Electronic Supplementary Material (ESI) for CrystEngComm

Polyoxoanion-enveloped Ag/ptz Inorganic-organic Hybrid System: From a Single to a Double Template

Table S1. Selected bond lengths (Å) and angles (°) of compounds **1** and **2**.

Compound **1**			
Ag(1)-N(5)#1	2.255(16)	N(5)#1-Ag(1)-N(3)	157.4(5)
Ag(1)-N(3)	2.260(14)	N(5)#1-Ag(1)-O(31)#2	96.4(5)
Ag(1)-O(1W)	2.52(2)	N(3)-Ag(1)-O(31)#2	80.3(4)
Ag(1)-O(31)#2	2.537(11)	N(6)-Ag(2)-N(4)	146.9(5)
Ag(1)-Ag(3)	3.172(2)	N(8)#3-Ag(3)-N(2)	141.7(5)
Ag(2)-N(6)	2.222(13)	N(8)#3-Ag(3)-N(12)	118.7(5)
Ag(2)-N(4)	2.236(14)	N(2)-Ag(3)-N(12)	98.9(5)
Ag(2)-O(2W)	2.487(14)	N(8)#3-Ag(3)-O(33)	86.2(4)
Ag(3)-N(8)#3	2.243(13)	N(2)-Ag(3)-O(33)	94.9(5)
Ag(3)-N(2)	2.249(15)	N(12)-Ag(3)-O(33)	100.0(4)
Ag(3)-N(12)	2.331(13)	N(8)#3-Ag(3)-Ag(1)	107.3(4)
Ag(3)-O(33)	2.542(10)	N(2)-Ag(3)-Ag(1)	66.4(4)
Ag(4)-N(10)#1	2.135(12)	N(12)-Ag(3)-Ag(1)	85.3(4)
Ag(4)-N(7)	2.143(12)	O(33)-Ag(3)-Ag(1)	161.1(2)
Ag(5)-N(11)	2.224(12)	N(10)#1-Ag(4)-N(7)	167.8(5)
Ag(5)-O(35)#4	2.276(11)	N(11)-Ag(5)-O(35)#4	138.0(4)
Ag(5)-N(9)#3	2.356(13)	N(11)-Ag(5)-N(9)#3	124.9(4)
Symmetry transformations used to generate equivalent atoms for **1**: #1 -x+3/2, y-1/2, z #2 -x+3/2, -y+3/2, z+1/2 #3 -x+3/2, -y+3/2, z-1/2 #4 -x+1,-y+1, z+1/2 #5 -x+1, y, z #6 -x+1, -y+1, z-1/2 #7 -x+3/2, y+1/2, z.			
Compound **2**			
Ag(1)-N(10)	2.181(19)	N(10)-Ag(1)-N(22)	122.8(6)
Ag(1)-N(22)	2.225(15)	N(10)-Ag(1)-Ag(7)	85.2(7)
Ag(2)-N(9)	2.205(16)	N(22)-Ag(1)-Ag(7)	103.4(4)
Ag(2)-N(12)	2.252(15)	N(9)-Ag(2)-N(12)	138.9(7)
Ag(2)-N(16)	2.340(16)	N(9)-Ag(2)-N(16)	118.8(7)
Ag(2)-O(12)#1	2.567(15)	N(12)-Ag(2)-N(16)	101.9(6)
Ag(3)-N(18)#3	2.145(18)	N(9)-Ag(2)-O(12)#1	87.2(6)
Ag(3)-N(21)	2.17(2)	N(12)-Ag(2)-O(12)#1	110.5(5)
Ag(3)-O(18)	2.593(14)	N(16)-Ag(2)-O(12)#1	73.9(5)
Ag(4)-N(17)#4	2.299(18)	N(18)#3-Ag(3)-N(21)	169.1(7)
Ag(4)-N(24)	2.358(15)	N(18)#3-Ag(3)-O(18)	83.8(6)
Ag(4)-N(11)#5	2.430(14)	N(21)-Ag(3)-O(18)	93.4(6)
Ag(5)-N(25)	2.263(15)	N(17)#4-Ag(4)-N(24)	110.6(6)
Ag(5)-N(23)	2.270(15)	N(17)#4-Ag(4)-N(11)#5	108.6(5)

Ag(5)-N(13)#6	2.307(16)	N(24)-Ag(4)-N(11)#5	106.2(5)
Ag(6)-N(20)	2.201(15)	N(25)-Ag(5)-N(23)	123.7(5)
Ag(6)-N(19)	2.208(15)	N(25)-Ag(5)-N(13)#6	120.6(5)
Ag(6)-N(15)	2.516(14)	N(23)-Ag(5)-N(13)#6	115.5(5)
Ag(7)-N(8)#4	2.116(17)	N(20)-Ag(6)-N(19)	148.0(5)
Ag(7)-N(7)	2.122(17)	N(20)-Ag(6)-N(15)	102.9(5)
		N(19)-Ag(6)-N(15)	108.6(5)
		N(8)#4-Ag(7)-N(7)	175.1(10)

Symmetry transformations used to generate equivalent atoms for **2**: #1 x, y-1, z #2 -x+3, -y-1, -z #3 -x+3, -y+1, -z+1 #4 -x+2,-y,-z #5 -x+3,-y,-z #6 x-1,y,z #7 x,y+1,z #8 x+1,y,z

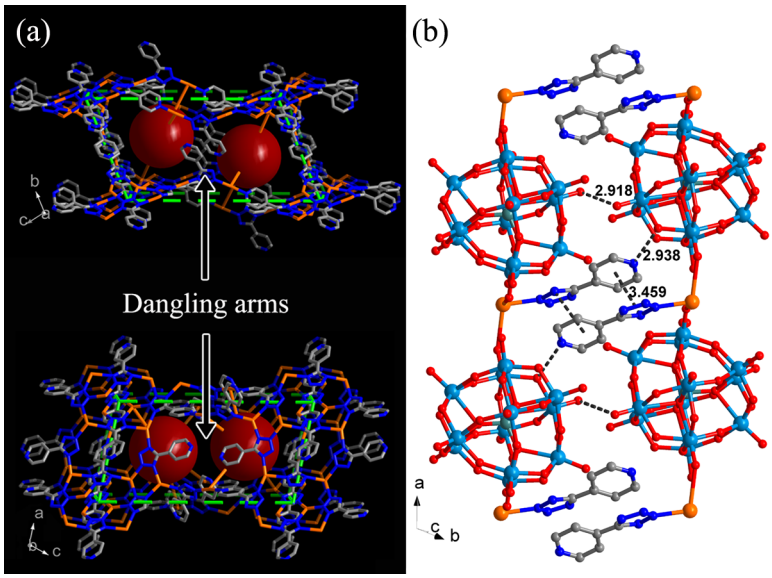


Fig. S1 (a) View of a couple of Keggin anions enveloped in the nanocage in compound **2**. (b) The π-π stacking and inter-molecular interaction between two L-e ligands rings and POM anions in compound **2**.

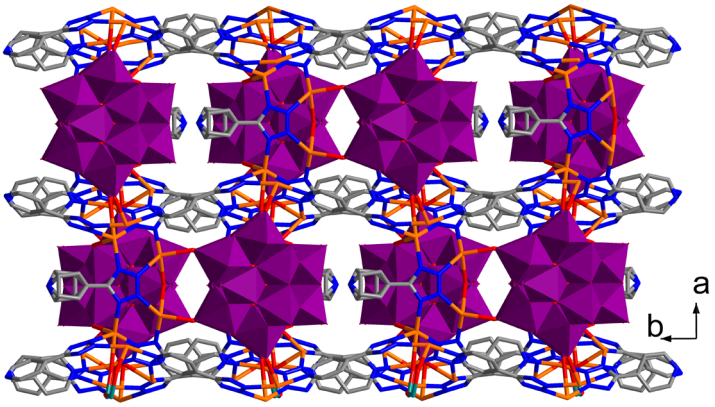


Fig. S2 Stick/ polyhedral view of compound **1** along the *c* axis, showing that the Wells–Dawson polyoxoanions insert in a horizontal way between the metal-organic layers.

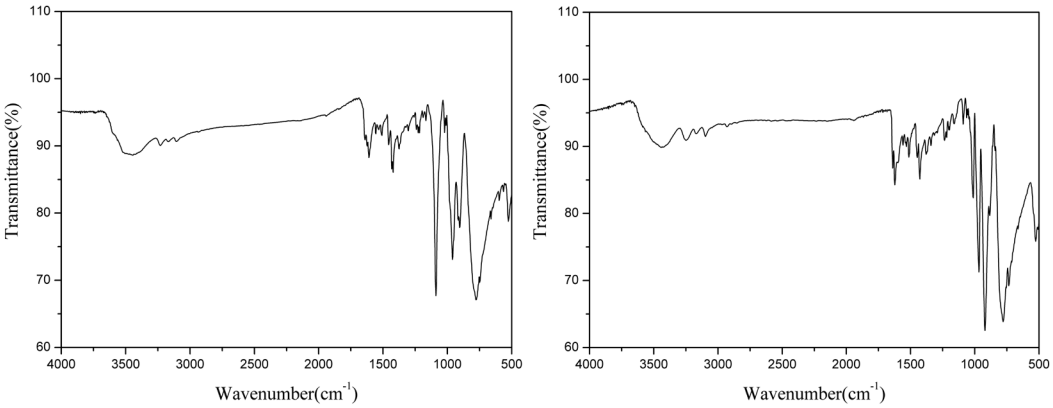


Fig. S3 The IR spectrums of compounds **1**(left) and **2**(right).

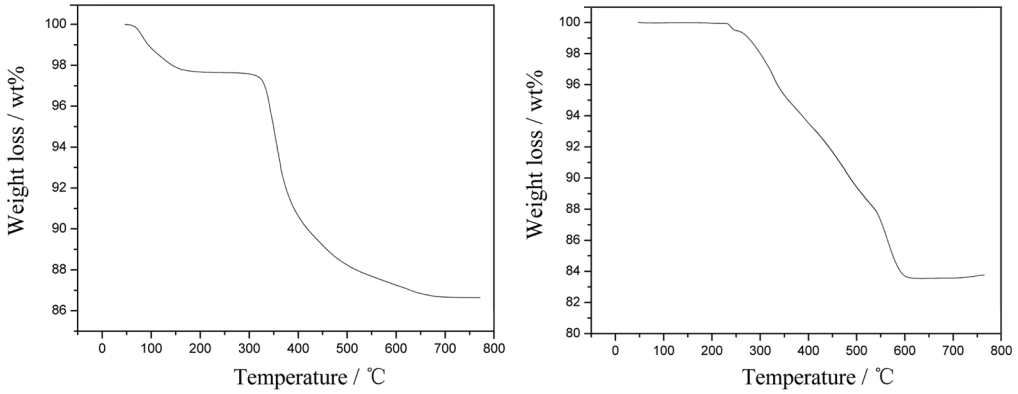


Fig. S4 TG curves of compounds **1**(left) and **2**(right).

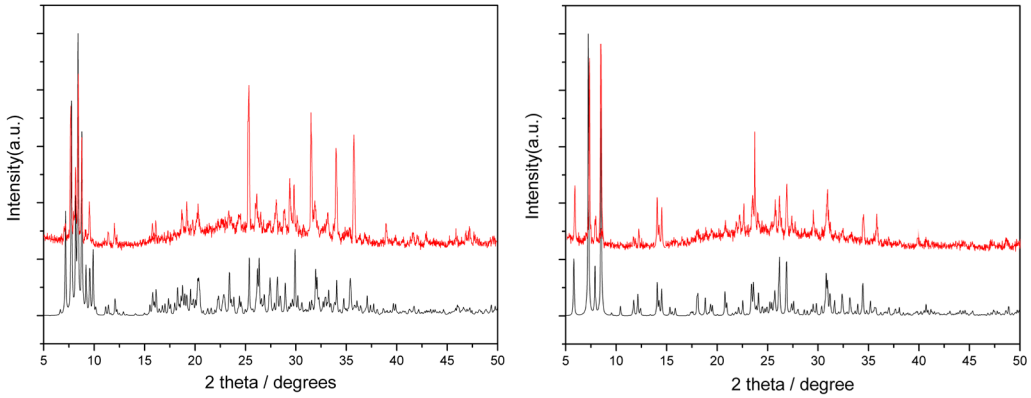
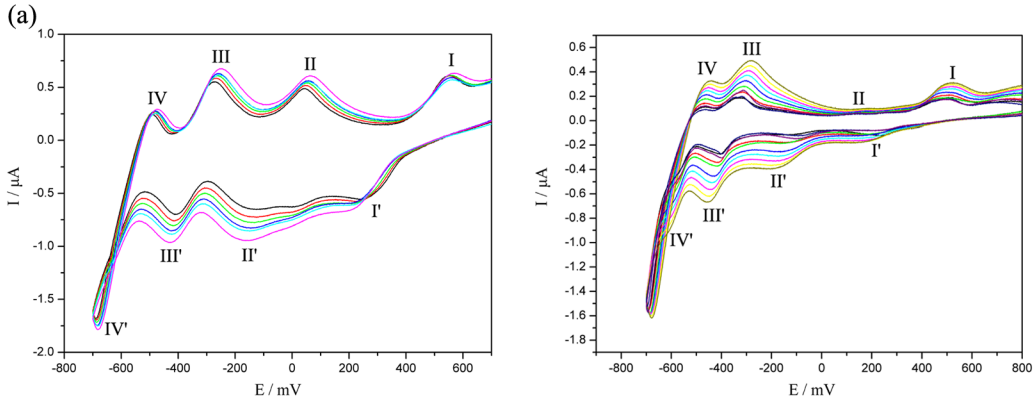


Fig. S5 The PXRD patterns for compounds **1**(left) and **2**(right).

(a)



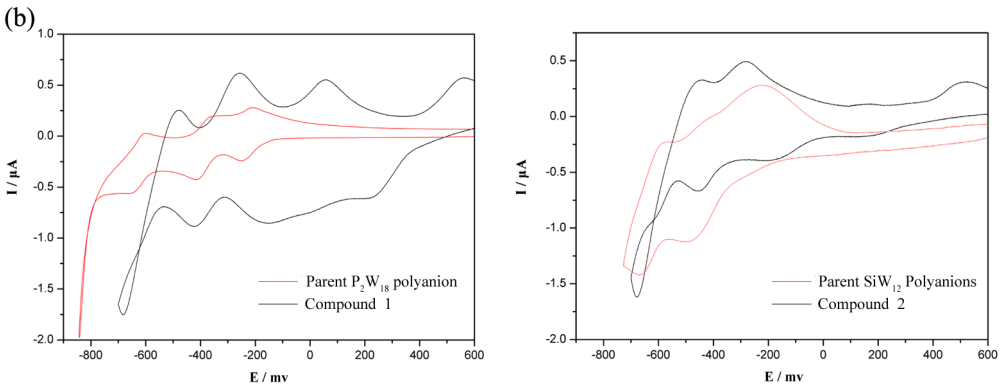


Fig. S6 (a) The cyclic voltammograms of the **1**–CPE(left) and **2**–CPE(right) in 1M H_2SO_4 at different scan rates (from inner to outer: 120, 140, 160, 180, 200, 220 and 480 $mV \cdot s^{-1}$ for **1**, 60, 80, 100, 120, 140, 160, 180, 200, 220 and 240 $mV \cdot s^{-1}$ for **2**). (b) The cyclic voltammograms of compound **1**, **2**, and parent P_2W_{18} and SiW_{12} polyoxoanions in 1 M H_2SO_4 (scan rate: 200 mV/s).