Supplementary Material (ESI) for CrystEngComm

Supporting Information

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

Xi-Li Li,*[a] Lai-Fu He,[a] Xiang-Li Feng,[a] You Song,*[b] Min Hu,[a] Li-Feng Han,[a] Xian-Jun Zheng,[a] Zhi-Hong Zhang[a] and Shao-Ming Fang*[a]

[a]*Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou, 450002, China. E-mail: lixl@zzuli.edu.cn; Fax: +86 371 63556510.*

[b]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing, 210093, China.*

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 $Dy_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}(\mu\text{-}\eta^2\text{-}acac)_8(\eta^2\text{-}acac)_{16}\cdot 6H_2O$ (1). an aqueous solution of NH_4acac (75 mL, 2 mol/L) was added slowly with stirring to a solution of 0.1 mmol $DyCl_3\cdot 6H_2O$ (0.38 g) in 10 mL cold

water. $NH_3 \cdot H_2O$ (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_2Cl_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 $Tb_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}(\mu\text{-}\eta^2\text{-}acac)_8(\eta^2\text{-}acac)_{16}\cdot 6H_2O$ (2). This compound was prepared using the same procedure as described above for the synthesis of **1**, but using $TbCl_3 \cdot 6H_2O$ (0.1 mmol, 0.37 g) in place of $DyCl_3 \cdot 6H_2O$. 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).

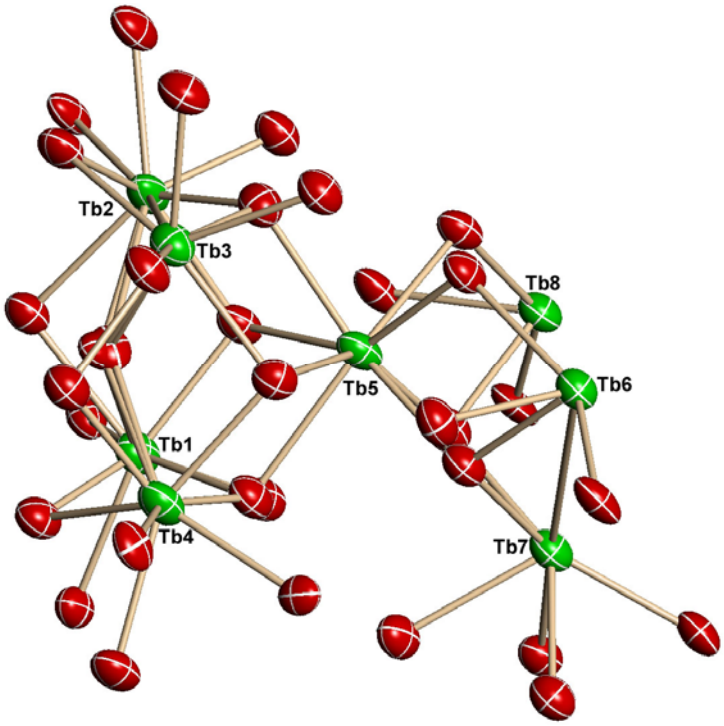


Figure S1. The asymmetrical unit of **2** showing thermal ellipsoids at the 50% probability level with labeling Tb atoms. All hydrogen atoms, carbon atoms and lattice water molecules are omitted for clarity. Tb: green; O: red.

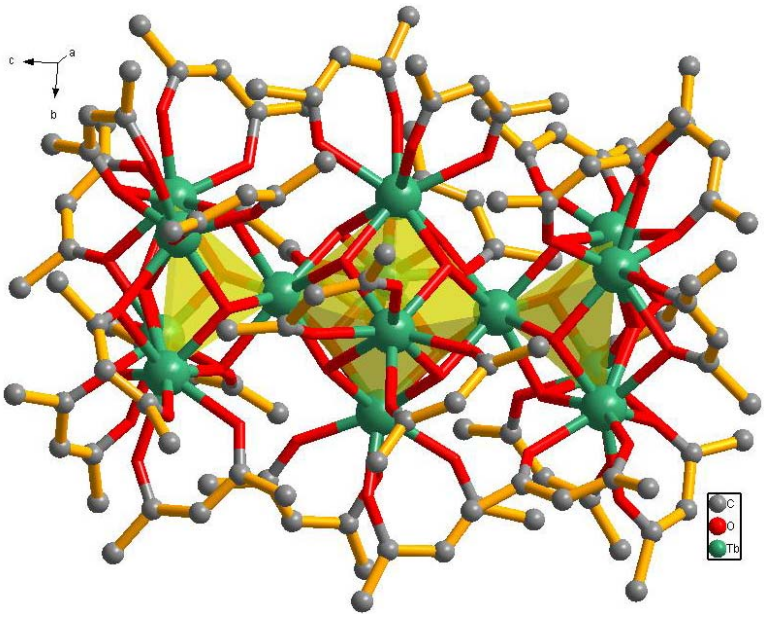


Figure S2. The molecular structure of **2**. Hydrogen atoms are omitted for clarity.

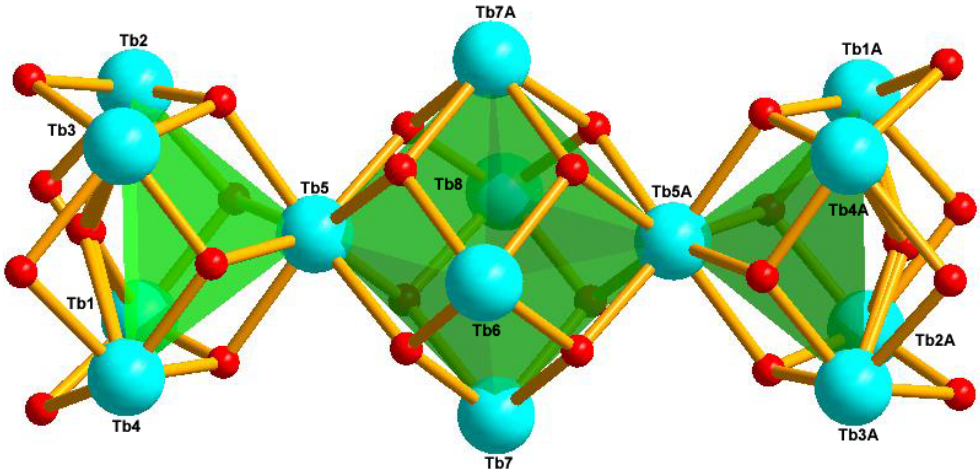
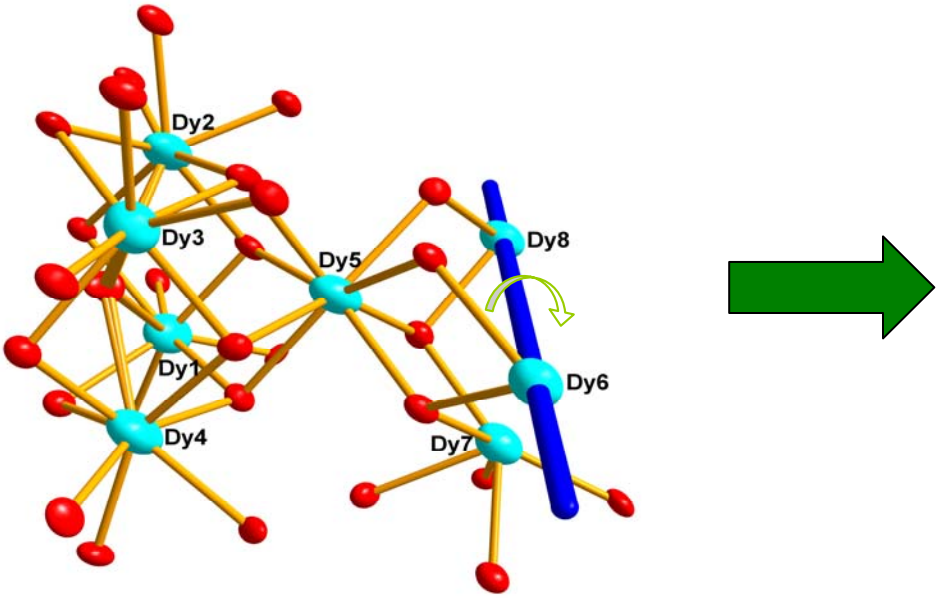
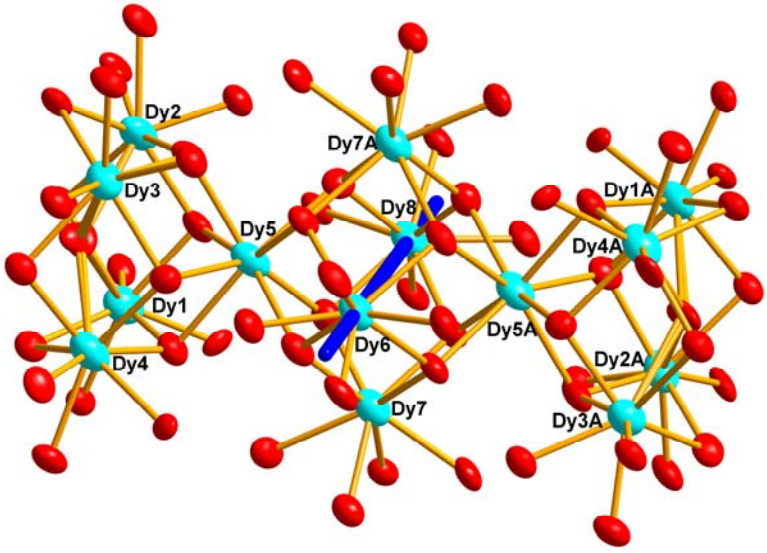


Figure S3. Polyhedral representation of the structure of $[Tb_{14}(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_{16}]^{24+}$ cluster core, in which one octahedral $[Tb_6(\mu_3\text{-}OH)_8]^{10+}$ unit shares two opposing apexes (Tb5 and Tb5A atoms) with two $[Tb_5(\mu_4\text{-}OH)(\mu_3\text{-}OH)_4]^{10+}$ square pyramid units. Tb: cyan; O: red.



(a)



(b)

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.