Supporting Information

Constructing Heterometallic Frameworks with Highly Connected Topology Based on Edge-to-Edge Hexanuclear Lanthanide Clusters

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Table S1 Selected bond lengths (Å) for compounds **1-2**.

Fig. S1 ORTEP drawing of **1** with 30% probability of thermal ellipsoids.

Fig. S2 The coordination environments of the Sm and Cu atoms in **1**.

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Table S1 Selected bond lengths (Å) for compounds **1-2**

Compound 1			
Sm(1)-O(2)A	2.302(1)	Sm(3)-O(16)	2.419(8)
Sm(1)-O(6)	2.329(9)	Sm(3)-O(16)C	2.360(1)
Sm(1)-O(7)	2.563(1)	Cu(1)-I(1)	2.615(1)
Sm(1)-O(8)	2.460(1)	Cu(1)-I(1)D	2.658(1)
Sm(1)-O(9)	2.316(7)	Cu(1)-I(2)	2.658(1)
Sm(1)-O(13)	2.407(1)	Cu(1)-N(1)D	2.053(7)
Sm(1)-O(14)	2.471(1)	Cu(2)-I(1)	2.664(1)
Sm(1)-O(15)	2.349(8)	Cu(2)-I(2)	2.640(1)
Sm(2)-O(1W)	2.586(1)	Cu(2)-I(3)	2.656(1)
Sm(2)-O(2W)	2.323(1)	Cu(2)-N(2)	2.040(8)
Sm(2)-O(3)	2.435(1)	Cu(3)-I(2)	2.655(1)
Sm(2)-O(4)	2.513(1)	Cu(3)-I(3)	2.657(1)
Sm(2)-O(12)	2.359(7)	Cu(3)-I(4)	2.651(1)
Sm(2)-O(14)	2.367(1)	Cu(3)-N(3)E	2.056(7)
Sm(2)-O(15)	2.377(8)	Cu(4)-I(3)	2.657(1)
Sm(2)-O(16)	2.377(1)	Cu(4)-I(4)	2.605(1)
Sm(3)-O(1)	2.387(7)	Cu(4)-I(4)F	2.683(1)
Sm(3)-O(3W)	2.533(1)	Cu(4)-N(4)G	2.026(9)
Sm(3)-O(5)B	2.359(8)	Cu(5)-N(5)	1.905(9)
Sm(3)-O(10)C	2.599(1)	Cu(5)-N(5)H	1.905(9)
Sm(3)-O(11)	2.357(7)	Cu(6)-N(6)	1.907(7)
Sm(3)-O(15)C	2.361(8)	Cu(6)-N(6)I	1.907(7)
Symmetry transformations used to generate equivalent atoms: A: *x*+1, *y*, *z*; B: *x*-1, *y*, *z*; C: -*x*, -*y*, -*z*+1; D: -*x*, -*y*+1, -*z*+2; E: *x*, *y*+1, *z*+1; F: -*x*+1, -*y*+2, -*z*+2; G: -*x*+1, -*y*+1, -*z*+1; H: -*x*+1, -*y*+1, -*z*+2; I: -*x*, -*y*, -*z*.			
Compound 2			
Sm(1)-O(1)	2.380(1)	Cu(2)-I(1)	2.676(2)
Sm(1)-O(1W)	2.495(1)	Cu(2)-I(2)	2.705(2)
Sm(1)-O(2W)	2.438(1)	Cu(2)-I(3)	2.662(2)
Sm(1)-O(4)	2.337(8)	Cu(2)-I(12)	2.681(3)
Sm(1)-O(17)	2.421(9)	Cu(3)-I(2)	2.687(2)
Sm(1)-O(21)A	2.275(8)	Cu(3)-I(3)	2.658(2)
Sm(1)-O(29)	2.427(8)	Cu(3)-I(4)	2.602(2)
Sm(2)-O(2)	2.369(9)	Cu(3)-N(11)C	2.018(1)
Sm(2)-O(5)	2.461(1)	Cu(4)-I(3)	2.681(2)
Sm(2)-O(7)	2.499(9)	Cu(4)-I(4)	2.668(2)
Sm(2)-O(15)	2.474(9)	Cu(4)-I(5)	2.660(1)
Sm(2)-O(16)	2.491(1)	Cu(4)-N(2)	2.033(1)
Sm(2)-O(29)	2.432(8)	Cu(5)-I(3)	2.837(2)
Sm(2)-O(30)	2.410(9)	Cu(5)-I(5)	2.592(2)
Sm(3)-O(14)A	2.408(9)	Cu(5)-I(6)	2.617(2)
Sm(3)-O(19)	2.432(8)	Cu(5)-N(10)D	2.040(1)

Sm(3)-O(23)	2.397(1)	Cu(6)-I(5)	2.666(2)
Sm(3)-O(25)	2.396(1)	Cu(6)-I(6)	2.626(2)
Sm(3)-O(29)	2.408(8)	Cu(6)-I(7)	2.673(2)
Sm(3)-O(30)	2.373(9)	Cu(6)-N(7)A	2.019(1)
Sm(3)-O(31)	2.445(8)	Cu(7)-I(7)	2.573(3)
Sm(4)-O(3)B	2.301(1)	Cu(7)-I(8)	2.658(3)
Sm(4)-O(8)	2.361(9)	Cu(7)-I(9)E	2.688(3)
Sm(4)-O(9)	2.397(8)	Cu(7)-N(6)	2.061(1)
Sm(4)-O(22)	2.424(7)	Cu(8)-I(7)F	2.591(4)
Sm(4)-O(30)	2.398(8)	Cu(8)-I(9)	2.652(4)
Sm(4)-O(31)	2.442(7)	Cu(8)-I(10)	2.635(4)
Sm(4)-O(32)	2.474(8)	Cu(8)-N(13)G	2.070(2)
Sm(5)-O(3W)	2.493(1)	Cu(9)-I(8)H	2.650(3)
Sm(5)-O(11)	2.473(1)	Cu(9)-I(10)	2.741(3)
Sm(5)-O(12)	2.510(1)	Cu(9)-I(11)	2.682(3)
Sm(5)-O(24)	2.436(1)	Cu(9)-N(1)	1.985(1)
Sm(5)-O(26)	2.331(1)	Cu(10)-I(1)	2.661(3)
Sm(5)-O(27)	2.362(1)	Cu(10)-I(2)	2.659(2)
Sm(5)-O(31)	2.407(8)	Cu(10)-I(9)	2.660(2)
Sm(5)-O(32)	2.494(8)	Cu(10)-N(3)A	2.055(1)
Sm(6)-O(4W)	2.488(1)	Cu(11)-I(1)	2.680(3)
Sm(6)-O(5W)	2.445(1)	Cu(11)-I(10)	2.688(3)
Sm(6)-O(10)	2.347(9)	Cu(11)-I(11)	2.719(3)
Sm(6)-O(13)	2.310(9)	Cu(11)-I(12)	2.665(3)
Sm(6)-O(20)B	2.366(9)	Cu(12)-I(8)H	2.549(5)
Sm(6)-O(28)	2.417(9)	Cu(12)-I(11)	2.657(5)
Sm(6)-O(32)	2.388(8)	Cu(12)-N(14)G	2.130(2)
Cu(1)-I(2)	2.735(3)	Cu(13)-N(12)D	1.909(1)
Cu(1)-I(9)	2.644(3)	Cu(13)-N(5)	1.890(1)
Cu(1)-I(12)	2.660(3)	Cu(14)-N(4)	1.913(1)
Cu(1)-N(8)C	2.077(1)	Cu(14)-N(9)D	1.940(1)

Symmetry transformations used to generate equivalent atoms: A: *x*-1, *y*, *z*; B: *x*+1, *y*, *z*; C: *x*-1, *y*, *z*+1; D: *x*, *y*, *z*+1; E: *x*, *y*+1, *z*; F: *x*, *y*-1, *z*; G: *x*, *y*-1, *z*+1; H: *x*+1, *y*-1, *z*.

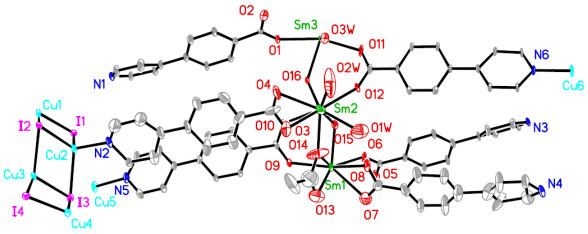

Fig. S1 ORTEP drawing of **1** with 30% probability of thermal ellipsoids. Lattice water molecules and ClO_4^- are omitted for clarity.

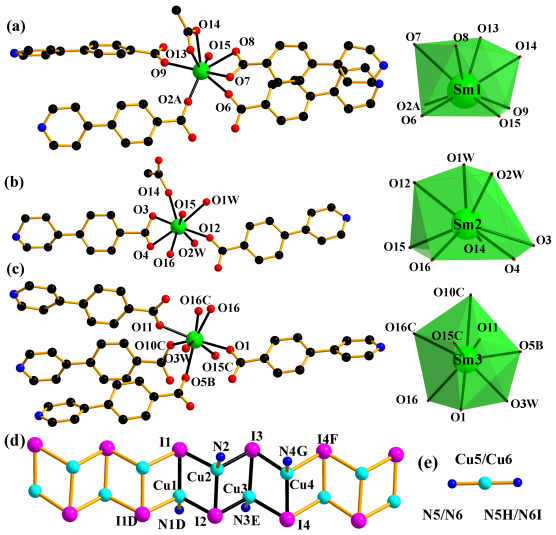

Fig. S2 The representation of the coordination environments of Sm (a-c) and Cu (d-e) atoms in compound **1**. Atoms having A-I in their labels are symmetry-generated. Symmetry codes A: *x*+1, *y*, *z*; B: *x*-1, *y*, *z*; C: -*x*, -*y*, -*z*+1; D: -*x*, -*y*+1, -*z*+2; E: *x*, *y*+1, *z*+1; F: -*x*+1, -*y*+2, -*z*+2; G: -*x*+1, -*y*+1, -*z*+1; H: -*x*+1, -*y*+1, -*z*+2; I: -*x*, -*y*, -*z*.

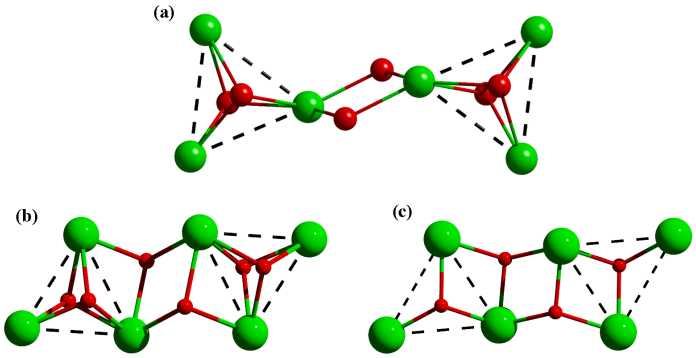

Fig. S3 The skeleton of Ln_6 clusters in the combination of two triangular cores: (a) Double-capped triangles in the head-to-head arrangement; (b) Double-capped triangles in the edge-to-edge arrange- ment; (c) Single-capped triangles in the edge-to-edge arrangement.

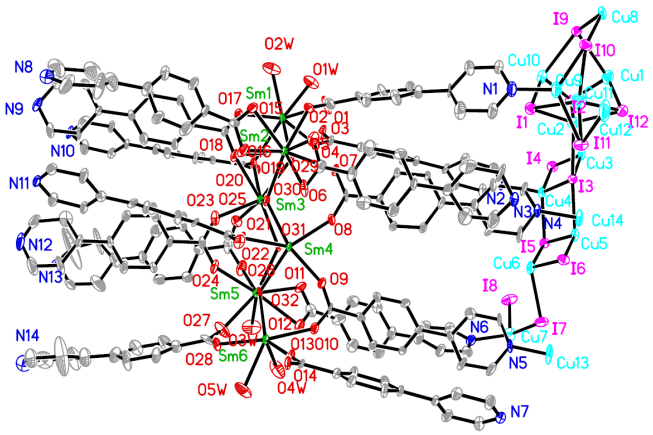

Fig. S4 ORTEP view of compound **2** with 30% probability of thermal ellipsoids. Lattice water molecules and ClO_4^- are omitted for clarity.

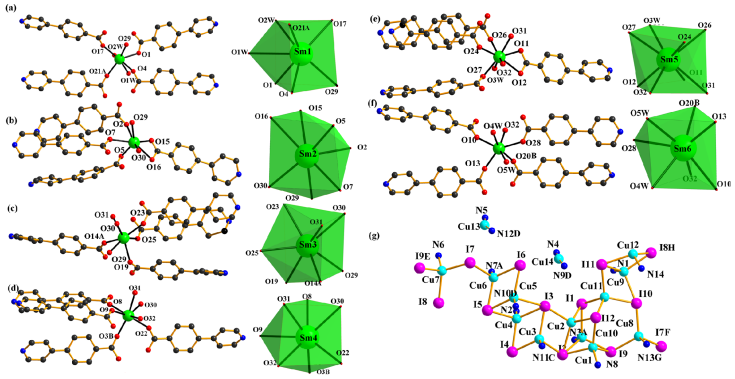

Fig. S5 The representation of the coordination environments of Sm (a-f) and Cu (g) atoms in compound **2**. Atoms having A-H in their labels are symmetry-generated. Symmetry codes A: *x*-1, *y*, *z*; B: *x*+1, *y*, *z*; C: *x*-1, *y*, *z*+1; D: *x*, *y*, *z*+1; E: *x*, *y*+1, *z*; F: *x*, *y*-1, *z*; G: *x*, *y*-1, *z*+1; H: *x*+1, *y*-1, *z*.

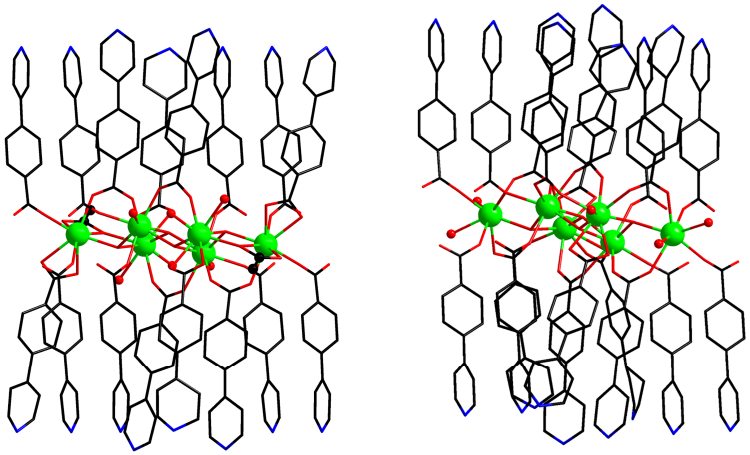

Fig. S6 The coordination environment of the $\{Sm_6\}^1$ core in **1** (left) and the $\{Sm_6\}^2$ core in **2** (right), showing that 16 L ligands, 2 CH_3COO^- and 6 coordination water molecules bond to the $\{Sm_6\}^1$ core, while 18 L ligands and 5 coordination water molecules bond to the $\{Sm_6\}^2$ core, respectively. If the above-mentioned CH_3COO^- and coordination water molecules are replaced by the same number of the L ligands, the number of the L ligands bonded to the $\{Sm_6\}^1$ and $\{Sm_6\}^2$ cores will up to 24 and 23 in **1** and **2**, respectively.

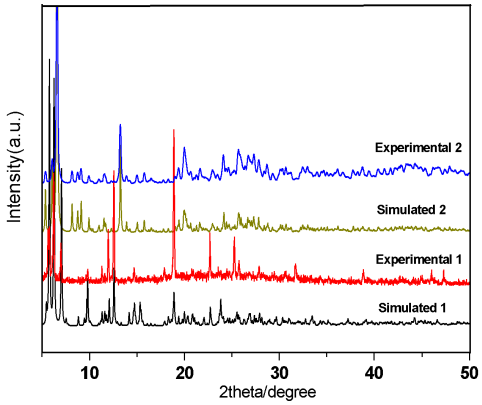

Fig. S7 The experimental and simulated PXRD patterns of compounds **1-2**.

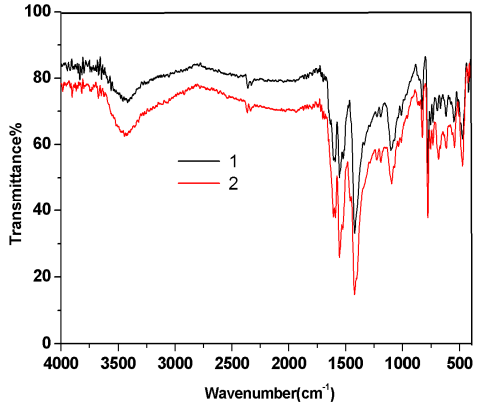

Fig. S8 Infrared spectra of compounds **1-2**.

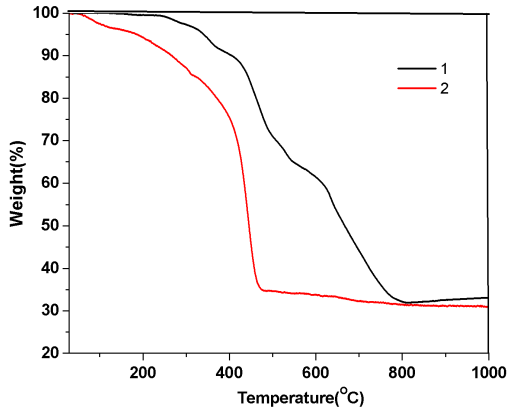

Fig. S9 TG curves of compounds **1-2**.

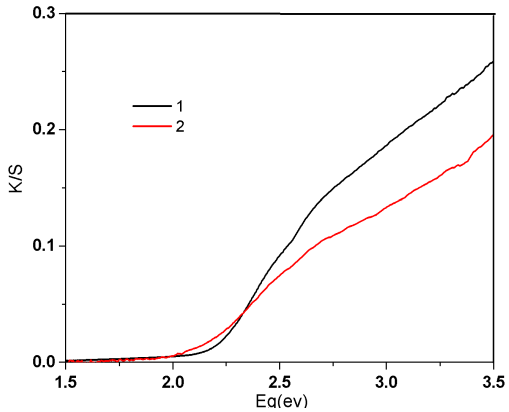

Fig. S10 Optical absorption spectra of compounds **1-2** from diffuse reflectance data.