Supplementary Material (ESI) for Dalton Transactions

Unprecedented double-bridging interpenetrating α-Po network based on a new heterometallic cluster $\{Cu_4Mo_6\}$

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Single-crystal X-ray diffraction

X-ray single-crystal diffraction data was collected on a Rigaku R-axis rapid IP area detector with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å). The program SAINT[1] was used for integration of the diffraction profiles. The crystal structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL[2]. Metal atoms were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. Hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

References

(1) Bruker AXS, *SAINT Software Reference Manua*l, Madison, WI, **1998.**

(2) Sheldrick, G. M. *SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures,* University of Göttingen, Germany, **1997**.

Electrochemical experiment

The electrochemical analysis was carried out using a CHI 440 Electrochemical Quartz Crystal Microbalance. A conventional three-electrode cell was used at room temperature. The modified electrode was used as working electrode. A SCE and a platinum wire were used as reference and auxiliary electrodes, respectively. The complex modified carbon paste electrode (**1**-CPE) was fabricated as follows: 0.5 g graphite powder and 0.03 g complex was mixed and ground together by agate mortar and pestle for approximately 30 min to achieve an even, dry mixture; to the mixture 0.2 ml paraffin oil was added and stirred with a glass rod; then the homogenized mixture was used to pack 3 mm inner diameter glass tube to a length of 0.8 cm. The electrical contact was established with the copper stick, and the surface of the modified CPE was wiped with weighing paper.

Table 1. Selected bond lengths [Å] and angles [°] for compound **1**

Cu(1)-O(11)	1.959(4)	Cu(1)-O(3)	1.959(4)
Cu(1)-N(3)	2.005(5)	Cu(1)-N(10)#1	2.040(5)
Cu(1)-N(1)	2.286(5)	Cu(2)-O(4)	1.948(4)
Cu(2)-N(7)	1.977(5)	Cu(2)-O(10)#2	2.009(4)
Cu(2)-O(2)	2.013(4)	Cu(2)-N(6)#3	2.216(5)
Mo(1)-O(1)	1.700(4)	Mo(1)-O(3)	1.763(4)
Mo(1)-O(2)	1.773(4)	Mo(1)-O(5)	2.013(4)
Mo(1)-O(4)	2.062(4)	Mo(2)-O(6)	1.716(4)
Mo(2)-O(7)	1.747(4)	Mo(2)-O(8)	1.829(4)
Mo(2)-O(4)	1.918(4)	Mo(2)-O(5)	2.084(4)
Mo(2)-Mo(3)	3.2047(8)	Mo(3)-O(9)	1.708(4)
Mo(3)-O(10)	1.767(4)	Mo(3)-O(11)	1.768(4)
Mo(3)-O(5)	2.066(4)	Mo(3)-O(8)	2.093(4)
O(11)-Cu(1)-O(3)	85.47(17)	O(11)-Cu(1)-N(3)	85.29(19)
O(3)-Cu(1)-N(3)	170.05(19)	O(11)-Cu(1)-N(10)#1	157.54(18)
O(3)-Cu(1)-N(10)#1	87.26(19)	N(3)-Cu(1)-N(10)#1	100.0(2)
O(11)-Cu(1)-N(1)	110.37(18)	O(3)-Cu(1)-N(1)	96.24(18)
N(3)-Cu(1)-N(1)	90.41(19)	N(10)#1-Cu(1)-N(1)	91.52(19)
O(4)-Cu(2)-N(7)	166.4(2)	O(4)-Cu(2)-O(10)#2	96.81(16)
N(7)-Cu(2)-O(10)#2	92.25(19)	O(4)-Cu(2)-O(2)	75.79(17)
N(7)-Cu(2)-O(2)	92.7(2)	O(10)#2-Cu(2)-O(2)	162.57(19)
O(4)-Cu(2)-N(6)#3	91.9(2)	N(7)-Cu(2)-N(6)#3	97.3(2)
O(10)#2-Cu(2)-N(6)#3	95.72(19)	O(2)-Cu(2)-N(6)#3	100.2(2)
O(1)-Mo(1)-O(3)	107.2(2)	O(1)-Mo(1)-O(2)	106.8(2)
O(3)-Mo(1)-O(2)	102.3(2)	O(1)-Mo(1)-O(5)	104.90(19)
O(3)-Mo(1)-O(5)	90.32(17)	O(2)-Mo(1)-O(5)	140.32(19)
O(1)-Mo(1)-O(4)	104.2(2)	O(3)-Mo(1)-O(4)	146.82(18)
O(2)-Mo(1)-O(4)	78.37(18)	O(5)-Mo(1)-O(4)	71.24(15)

O(6)-Mo(2)-O(7)	108.0(2)	O(6)-Mo(2)-O(8)	104.0(2)
O(7)-Mo(2)-O(8)	99.2(2)	O(6)-Mo(2)-O(4)	103.8(2)
O(7)-Mo(2)-O(4)	94.56(18)	O(8)-Mo(2)-O(4)	143.24(18)
O(7)-Mo(2)-O(5)	142.98(19)	O(8)-Mo(2)-O(5)	75.93(16)
O(4)-Mo(2)-O(5)	72.64(16)	O(6)-Mo(2)-O(5)	108.77(18)
O(9)-Mo(3)-O(10)	103.9(2)	O(9)-Mo(3)-O(11)	103.1(2)
O(10)-Mo(3)-O(11)	105.76(19)	O(9)-Mo(3)-O(5)	101.04(19)
O(10)-Mo(3)-O(5)	146.12(17)	O(11)-Mo(3)-O(5)	90.27(17)
O(9)-Mo(3)-O(8)	95.3(2)	O(10)-Mo(3)-O(8)	84.16(17)
O(11)-Mo(3)-O(8)	156.05(17)	O(5)-Mo(3)-O(8)	71.01(15)

*Symmetry mode, #1 -x+2,-y+1,-z+2; #2 -x+2,-y+2,-z+2; #3 x+1,y+1,z+1.

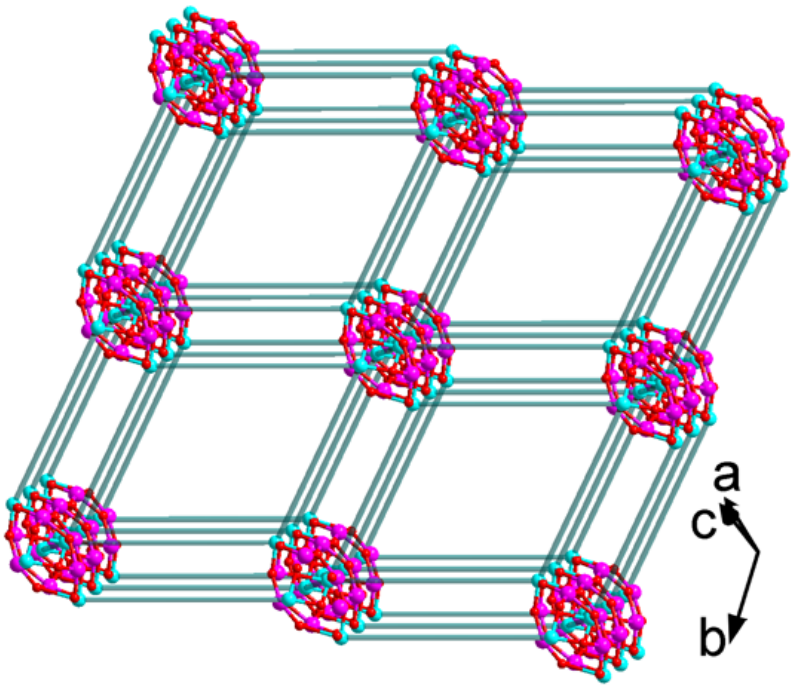

Figure S1. The organic-inorganic hybrid network based on the bimetallic cluster.

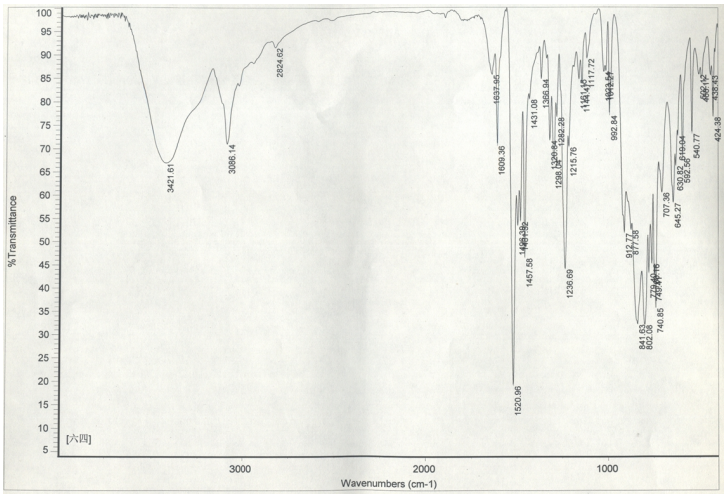

Figure S2. IR plot for **1**.

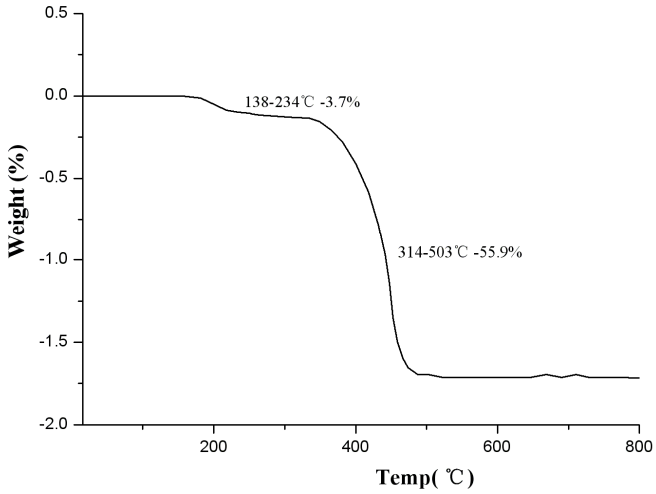

Figure S3. TG plot for **1** vs. temperature.

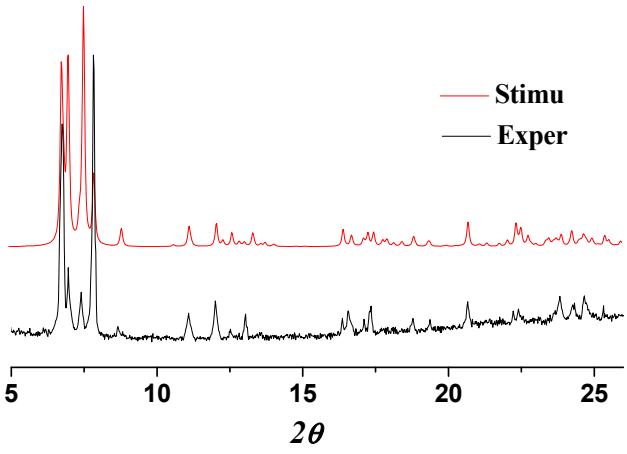

Figure S4. XRPD plot for **1** at room temperature.