Supporting Information

Bilayer architecture based on heterometallic hexanuclear units

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Table S1 Selected bond lengths (Å) for compound **1**[a]

Eu-O(1)	2.393(7)	Cu(1)-O(9)	1.950(7)
Eu-O(1W)	2.506(9)	Cu(1)-O(10)	1.932(6)
Eu-O(4)	2.398(7)	Cu(1)-O(14)	2.842(3)
Eu-O(5)	2.361(7)	Cu(2)-N(2)C	2.010(9)
Eu-O(6)A	2.483(7)	Cu(2)-O(2)	1.971(7)
Eu-O(7)	2.374(8)	Cu(2)-O(6)A	2.502(7)
Eu-O(8)A	2.468(7)	Cu(2)-O(9)	1.972(7)
Eu-O(10)	2.409(7)	Cu(2)-O(10)	1.936(6)
Cu(1)-N(1)B	1.982(8)	Cu(2)-O(13)	2.557(2)
Cu(1)-O(3)	1.976(7)	Cu(3)-N(3)	2.036(1)
Cu(1)-O(8)A	2.506(7)	Cu(3)-N(4)D	2.030(5)

[a] Symmetry transformations used to generate equivalent atoms: A: -*x*+2, -*y*+1, -*z*; B: *x*, *y*-1, *z*; C: *x*, *y*, *z*-1; D: *x*, *y*-1, *z*+1.

Table S2 BVS for Eu, Cu and hydroxyl oxygen atoms in **1**[a]

Atom	**BVS**
Eu	2.84
Cu1	1.95
Cu2	1.95
Cu3	0.64
O9	0.85
O10	1.37

[a] BVS=exp[(R1-d)/0.37]

Table S3 Hydrogen bond lengths (Å) and bond angles (°) for compounds **1**[a]

D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<DHA**
O9-H(0B)···O2W	0.90	2.29	2.87(1)	122.4
O10-H(0A)···O3W	0.96	1.90	2.85(2)	168.3
O4W-H(42)···O5^{A}	0.83	2.37	3.14(1)	157.1

[a] Symmetry code: A: -*x*+2, -*y*+1, -*z*+3.

Supporting Figures:

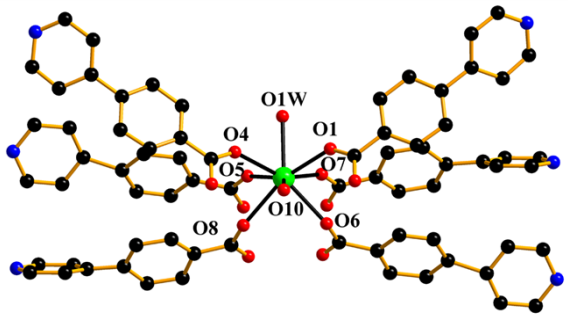


Fig. S1 The ball-stick view of the coordination environment of Eu ion. Atoms having "A" in their labels are symmetry-generated. Symmetry code A: -*x*+2, -*y*+1, -*z*.

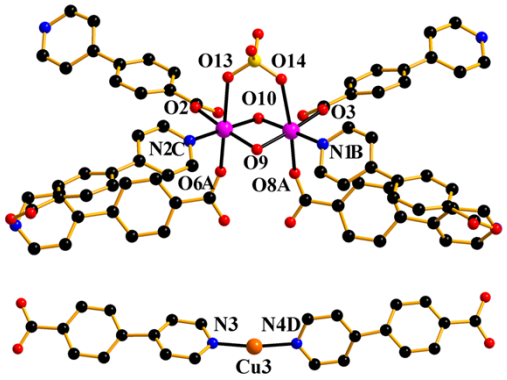
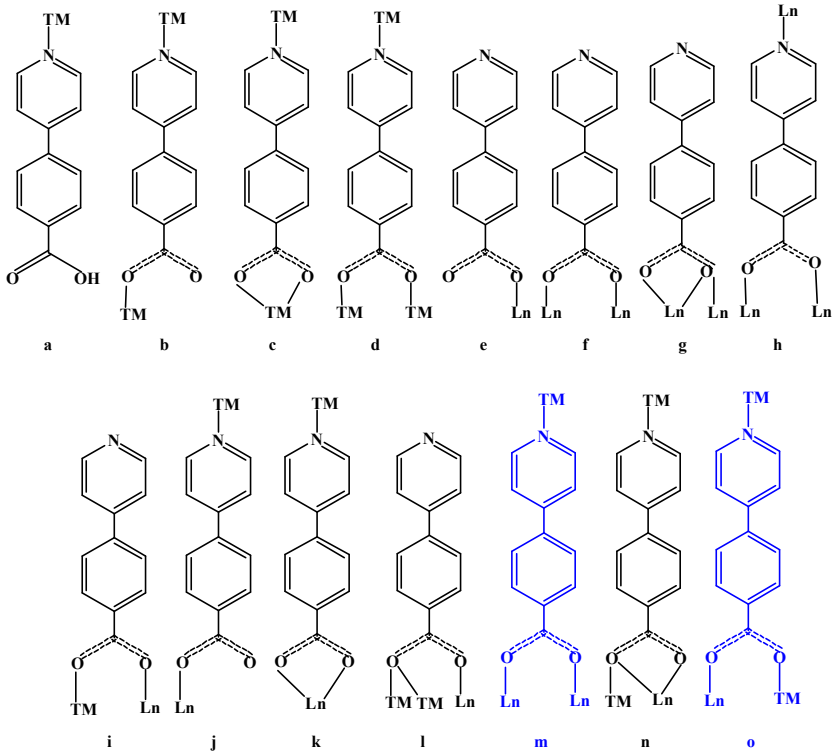


Fig. S2 The ball-stick view of the coordination environments of the Cu^{II} (up) and Cu^{I} (down) in compound **1**. Atoms having B-D in their labels are symmetry-generated. Symmetry codes B: *x*, *y*-1, *z*; C: *x*, *y*, *z*-1; D: *x*, *y*-1, *z*+1.



Scheme S1 The coordination modes of HL ligands and related references.

The mode (a) is seen in the reference 1; The mode (b) is given in the reference 2; The mode (c) is found in the reference

2a,c,3; The mode (d) is seen in the reference 2b,4; The modes (e,i,l,n) are seen in the reference 5; The modes (f-h) are seen in the reference 6; The mode (j) is seen in the reference 7; The mode (k) is seen in the reference 7,8; The mode (m) is seen in the reference 7,9 and herein; The mode (o) is seen in the reference herein.

1 (*a*) R. Sekiya, S. Nishikiori and K. Ogura, *Inorg. Chem.,* 2006, **45**, 9233; (*b*) R. Sekiya and S. Nishikiori, *Cryst. Growth Des.,* 2011, **11**, 5574; (*c*) G. C. Ou, J. Z. Gu, T. B. Lu and R. L. Luck, *J. Mol. Struct.,* 2005, **740**, 143; (*d*) P. Teo, L. L. Koh and T. S. A. Hor, *Inorg. Chem.,* 2008, **47**, 6464; (*e*) X. L. Jia, J. Zhou, S. T. Zheng and G. Y. Yang, *J. Cluster Sci.,* **2009**, **20**, 555; (*f*) R. Sekiya and S. Nishikiori, K. Ogura, *Chem. Lett.,* 2006, **35**, 614.

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6 (*a*) Z. L. Wang, W. H. Fang and G. Y. Yang, *Chinese. J. Struct. Chem.,* 2009, **28**, 1453; (*b*) Z. L. Wang, W. H. Fang and G. Y. Yang, *J. Cluster Sci.,* 2009, **20**, 725; (*c*) W. H. Fang, Z. L. Wang and G. Y. Yang, *J. Cluster Sci.,* 2010, **21**, 187; (*d*) W. H. Fang, L. Cheng, L. Huang and G. Y. Yang, *Inorg. Chem.,* 2013, **52**, 6.

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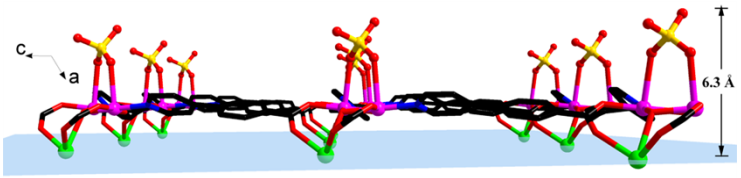

Fig. S3 Side view shows the thickness of the monolayers along the *b* axis.

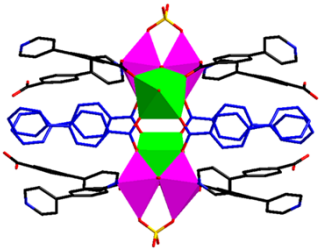

Fig. S4 The coordination environment of $Eu^{III}_2Cu^{II}_4$ core in **1**. Twelve ligands: four in mode I (blue), eight in mode II (black).

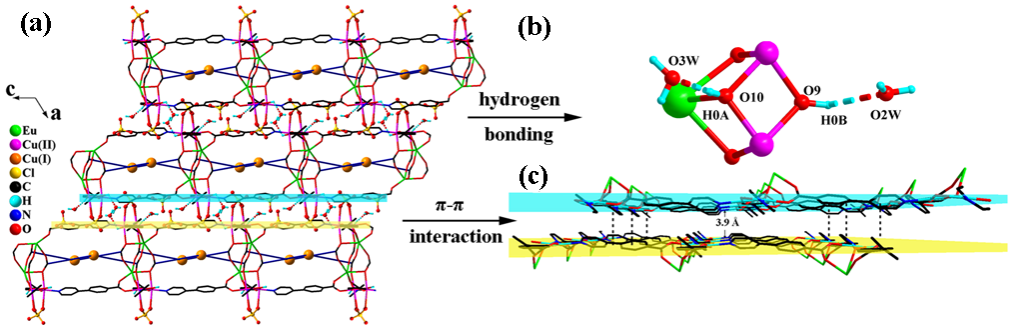

Fig. S5 (a) Superamolecular structure of compound **1**. (b-c) Emphasized hydrogen bonding and π-π interaction. Perchlorate groups are omitted for clarity.

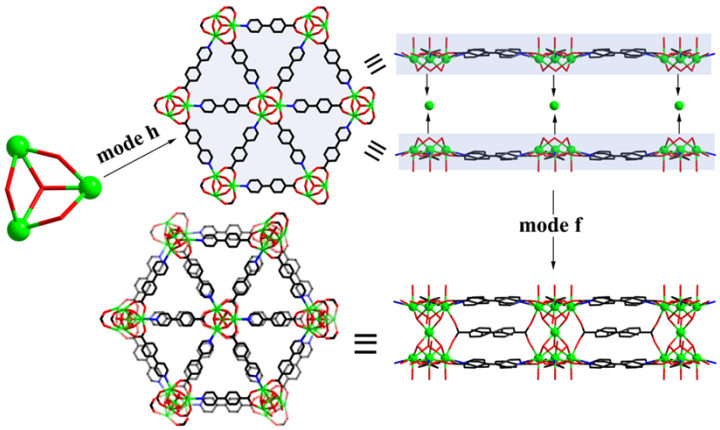

Fig. S6 The bilayer architecture in **1'** (ref. 16).

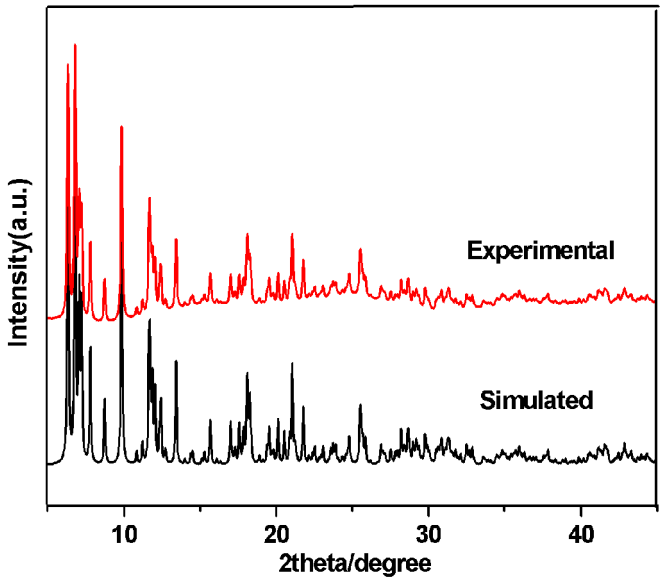

Fig. S7 Simulated and experimental PXRD patterns of **1**.

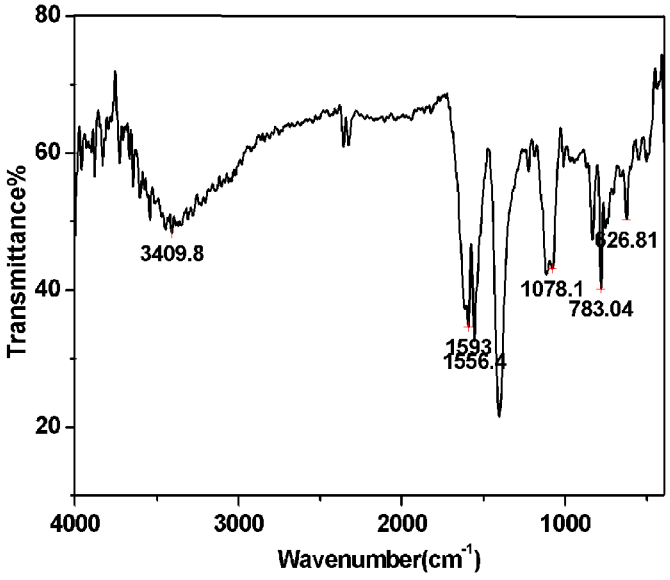

Fig. S8 The IR spectrum of compound **1**.

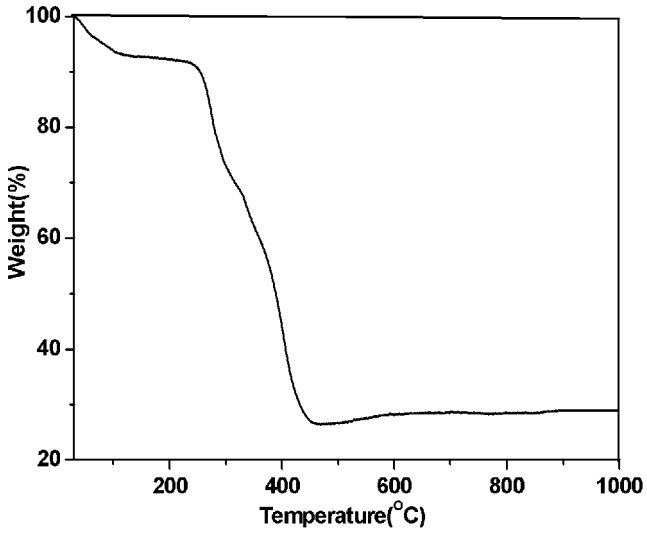

Fig. S9 TGA curve of compound **1**.

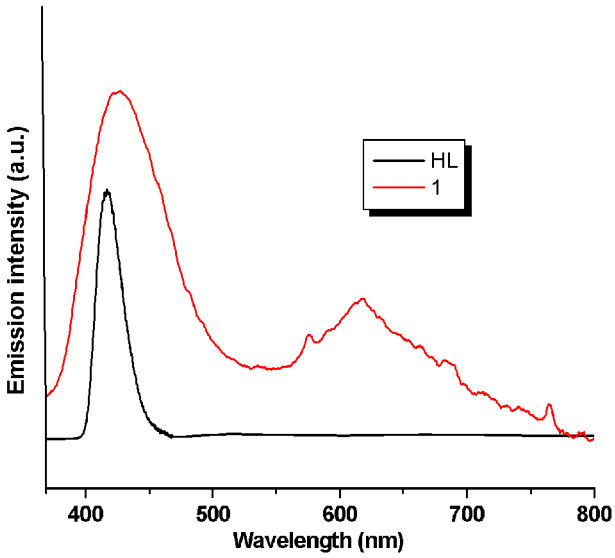

Fig. S10 Solid-state emission spectra of HL and compound **1** at room temperature.