Electronic Supplementary Material (ESI) for CrystEngComm.

Two unusual organic-inorganic hybrid 3-D frameworks based on Keggin-type heteropoly blues anion-chain, 40-membered macrocycles, and sodium as linker units

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1. Structural figures

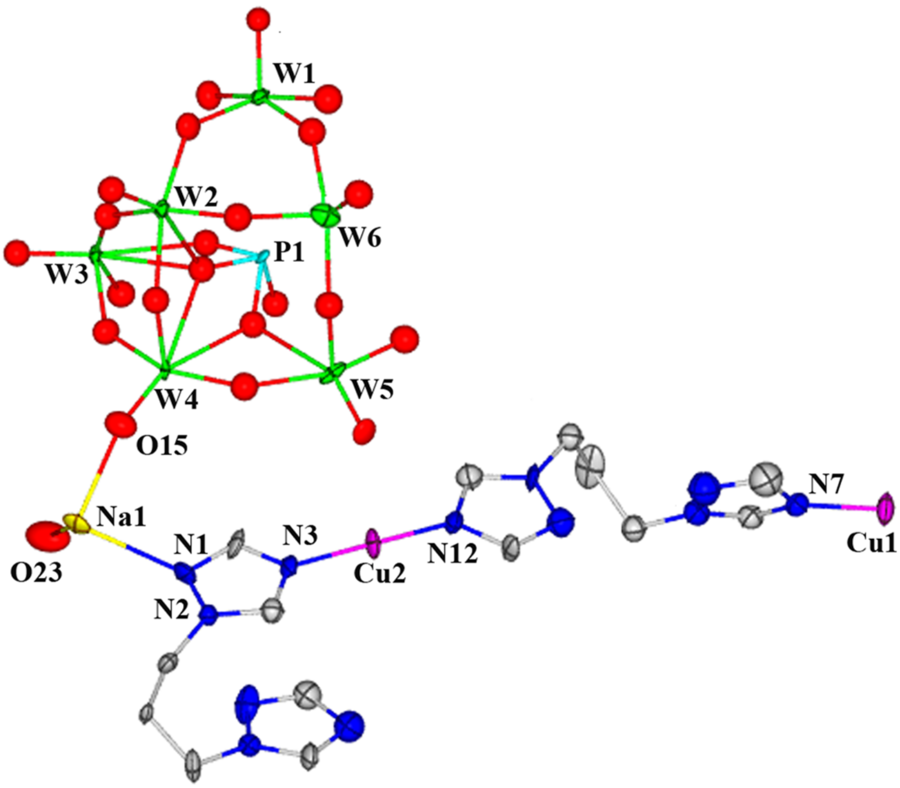

Figure S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoid.

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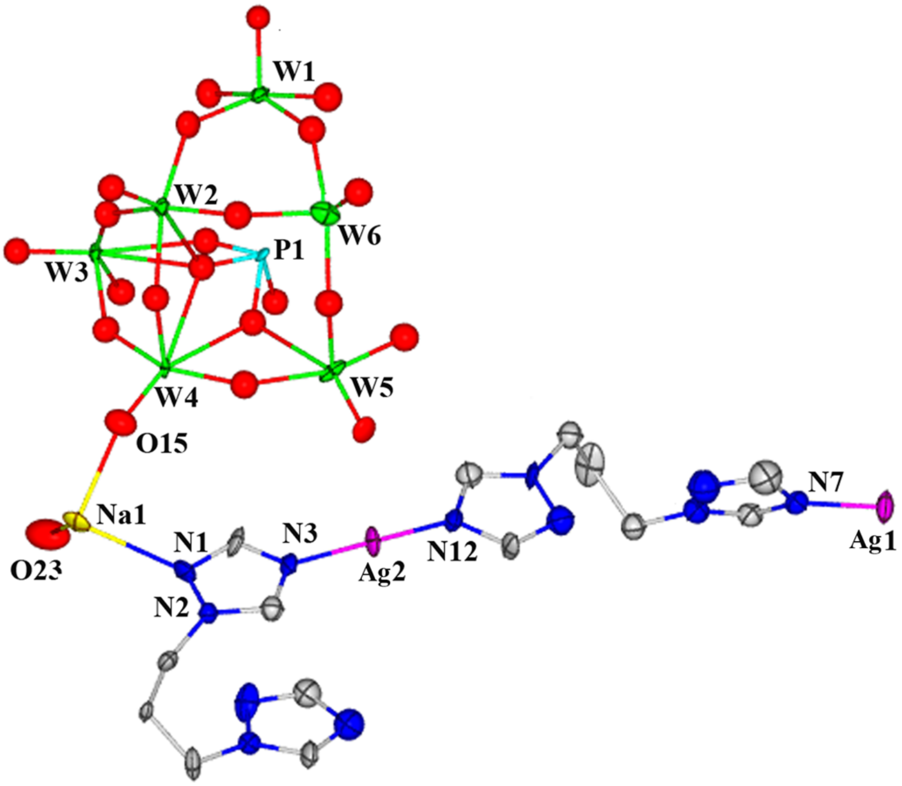

Figure S2 ORTEP view of the basic units in compound **2** with 50% thermal ellipsoid.

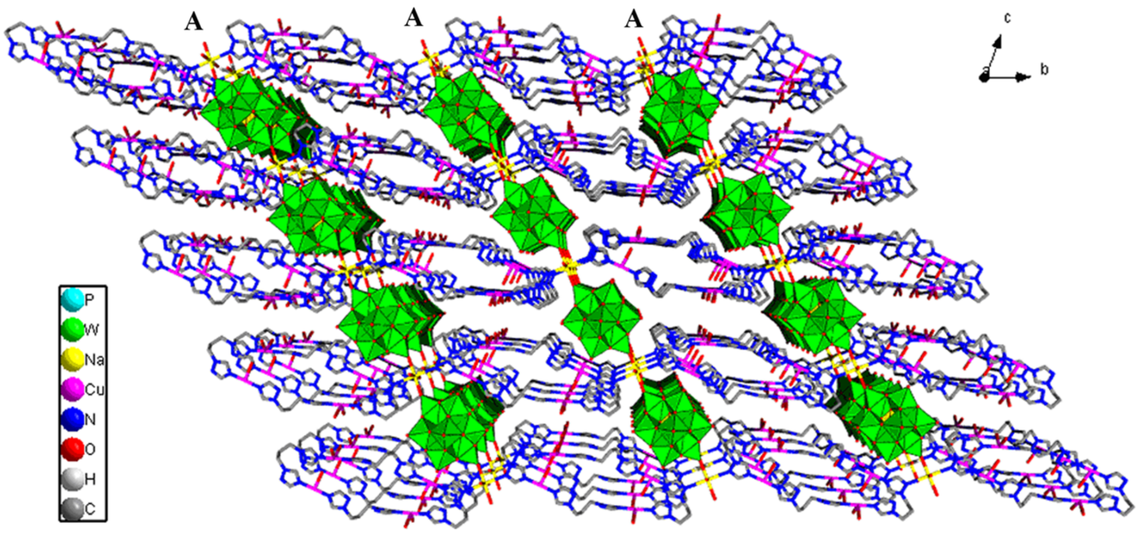

Figure S3 The 3D framework formed by $\{Na(H_2O)_2\}$, 40-membered macrocycles and 2D layer in A-A mode via Na-N bond (The Keggin cluster linked with Cu atoms of 40-membered macrocycles are omitted for clarity (B layer)).

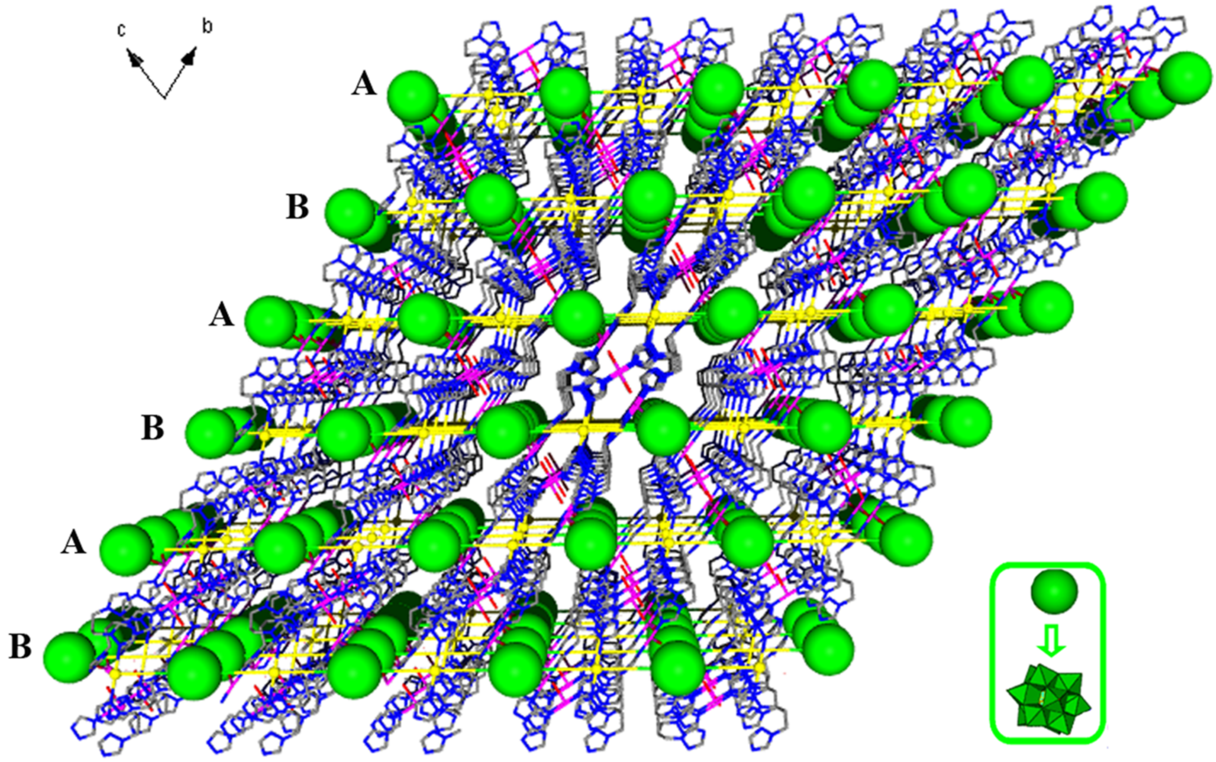

Figure S4. The simplified 3-D framework view of compound **1** formed by $\{Na(H_2O)_2\}$, 40-membered macrocycles and 2D layer in A-B-A-B mode.

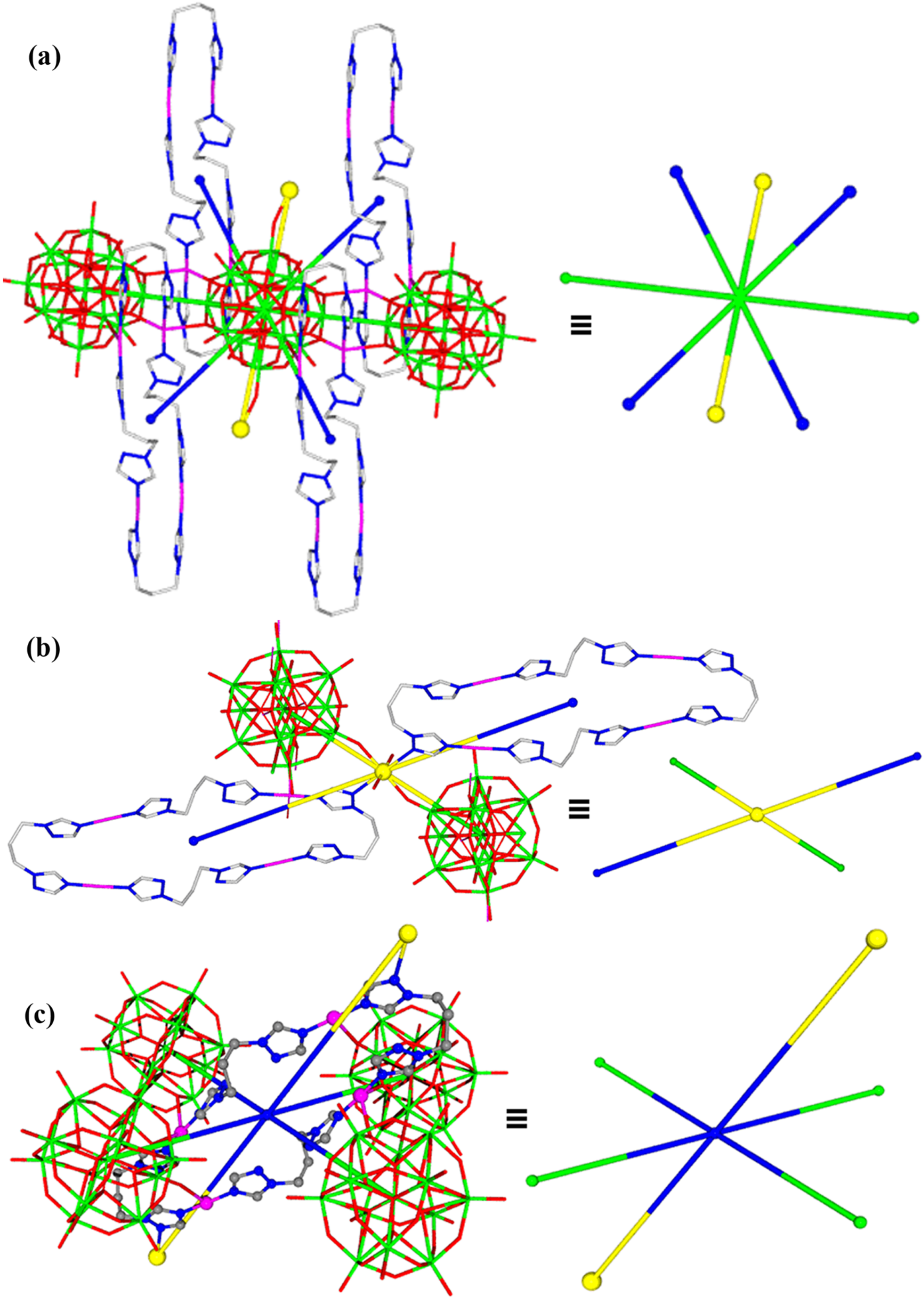

Figure S5 The details of simplify for Topology of compound **1**

2. Structural data

Table S1 Selected bond lengths (Å) and bond angles (º) of compound **1**

W(1)-O(1)	1.70(2)	W(2)-O(6)	1.68(3)	W(3)-O(10)	1.69(2)
W(1)-O(4)	1.83(3)	W(2)-O(9)	1.82(3)	W(3)-O(11)	1.85(3)
W(1)-O(2)	1.88(3)	W(2)-O(7)	1.91(2)	W(3)-O(12)	1.87(2)
W(1)-O(3)	1.93(3)	W(2)-O(5)	1.92(3)	W(3)-O(7)	1.92(2)
W(1)-O(5)	1.92(3)	W(2)-O(8)	1.93(2)	W(3)-O(19)#1	1.91(3)
W(1)-O(22)#1	2.39(4)	W(2)-O(22)#1	2.36(4)	W(3)-O(14)	2.37(4)
W(4)-O(15)	1.67(3)	W(5)-O(18)	1.72(2)	W(6)-O(9)	1.91(3)
W(4)-O(16)	1.86(3)	W(5)-O(20)	1.84(3)	W(6)-O(20)	1.91(3)
W(4)-O(8)	1.88(3)	W(5)-O(19)	1.88(3)	W(6)-O(4)	1.93(3)
W(4)-O(2)#1	1.87(3)	W(5)-O(3)#1	1.91(3)	W(6)-O(11)#1	1.93(3)
W(4)-O(12)	1.92(2)	W(5)-O(16)	1.921(3)	W(6)-O(21)	1.940(2)
W(4)-O(17)	2.37(5)	W(5)-O(14)#1	2.48(4)	W(6)-O(22)#1	2.52(4)
P(1)-O(13)	1.45(4)	P(1)-O(17)#1	1.51(4)	P(1)-O(14)#1	1.51(4)
P(1)-O(13)#1	1.45(4)	P(1)-O(17)	1.51(5)	P(1)-O(14)	1.51(4)
P(1)-O(22)#1	1.59(4)	Na(1)-O(15)	2.31(3)	Na(1)-O(23)#3	2.38(4)
P(1)-O(22)	1.59(4)	Na(1)-O(15)#3	2.31(3)	Na(1)-O(23)	2.38(4)
Na(1)-N(1)	2.74(3)	Cu(1)-N(6)#2	1.88(4)	Cu(2)-N(12)	1.88(3)
Na(1)-N(1)#3	2.74(3)	Cu(1)-N(7)	1.88(3)	Cu(2)-N(3)	1.89(3)
O(1)-W(1)-O(4)	102.8(13)	O(6)-W(2)-O(9)	105.0(13)	O(10)-W(3)-O(11)	102.3(13)
O(1)-W(1)-O(2)	102.0(13)	O(6)-W(2)-O(7)	101.9(12)	O(10)-W(3)-O(12)	101.2(12)
O(1)-W(1)-O(3)	101.1(15)	O(6)-W(2)-O(5)	100.5(13)	O(10)-W(3)-O(7)	102.9(12)
O(1)-W(1)-O(5)	99.8(12)	O(6)-W(2)-O(8)	100.6(12)	O(10)-W(3)-O(19)#1	102.2(13)
O(1)-W(1)-O(22)#1	161.1(14)	O(6)-W(2)-O(22)#1	162.9(14)	O(10)-W(3)-O(14)	163.2(14)
O(15)-W(4)-O(16)	100.4(14)	O(18)-W(5)-O(20)	103.2(12)	O(9)-W(6)-O(20)	89.0(12)
O(15)-W(4)-O(8)	101.8(12)	O(18)-W(5)-O(19)	102.3(12)	O(9)-W(6)-O(4)	87.5(12)
O(15)-W(4)-O(2)#1	102.9(13)	O(18)-W(5)-O(3)#1	100.5(15)	O(9)-W(6)-O(11)#1	158.0(12)
O(15)-W(4)-O(12)	102.5(13)	O(18)-W(5)-O(16)	100.9(12)	O(9)-W(6)-O(21)	99.0(8)
O(15)-W(4)-O(17)	159.4(15)	O(18)-W(5)-O(14)#1	161.8(13)	O(9)-W(6)-O(22)#1	61.9(13)
O(17)#1-P(1)-O(17)	180	O(17)#1-P(1)-O(14)	75(2)	O(17)-P(1)-O(22)#1	109(2)
O(17)#1-P(1)-	105(2)	O(17)-P(1)-O(14)	105(2)	O(17)#1-P(1)-O(22)	109(2)
O(17)-P(1)-O(14)#1	75(2)	O(17)#1-P(1)-O(22)#1	71(2)	O(17)-P(1)-O(22)	71(2)
O(15)-Na(1)-O(15)#3	180	O(15)#3-Na(1)-O(23)#3	93.0(11)	O(15)#3-Na(1)-O(23)	87.0(11)
O(15)-Na(1)-O(23)#3	87.0(11)	O(15)-Na(1)-O(23)	93.0(11)	O(15)-Na(1)-N(1)	90.2(10)
O(15)#3-Na(1)-N(1)	89.8(10)	O(15)-Na(1)-N(1)#3	89.8(10)	O(15)#3-Na(1)-N(1)#3	90.2(10)

Table S2 Selected bond lengths (Å) and bond angles (º) of compound **2**

W(1)-O(1)	173(2)	W(2)-O(6)	1.68(3)	W(3)-O(10)	1.69(2)
W(1)-O(4)	1.88(3)	W(2)-O(9)	1.83(2)	W(3)-O(11)	1.84(3)
W(1)-O(2)	1.86(3)	W(2)-O(5)	1.91(3)	W(3)-O(12)	1.88(3)
W(1)-O(5)	1.89(3)	W(2)-O(8)	1.92(3)	W(3)-O(7)	1.92(3)
W(1)-O(3)	1.94(3)	W(2)-O(7)	1.94(3)	W(3)-O(19)#1	1.94(3)
W(1)-O(22)#1	2.37(6)	W(2)-O(22)#1	2.39(6)	W(3)-O(14)	2.40(6)
W(4)-O(15)	1.70(3)	W(5)-O(18)	1.71(2)	W(6)-O(9)	1.93(2)
W(4)-O(8)	1.87(3)	W(5)-O(19)	1.83(3)	W(6)-O(11)#1	1.91(3)
W(4)-O(16)	1.87(3)	W(5)-O(20)	1.89(3)	W(6)-O(20)	1.93(3)
W(4)-O(2)#1	1.92(3)	W(5)-O(3)#1	1.93(3)	W(6)-O(4)	1.94(3)

W(4)-O(12)	1.93(3)	W(5)-O(16)	1.95(3)	W(6)-O(21)	1.9403(18)
W(4)-O(17)	2.36(6)	W(5)-O(14)#1	2.45(6)	W(6)-O(22)#1	2.47(6)
P(1)-O(13)#1	1.49(6)	P(1)-O(17)#1	1.54(6)	P(1)-O(14)	1.56(6)
P(1)-O(13)	1.49(6)	P(1)-O(17)	1.54(6)	P(1)-O(14)#1	1.56(6)
P(1)-O(22)	1.63(6)	Na(1)-O(15)#4	2.30(3)	Na(1)-O(23)#4	2.38(4)
P(1)-O(22)#1	1.63(6)	Na(1)-O(15)	2.30(3)	Na(1)-O(23)	2.38(4)
Na(1)-N(1)	2.76(3)	Ag(1)-N(7)	1.88(3)	Ag(2)-N(3)	1.90(3)
Na(1)-N(1)#4	2.76(3)	Ag(1)-N(6)#2	1.92(4)	Ag(2)-N(12)	1.91(3)
O(1)-W(1)-O(4)	103.1(13	O(6)-W(2)-O(9)	103.5(14)	O(10)-W(3)-O(11)	102.7(14)
O(1)-W(1)-O(2)	102.6(13	O(6)-W(2)-O(5)	101.1(13)	O(10)-W(3)-O(12)	102.0(13)
O(1)-W(1)-O(5)	102.3(13	O(6)-W(2)-O(8)	102.1(13)	O(10)-W(3)-O(7)	102.3(13)
O(1)-W(1)-O(3)	98.8(13)	O(6)-W(2)-O(7)	100.4(13)	O(10)-W(3)-O(19)#1	104.6(13)
O(1)-W(1)-O(22)#1	161.4(17	O(6)-W(2)-O(22)#1	160.2(17)	O(10)-W(3)-O(14)	160.0(17)
O(15)-W(4)-O(8)	102.6(13	O(18)-W(5)-O(19)	104.2(13)	O(9)-W(6)-O(11)#1	156.9(13)
O(15)-W(4)-O(16)	99.3(13)	O(18)-W(5)-O(20)	102.7(13)	O(9)-W(6)-O(20)	89.6(12)
O(15)-W(4)-O(2)#1	103.9(14	O(18)-W(5)-O(3)#1	98.7(13)	O(9)-W(6)-O(4)	87.6(11)
O(15)-W(4)-O(12)	102.8(13	O(18)-W(5)-O(16)	100.7(12)	O(9)-W(6)-O(21)	98.2(9)
O(15)-W(4)-O(17)	158.5(17	O(18)-W(5)-O(14)#1	160.7(16)	O(9)-W(6)-O(22)#1	63.2(16)
O(17)#1-P(1)-O(17)	180	O(17)#1-P(1)-O(14)#1	106(3)	O(17)-P(1)-O(22)	71(3)
O(17)#1-P(1)-O(14)	74(3)	O(17)-P(1)-O(14)#1	74(3)	O(17)#1-P(1)-O(22)#1	71(3)
O(17)-P(1)-O(14)	106(3)	O(17)#1-P(1)-O(22)	109(3)	O(17)-P(1)-O(22)#1	109(3)
O(15)#4-Na(1)-O(15)	180	O(15)#4-Na(1)-O(23)#4	92.4(11)	O(15)-Na(1)-O(23)#4	87.6(11)
O(15)#4-Na(1)-O(23)	87.6(11)	O(15)-Na(1)-O(23)	92.4(11)	O(15)#4-Na(1)-N(1)	90.1(9)
O(15)-Na(1)-N(1)	89.9(9)	O(15)#4-Na(1)-N(1)#4	89.9(9)	O(15)-Na(1)-N(1)#4	90.1(9)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z；#2 -x+1/2,-y+1/2,-z

3. Physical characterization

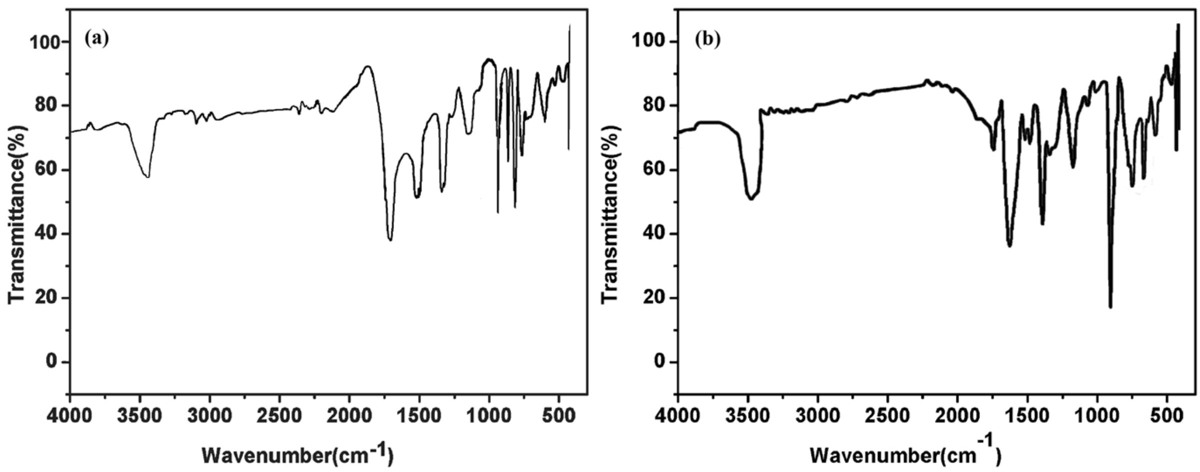

Figure S6 IR spectra of **(a)** compound **1** and **(b)** compound **2**

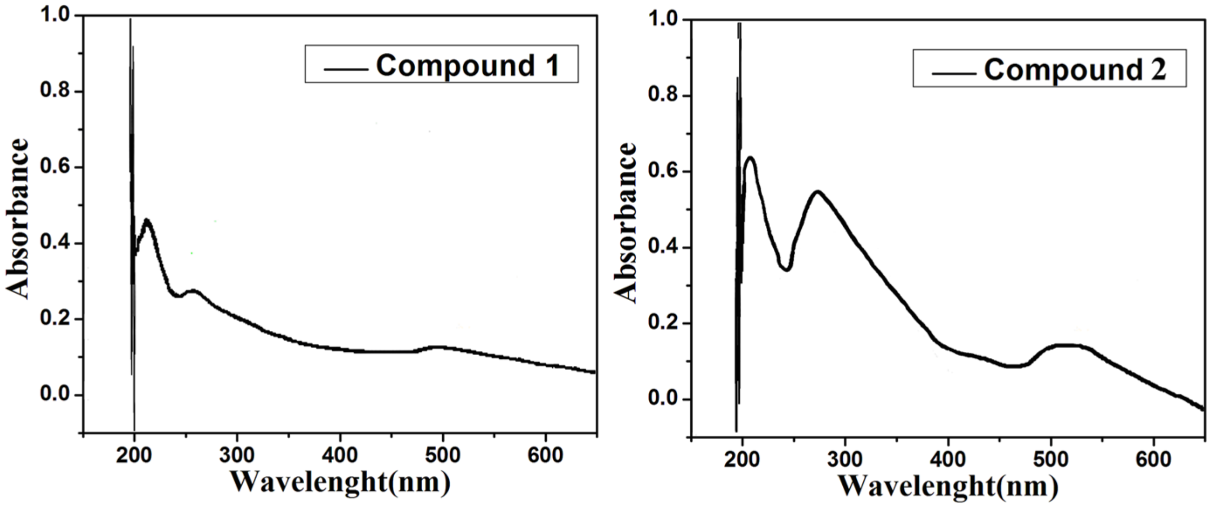

Figure S7 Solid state UV-vis spectra of compound **1** and compound **2**

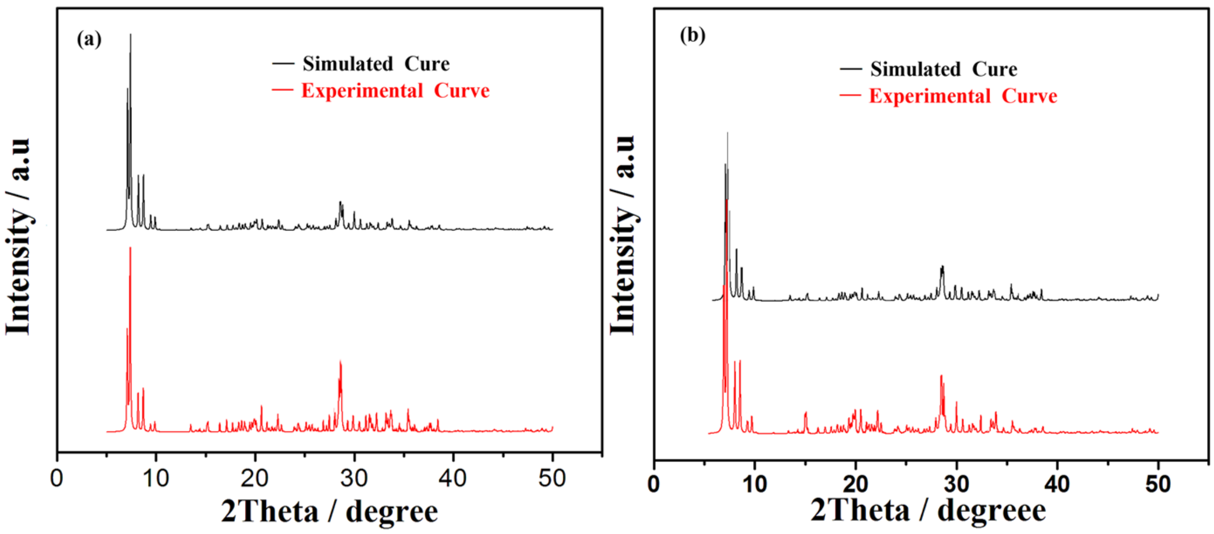

Figure S8 The PXRD contrast curves of **(a)** compound **1** and **(b)** compound **2**

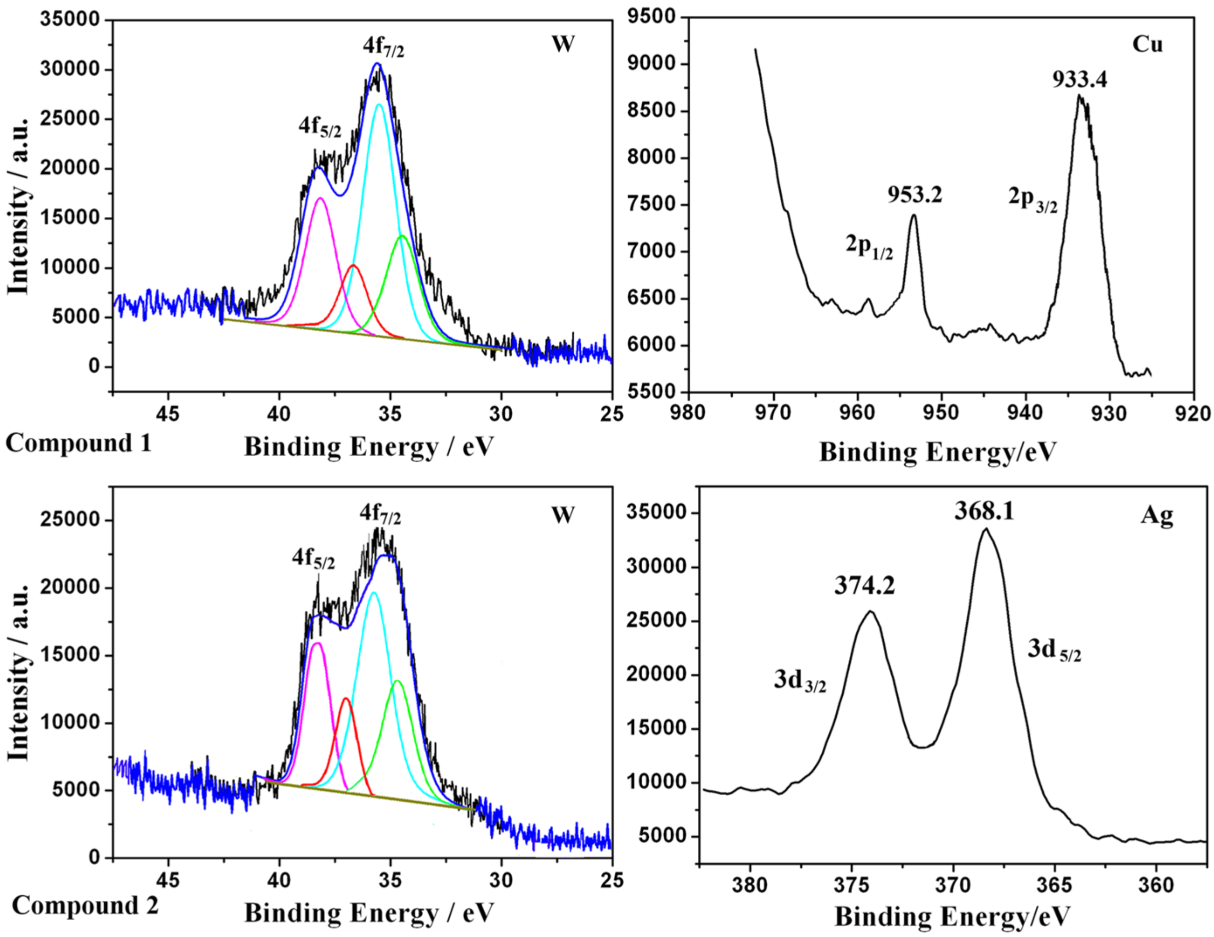

Figure S9 The XPS spectra of W and Cu/Ag in compound **1** and compound **2.**

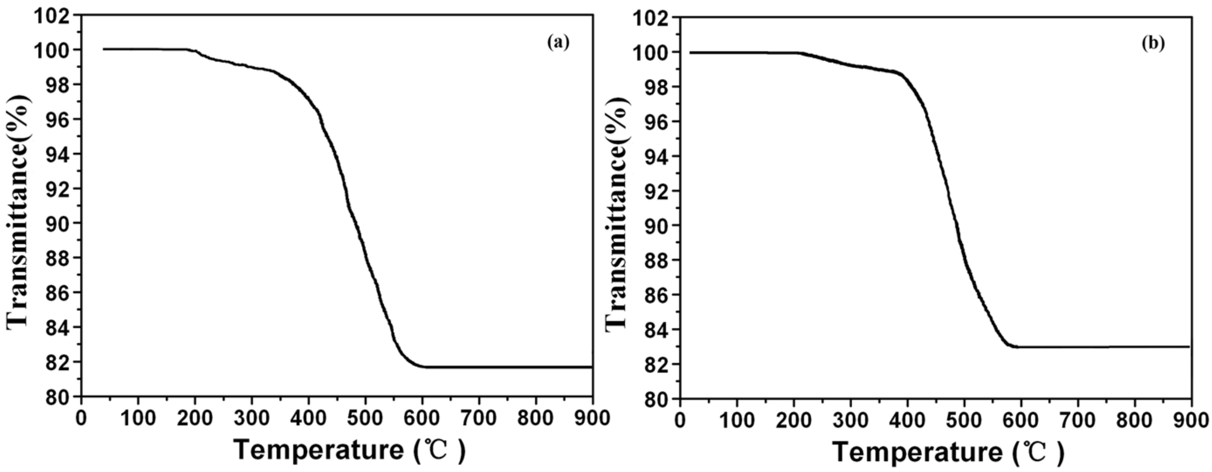

Figure S10 TG curve of **(a)** compound **1** and **(b)** compound **2.**

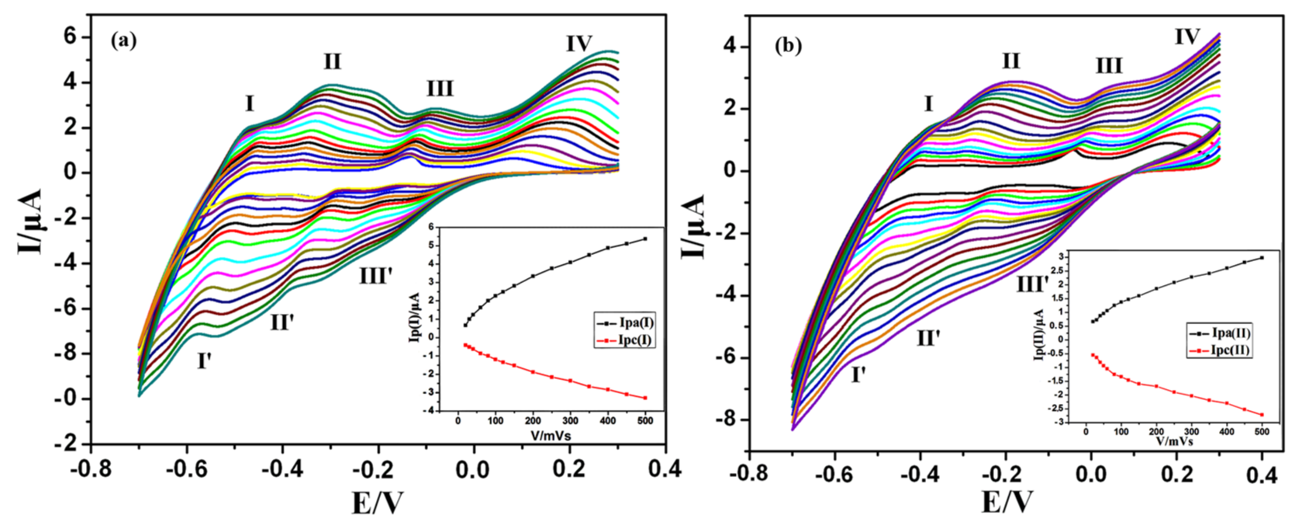

Figure S11 Cyclic voltammograms of **(a) 1-CPE** and **(b) 2-CPE** (scan rates from inner to outer: 20, 30, 40, 60, 80, 100, 120, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}). Potentials vs. SCE. (Insert plots: The dependence of anodic peak II current on scan rates.)

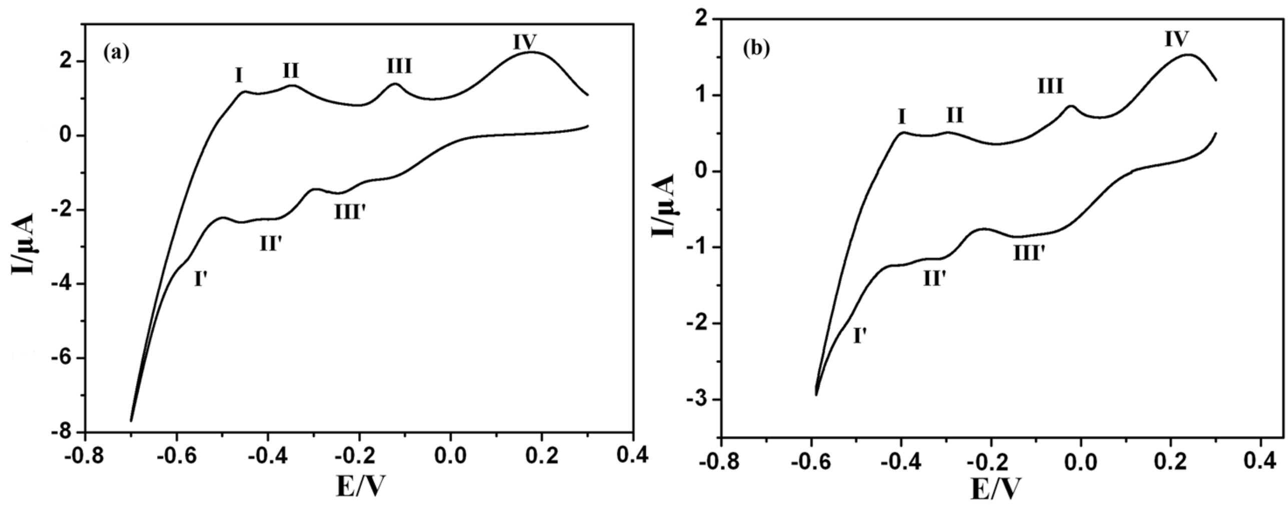

Figure S12 Cyclic voltammograms of (a) **1-CPE** and (b) **2-CPE** in the 1.0 M H_2SO_4 solution at scan rate of 40 mV s^{-1}; Potentials vs. SCE.