2}$ , g = 4/3).<sup>27</sup> When the temperature was lowered, the  $\gamma_{M}T$  for I gradually decreased to 79.9 cm<sup>3</sup> mol<sup>-1</sup> K at *ca.* 12 K, which is ascribed primarily to the progressive depopulation of excited Stark sublevels.<sup>28</sup> At temperatures less than 12 K, the  $\chi_M T$  began to increase abruptly and reached 89.5 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K, which obviously suggests the presence of intramolecular ferromagnetic interactions between the metal centers.<sup>29</sup> Unlike the  $\chi_{M}T$  for I, those for II and III gradually decreased to 73.3  $\text{cm}^3 \text{ mol}^{-1}$  K for II and 75.2  $\text{cm}^3 \text{ mol}^{-1}$  K for III as the T was decreased to 2 K. The intramolecular  $Dy \cdots Dy$ separations in I were very similar to those in II and III, and the intermolecular Dy ... Dy separation in I was significantly longer than those in **II** and **III**; the difference between the  $\chi_{M}T$  vs. T curves of I, II, and III in the lower-temperature range is thus attributed to the significantly longer intermolecular separation in I compared to those in II and III and to antiferromagnetic dipole-dipole interactions between the clusters in **II** and **III**.<sup>30</sup> This deduction is consistent with the conclusion that intermolecular magnetic interaction can be influenced by intermolecular separation and interaction.31

The field (*H*) dependence of the magnetizations (*M*) of **I–III** at low temperatures (2–10 K) were also measured (ESI,† Fig. S5). The magnetization values at 2 K and 7 T for **I**, **II**, and **III** reached 35.4, 34.8, and 33.8  $N\mu_{\rm B}$ , respectively, without saturation, suggesting the presence of low-lying excited states. The lack of saturation of *M vs. H* suggests the presence of significant anisotropy and/or low-lying excited states for **I–III**, consistent with the observed non-superposition of the *M vs. H/T* curves at different magnetic fields (ESI,† Fig. S6).<sup>32</sup>

To investigate the dynamics of magnetization for I–III, alternating-current (ac) magnetic susceptibility measurements were performed over the temperature range 2.0–5.0 K with a

zero dc field at various frequencies from 1 to 1500 Hz (ESI,† Fig. S7). Clusters I to III displayed frequency-dependent in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) signals at temperatures less than 5.0 K, indicating the presence of slow relaxation of the magnetization that is characteristic of SMMs.<sup>33</sup> However, the out-of-phase ( $\chi''$ ) signal for I exhibited peaks at temperatures less than 2.8 K. In contrast, no such peaks were observed for II and III in the same temperature range, indicating that I exhibits a slightly stronger frequency dependence than II and III. Considering that tunneling would make all the maxima to fall at the same temperature but not to disappear, the difference in the frequency-dependent out-of-phase ( $\chi''$ ) signals between I and II or III is probably related to the disorder of the  $NH_4^+$  in the crystal lattice. Although the energy barriers for I, II, and III could not be obtained by fitting the Arrhenius expression, if only one characteristic relaxation process is assumed to occur, the energy barrier and  $\tau_0$  values can be approximated from fits of the ac susceptibility data by adopting the Debye model and the equation  $\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/k_BT$ , which has been applied for cluster compounds.<sup>34</sup> This analysis gave  $\tau_0 \approx 7 \times 10^{-5}$  s and  $E_a \approx 23$  K for I,  $\tau_0 \approx 7 \times 10^{-5}$  s and  $E_a \approx 9$  K for II, and  $\tau_0 \approx 7 \times 10^{-5}$  s and  $E_a \approx 10$  K for III (ESI,† Fig. S8).

In conclusion, we have reported three polynuclear lanthanide clusters, **I**, **II**, and **III**. Cluster **I** has  $S_4$  symmetry and crystallizes in a centrosymmetric space group, whereas clusters **II** and **III** have  $C_2$  symmetry and crystallize in a chiral space group. Cluster **I** can reversibly transform into **II** and **III** if the NH<sub>4</sub><sup>+</sup> cation in **I** is replaced with Et<sub>3</sub>NH<sup>+</sup> and Me<sub>4</sub>N<sup>+</sup>, respectively. These results indicate that symmetry breaking can be achieved through the symmetric operation of achiral clusters with  $S_4$  symmetry. Magnetic studies revealed existence of ferromagnetic interactions within the clusters and anti-ferromagnetic interactions between the chiral clusters in the lower-temperature range.

We acknowledge the 973 Project from MSTC (grant no. 2012CB821704 and 2014CB845601) and the NNSFC (grant no. 21390391) and the Doctoral Fund of Ministry of Education of China (20120121110012) for the financial support.

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