Supporting Information

Two chiral tetradecanuclear hydroxo-lanthanide clusters with luminescent and magnetic properties

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Materials and methods. All reagents were of commercial origin and were used as received. The C and H microanalyses were carried out with a Perkin-Elmer 240C analyzer. Infrared spectra were performed on TENSOR27 Bruker spectrophotometer with KBr pellets in the 4000 – 400 cm\(^{-1}\) region. Magnetic susceptibility measurements for the crystalline samples were obtained with the use of a Quantum Design MPMS-XL7 SQUID magnetometer in the temperature range 1.8–300 K. The photoluminescence spectra were recorded on a HITACHI F7000 Fluorescence Spectrophotometer at room temperature.

Synthesis of Dy\(_{14}(\mu_4\text{-OH})_2(\mu_3\text{-OH})_{16}(\mu-\eta^2\text{-acac})_8(\eta^2\text{-acac})_{16}\cdot6\text{H}_2\text{O}\) (1). an aqueous solution of NH\(_4\)acac (75 mL, 2 mol/L) was added slowly with stirring to a solution of 0.1 mmol DyCl\(_3\cdot6\text{H}_2\text{O}\) (0.38 g) in 10 mL cold
water. NH$_3$·H$_2$O (1.0 M) was added to keep pH value being 7.0-7.5 and result in white precipitate. Stirring was continued for about 5 hours. The white precipitate was filtered, washed with sufficient water and air-dried in about 67% yield (based on DyCl$_3$). The block colorless crystals of 1 were obtained by recrystallization using CH$_2$Cl$_2$/petroleum ether mixed solvents (10 mL). Elemental analysis (%) calcd. for 1 (C$_{120}$H$_{198}$O$_{72}$Dy$_{14}$): C 28.42, H 3.91; Found: C 28.76, H 3.69. IR data (KBr, cm$^{-1}$): ν 1617 s(C=O stretching), ν 3473 m(O−H stretching), ν 1517 s(enol C=C stretching in acac).

**Synthesis of Tb$_{14}$($\mu$$_4$-OH)$_2$(μ$_3$-OH)$_{16}$($\mu$-η$^2$-acac)$_8$(η$^2$-acac)$_{16}$·6H$_2$O (2).**

This compound was prepared using the same procedure as described above for the synthesis of 1, but using TbCl$_3$·6H$_2$O (0.1 mmol, 0.37 g) in place of DyCl$_3$·6H$_2$O. The product was obtained as white solids in about 71% yield (based on TbCl$_3$). The block colorless crystals of 2 were obtained using the same method as that of 1. Anal. Calcd. (found) for 2, C$_{120}$H$_{198}$O$_{72}$Tb$_{14}$ (%): C, 28.69(28.57); H, 3.95(3.72). IR data (KBr, cm$^{-1}$): ν 1617 s(C=O stretching), ν 3473 m(O−H stretching), ν 1517 s(enol C=C stretching in acac).
Figure S1. The asymmetrical unit of 2 showing thermal ellipsoids at the 50% probability level with labeling Tb atoms. All hydrogen atoms, carbon atoms and lattice water molecules are omitted for clarity. Tb: green; O: red.

Figure S2. The molecular structure of 2. Hydrogen atoms are omitted for clarity.
Figure S3. Polyhedral representation of the structure of $[\text{Tb}_{14}(\mu_4\text{-OH})_2(\mu_3\text{-OH})_{16}]^{24+}$ cluster core, in which one octahedral $[\text{Tb}_6(\mu_3\text{-OH})_8]^{10+}$ unit shares two opposing apexes (Tb5 and Tb5A atoms) with two $[\text{Tb}_5(\mu_4\text{-OH})(\mu_3\text{-OH})_4]^{10+}$ square pyramid units. Tb: cyan; O: red.
Scheme S1. The representation of structural formation of chiral complex 1, in which the asymmetric unit of 1 (a) changes to its chiral structure (b) by the $C_2$ chiral axis passing through the Dy6 and Dy8. All hydrogen atoms, carbon atoms and lattice water molecules are omitted for clarity. O: red; Dy: Cyan; $C_2$ chiral axis: blue.