Supporting Information

Construction of two novel borotungstates modified by different ligands connected with single/double bridge

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1.Structural figures

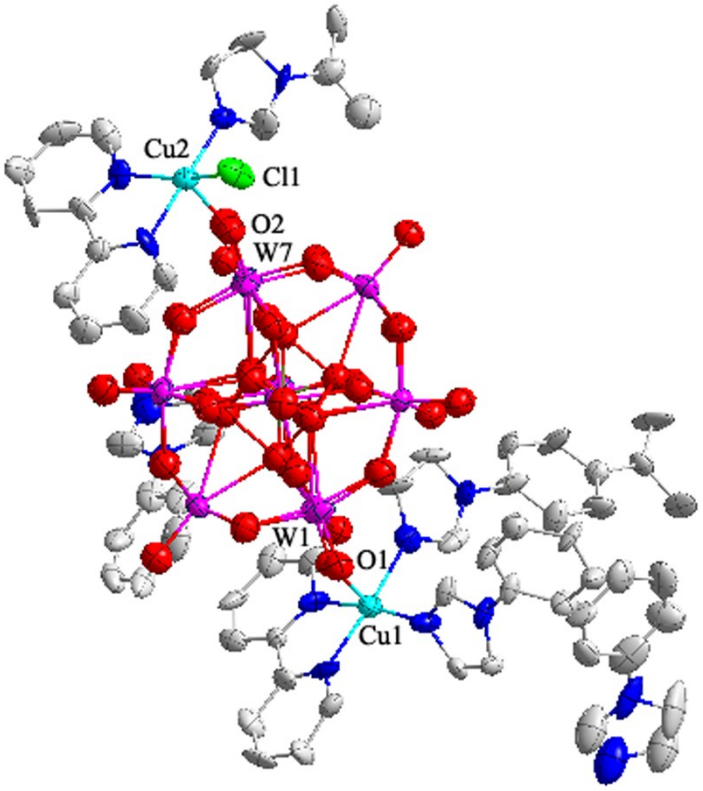

Figure S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoid.

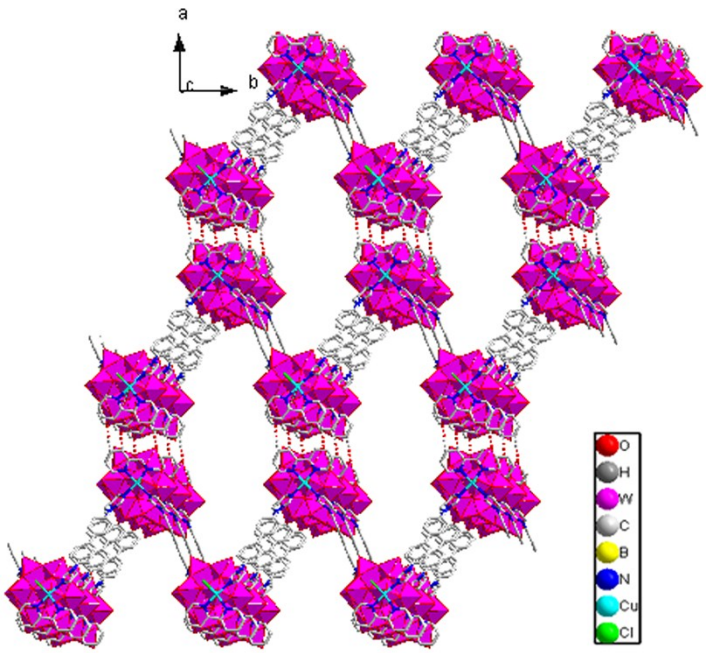

Figure S2 The 3-D supramolecular network on the ab plane of compound **1**.

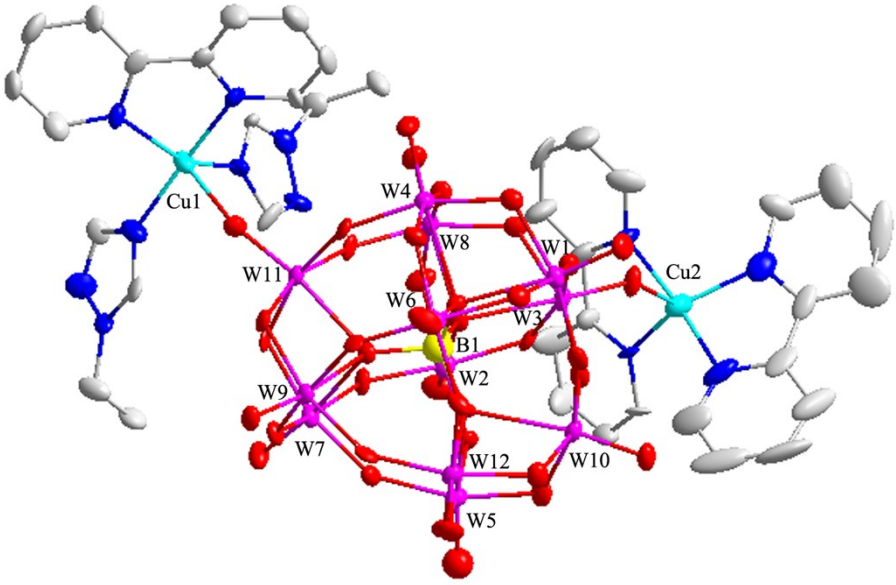

Figure S3 ORTEP view of the basic units in compound **2** with 50% thermal ellipsoid.

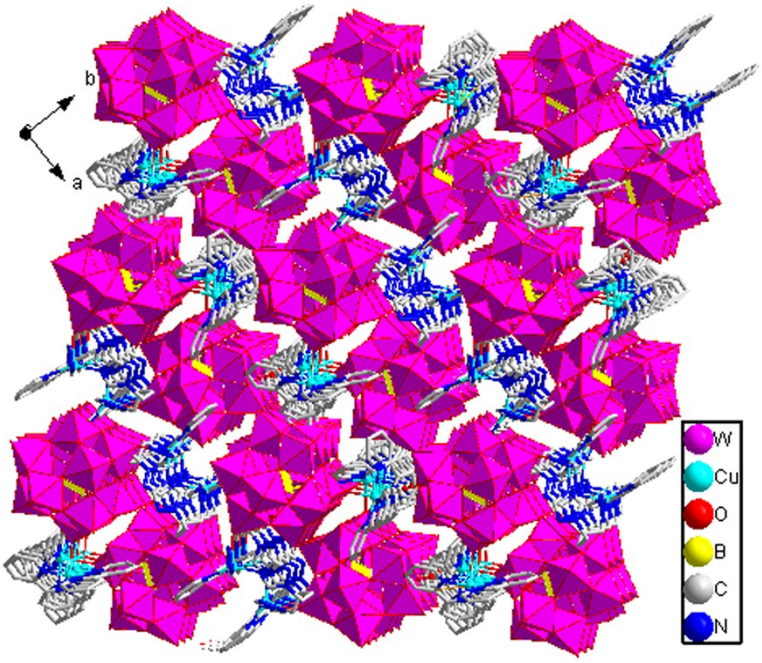

Figure S4 The 3-D supramolecular network on the ab plane of compound **3** linked by weak interaction.

2.Structural data

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

W(1)-O(1)	1.74(3)	W(5)-O(21)	2.46(7)	W(10)-O(39)	2.44(7)
W(1)-O(32)	1.84(3)	W(6)-O(19)	1.69(3)	W(10)-O(40)	2.46(7)
W(1)-O(29)	1.85(4)	W(6)-O(26)	1.82(3)	W(11)-O(5)	1.69(4)
W(1)-O(11)	1.89(4)	W(6)-O(23)	1.85(3)	W(11)-O(22)	1.91(3)
W(1)-O(13)	1.88(4)	W(6)-O(38)	1.90(4)	W(11)-O(45)	1.93(3)
W(1)-O(37)	2.42(7)	W(6)-O(28)	1.93(3)	W(11)-O(17)	1.94(3)
W(1)-O(33)	2.43(7)	W(6)-O(40)	2.40(7)	W(11)-O(25)	1.94(3)
W(2)-O(8)	1.65(4)	W(6)-O(21)	2.47(7)	W(11)-O(36)	2.36(7)
W(2)-O(7)	1.85(3)	W(7)-O(2)	1.70(3)	W(11)-O(41)	2.38(7)
W(2)-O(17)	1.88(4)	W(7)-O(30)	1.87(3)	W(12)-O(16)	1.67(4)
W(2)-O(32)	1.90(3)	W(7)-O(44)	1.89(3)	W(12)-O(31)	1.84(4)
W(2)-O(15)	1.95(4)	W(7)-O(14)	1.93(3)	W(12)-O(9)	1.86(3)
W(2)-O(37)	2.43(7)	W(7)-O(22)	1.93(3)	W(12)-O(34)	1.91(4)
W(2)-O(36)	2.46(7)	W(7)-O(41)	2.39(7)	W(12)-O(29)	1.94(3)
W(3)-O(18)	1.72(3)	W(7)-O(39)	2.46(7)	W(12)-O(33)	2.38(7)
W(3)-O(6)	1.85(3)	W(8)-O(20)	1.67(3)	W(12)-O(24)	2.44(7)
W(3)-O(45)	1.91(3)	W(8)-O(15)	1.85(3)	B(1)-O(37)	1.46(8)
W(3)-O(44)	1.91(3)	W(8)-O(34)	1.88(4)	B(1)-O(21)	1.47(8)
W(3)-O(23)	1.94(3)	W(8)-O(35)	1.92(3)	B(1)-O(24)	1.50(8)
W(3)-O(41)	2.43(7)	W(8)-O(25)	1.92(4)	B(1)-O(33)	1.51(8)
W(3)-O(21)	2.43(7)	W(8)-O(36)	2.38(7)	B(1)-O(40)	1.52(8)
W(4)-O(4)	1.69(4)	W(8)-O(24)	2.40(7)	B(1)-O(39)	1.56(8)
W(4)-O(38)	1.86(4)	W(9)-O(42)	1.70(4)	B(1)-O(36)	1.56(8)
W(4)-O(11)	1.87(4)	W(9)-O(14)	1.87(3)	B(1)-O(41)	1.58(8)

W(4)-O(12)	1.93(3)	W(9)-O(43)	1.88(4)	Cu(1)-O(1)	2.36(3)
W(4)-O(31)	1.96(4)	W(9)-O(35)	1.88(3)	Cu(2)-O(2)	2.26(3)
W(4)-O(33)	2.39(7)	W(9)-O(9)	1.92(3)	Cu(1)-N(2)	1.94(4)
W(4)-O(40)	2.43(7)	W(9)-O(39)	2.35(7)	Cu(1)-N(5)	2.00(3)
W(5)-O(3)	1.67(4)	W(9)-O(24)	2.48(7)	Cu(1)-N(3)	2.03(3)
W(5)-O(6)	1.89(3)	W(10)-O(10)	1.67(3)	Cu(1)-N(4)	2.05(4)
W(5)-O(13)	1.91(4)	W(10)-O(43)	1.87(4)	Cu(2)-N(13)	1.98(3)
W(5)-O(28)	1.93(3)	W(10)-O(12)	1.89(4)	Cu(2)-N(6)	1.99(3)
W(5)-O(7)	1.93(4)	W(10)-O(30)	1.90(3)	Cu(2)-N(8)	2.02(3)
W(5)-O(37)	2.45(7)	W(10)-O(26)	2.01(3)	Cu(2)-Cl(1)	2.250(12)
O(1)-W(1)-O(32)	100.6(16)	O(19)-W(6)-O(26)	98.9(17)	O(5)-W(11)-O(22)	97.7(16)
O(1)-W(1)-O(29)	98.6(16)	O(19)-W(6)-O(23)	97.6(16)	O(5)-W(11)-O(45)	97.4(16)
O(1)-W(1)-O(11)	99.1(16)	O(19)-W(6)-O(38)	102.6(16)	O(5)-W(11)-O(17)	97.7(16)
O(1)-W(1)-O(13)	98.6(15)	O(19)-W(6)-O(28)	94.7(16)	O(5)-W(11)-O(25)	97.0(16)
O(1)-W(1)-O(37)	157(2)	O(19)-W(6)-O(40)	161(2)	O(5)-W(11)-O(36)	159(2)
O(1)-W(1)-O(33)	159(2)	O(19)-W(6)-O(21)	158(2)	O(5)-W(11)-O(41)	158(2)
O(8)-W(2)-O(7)	101.7(17)	O(2)-W(7)-O(30)	98.0(15)	O(16)-W(12)-O(31)	99.3(17)
O(8)-W(2)-O(17)	97.5(17)	O(2)-W(7)-O(44)	101.3(15)	O(16)-W(12)-O(9)	99.8(16)
O(8)-W(2)-O(32)	101.1(17)	O(2)-W(7)-O(14)	96.9(15)	O(16)-W(12)-O(34)	99.6(17)
O(8)-W(2)-O(15)	96.9(17)	O(2)-W(7)-O(22)	97.7(15)	O(16)-W(12)-O(29)	98.9(16)
O(8)-W(2)-O(37)	160(2)	O(2)-W(7)-O(41)	159(2)	O(16)-W(12)-O(33)	159(2)
O(8)-W(2)-O(36)	157(2)	O(2)-W(7)-O(39)	156(2)	O(16)-W(12)-O(24)	159(2)
O(18)-W(3)-O(6)	101.7(15)	O(20)-W(8)-O(15)	98.9(16)	N(2)-Cu(1)-N(5)	96.0(16)
O(18)-W(3)-O(45)	99.8(15)	O(20)-W(8)-O(34)	98.1(16)	N(2)-Cu(1)-N(3)	169.9(13)
O(18)-W(3)-O(44)	99.7(15)	O(20)-W(8)-O(35)	99.0(15)	N(2)-Cu(1)-N(4)	92.0(14)
O(18)-W(3)-O(23)	97.2(15)	O(20)-W(8)-O(25)	98.1(16)	N(2)-Cu(1)-O(1)	84.4(14)
O(18)-W(3)-O(41)	159(2)	O(20)-W(8)-O(36)	160(2)	N(13)-Cu(2)-N(6)	174.8(13)
O(18)-W(3)-O(21)	159(2)	O(20)-W(8)-O(24)	158(2)	N(13)-Cu(2)-N(8)	80.0(14)
O(4)-W(4)-O(38)	99.7(16)	O(42)-W(9)-O(14)	100.0(17)	N(13)-Cu(2)-Cl(1)	93.0(10)
O(4)-W(4)-O(11)	102.7(16)	O(42)-W(9)-O(43)	102.4(17)	N(13)-Cu(2)-O(2)	89.8(14)
O(4)-W(4)-O(12)	95.7(16)	O(42)-W(9)-O(35)	99.6(17)	Cl(1)-Cu(2)-O(2)	106.1(10)
O(4)-W(4)-O(31)	101.5(16)	O(42)-W(9)-O(9)	100.8(16)	O(37)-B(1)-O(21)	72(4)
O(4)-W(4)-O(33)	161(2)	O(42)-W(9)-O(39)	161(2)	O(37)-B(1)-O(24)	110(4)
O(4)-W(4)-O(40)	156(2)	O(42)-W(9)-O(24)	158(2)	O(37)-B(1)-O(33)	75(4)
O(3)-W(5)-O(6)	100.8(16)	O(10)-W(10)-O(43)	102.6(17)	O(37)-B(1)-O(40)	110(4)
O(3)-W(5)-O(13)	102.3(16)	O(10)-W(10)-O(12)	97.2(17)	O(37)-B(1)-O(39)	176(5)
O(3)-W(5)-O(28)	95.4(16)	O(10)-W(10)-O(30)	100.0(16)	O(37)-B(1)-O(36)	73(4)
O(3)-W(5)-O(7)	101.5(16)	O(10)-W(10)-O(26)	98.0(16)	O(37)-B(1)-O(41)	109(4)
O(3)-W(5)-O(37)	160(2)	O(10)-W(10)-O(39)	160(2)		
O(3)-W(5)-O(21)	159(2)	O(10)-W(10)-O(40)	157(2)		

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

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

W(1)-O(35)	1.717(11)	W(5)-O(22)	2.377(10)	W(10)-O(11)	1.934(13)
W(1)-O(16)	1.849(12)	W(6)-O(17)	1.710(12)	W(10)-O(22)	2.413(11)
W(1)-O(6)	1.869(11)	W(6)-O(11)	1.856(12)	W(11)-O(25)	1.730(12)
W(1)-O(8)	1.935(11)	W(6)-O(34)	1.894(10)	W(11)-O(7)	1.887(10)
W(1)-O(1)	1.938(11)	W(6)-O(2)	1.927(12)	W(11)-O(31)	1.894(12)
W(1)-O(36)	2.368(11)	W(6)-O(16)	1.960(11)	W(11)-O(9)	1.922(12)
W(2)-O(10)	1.720(11)	W(6)-O(20)	2.301(11)	W(11)-O(4)	1.929(10)
W(2)-O(1)	1.875(12)	W(7)-O(32)	1.728(12)	W(11)-O(3)	2.292(11)
W(2)-O(7)	1.901(10)	W(7)-O(19)	1.865(11)	W(12)-O(27)	1.719(10)

W(2)-O(39)	1.911(11)	W(7)-O(12)	1.903(10)	W(12)-O(21)	1.885(11)
W(2)-O(14)	1.917(11)	W(7)-O(29)	1.921(10)	W(12)-O(30)	1.891(12)
W(2)-O(36)	2.347(10)	W(7)-O(9)	1.942(12)	W(12)-O(28)	1.915(12)
W(3)-O(26)	1.710(12)	W(7)-O(3)	2.376(11)	W(12)-O(13)	1.920(12)
W(3)-O(15)	1.882(10)	W(8)-O(33)	1.717(12)	W(12)-O(22)	2.359(9)
W(3)-O(8)	1.897(11)	W(8)-O(14)	1.906(10)	Cu(1)-N(3)	1.971(15)
W(3)-O(29)	1.917(11)	W(8)-O(38)	1.909(10)	Cu(1)-N(1)	1.990(16)
W(3)-O(39)	1.951(12)	W(8)-O(31)	1.915(12)	Cu(1)-N(7)	1.996(14)
W(3)-O(36)	2.346(10)	W(8)-O(2)	1.927(12)	Cu(1)-N(5)	2.000(13)
W(4)-O(37)	1.712(11)	W(8)-O(20)	2.356(10)	Cu(1)-O(25)	2.300(11)
W(4)-O(21)	1.902(12)	W(9)-O(24)	1.719(10)	Cu(2)-O(35)	2.393(11)
W(4)-O(38)	1.905(11)	W(9)-O(28)	1.866(12)	Cu(2)-N(10)	1.959(16)
W(4)-O(23)	1.910(12)	W(9)-O(23)	1.888(12)	Cu(2)-N(2)	1.966(16)
W(4)-O(34)	1.915(12)	W(9)-O(12)	1.926(10)	Cu(2)-N(11)	1.969(14)
W(4)-O(20)	2.426(9)	W(9)-O(4)	1.933(11)	Cu(2)-N(9)	2.001(18)
W(5)-O(40)	1.674(16)	W(9)-O(3)	2.398(9)	Cu(2)-O(35)	2.393(11)
W(5)-O(5)	1.886(12)	W(10)-O(18)	1.678(12)	B(1)-O(3)	1.55(3)
W(5)-O(15)	1.911(10)	W(10)-O(6)	1.913(10)	B(1)-O(20)	1.51(3)
W(5)-O(19)	1.918(11)	W(10)-O(5)	1.931(12)	B(1)-O(22)	1.50(3)
W(5)-O(13)	1.918(9)	W(10)-O(30)	1.932(10)	B(1)-O(36)	1.55(3)
O(35)-W(1)-O(16)	101.1(5)	O(40)-W(5)-O(22)	172.1(6)	O(18)-W(10)-O(11)	101.8(6)
O(35)-W(1)-O(6)	99.5(5)	O(17)-W(6)-O(11)	101.4(6)	O(18)-W(10)-O(22)	171.3(5)
O(35)-W(1)-O(8)	97.3(5)	O(17)-W(6)-O(34)	97.5(5)	O(25)-W(11)-O(7)	99.9(5)
O(35)-W(1)-O(1)	100.4(5)	O(17)-W(6)-O(2)	95.2(6)	O(25)-W(11)-O(31)	100.2(5)
O(35)-W(1)-O(36)	170.7(4)	O(17)-W(6)-O(16)	99.8(5)	O(25)-W(11)-O(9)	95.2(5)
O(10)-W(2)-O(1)	99.4(5)	O(17)-W(6)-O(20)	169.3(5)	O(25)-W(11)-O(4)	97.8(5)
O(10)-W(2)-O(7)	100.7(5)	O(32)-W(7)-O(19)	100.8(5)	O(25)-W(11)-O(3)	171.3(5)
O(10)-W(2)-O(39)	97.4(5)	O(32)-W(7)-O(12)	98.2(5)	O(27)-W(12)-O(21)	101.5(5)
O(10)-W(2)-O(14)	100.0(5)	O(32)-W(7)-O(29)	99.8(5)	O(27)-W(12)-O(30)	96.5(5)
O(10)-W(2)-O(36)	172.5(5)	O(32)-W(7)-O(9)	96.4(5)	O(27)-W(12)-O(28)	101.9(5)
O(26)-W(3)-O(15)	101.2(6)	O(32)-W(7)-O(3)	170.0(5)	O(27)-W(12)-O(13)	96.7(5)
O(26)-W(3)-O(8)	98.9(6)	O(33)-W(8)-O(14)	100.5(5)	O(27)-W(12)-O(22)	169.3(5)
O(26)-W(3)-O(29)	99.1(6)	O(33)-W(8)-O(38)	98.5(5)	N(3)-Cu(1)-N(1)	173.0(6)
O(26)-W(3)-O(39)	96.3(6)	O(33)-W(8)-O(31)	99.9(6)	N(3)-Cu(1)-N(7)	97.6(6)
O(26)-W(3)-O(36)	170.9(5)	O(33)-W(8)-O(2)	98.8(6)	N(3)-Cu(1)-N(5)	91.3(6)
O(37)-W(4)-O(21)	102.1(5)	O(33)-W(8)-O(20)	171.0(5)	N(3)-Cu(1)-O(25)	90.7(6)
O(37)-W(4)-O(38)	99.1(6)	O(24)-W(9)-O(28)	103.1(5)	N(10)-Cu(2)-N(2)	101.4(7)
O(37)-W(4)-O(23)	100.8(5)	O(24)-W(9)-O(23)	100.1(5)	N(10)-Cu(2)-N(11)	82.5(6)
O(37)-W(4)-O(34)	99.6(6)	O(24)-W(9)-O(12)	99.6(5)	N(10)-Cu(2)-N(9)	141.7(6)
O(37)-W(4)-O(20)	170.1(5)	O(24)-W(9)-O(4)	96.9(5)	N(10)-Cu(2)-O(35)	117.0(5)
O(40)-W(5)-O(5)	96.7(7)	O(24)-W(9)-O(3)	169.6(5)	O(22)-B(1)-O(20)	112.0(19)
O(40)-W(5)-O(15)	99.7(6)	O(18)-W(10)-O(6)	100.7(5)	O(22)-B(1)-O(36)	110(2)
O(40)-W(5)-O(19)	102.5(7)	O(18)-W(10)-O(5)	97.8(6)	O(22)-B(1)-O(3)	109(2)
O(40)-W(5)-O(13)	100.4(6)	O(18)-W(10)-O(30)	100.4(5)		

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

Table S3 Selected Hydrogen Bond Lengths ( ) and Bond Angles (°) of complexes **1**

D-H...A		d(D-H)	d(H...A)	<D-H...A	d(D...A)	Symmetry
1	O1W-H1WB...O23	0.85	2.36	133.3	3.01(4)	
	O1W-H1WA...O18	0.85	2.86	105.8	3.20(7)	
	O2W-H2WB...O10	0.85	2.52	123.9	3.07(7)	

3.Physical characterization

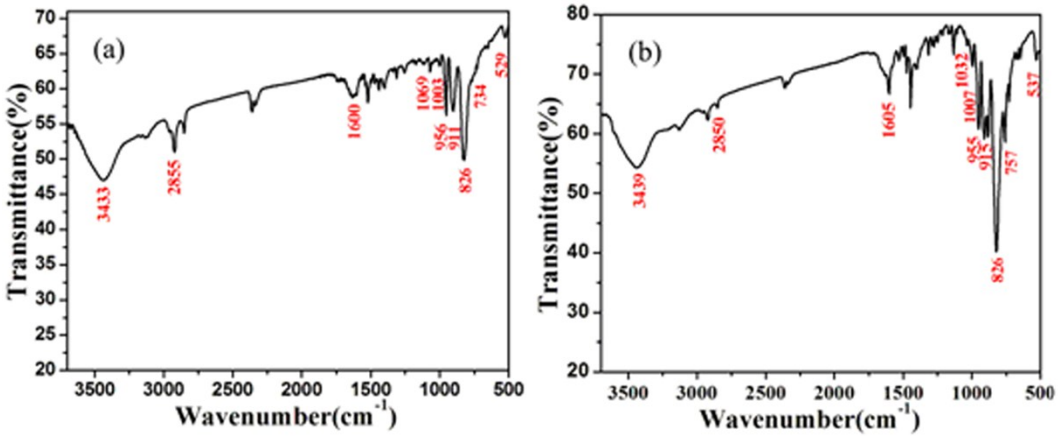

Figure S5 IR spectra of (a) compound **1** and (b)compound **2**.

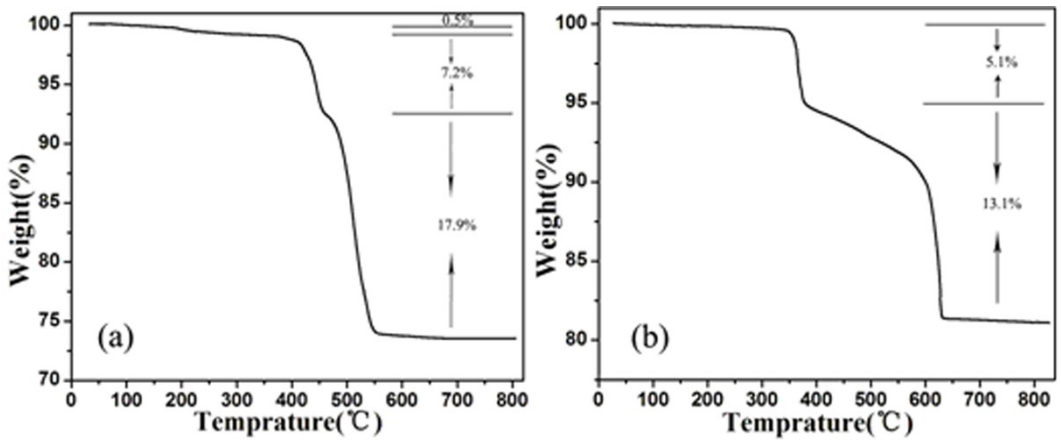

Figure S6 TG of (a) compound **1** and (b) compound **2**.

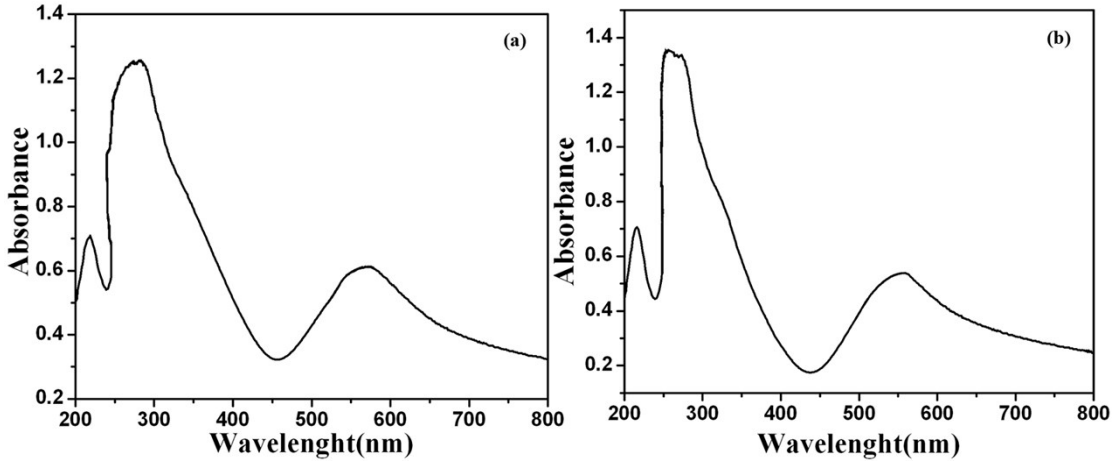

Figure S7 The UV-vis absorption spectra of (a) compound **1** and (b) compound **2** in solide state at room temperature.

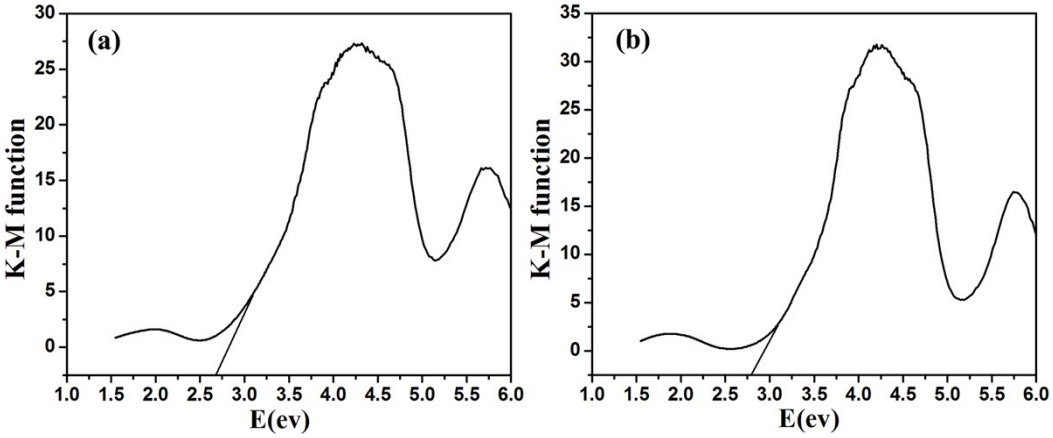

Figure S8 The diffuse reflectance spectra of (a) compound **1** and (b) compound **2**.

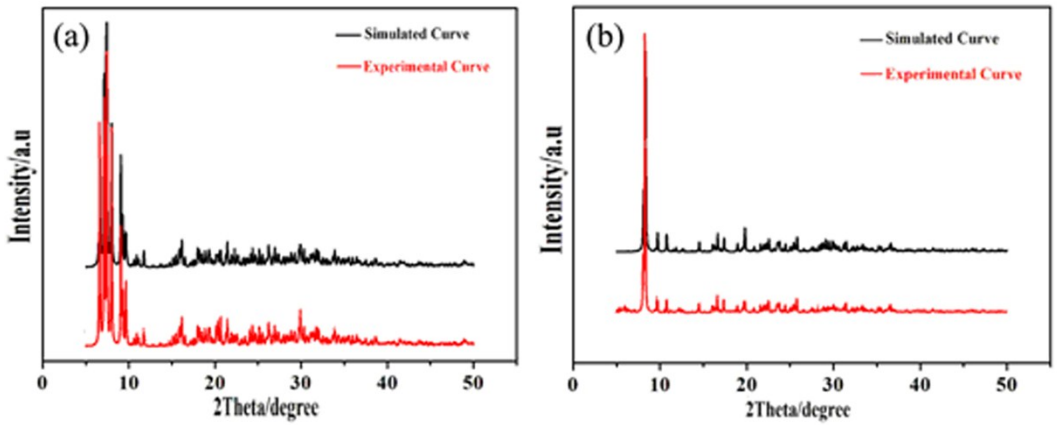

Figure S9 The PXRD contrast curves of **(a)** compound **1**and **(b)** compound **2**.

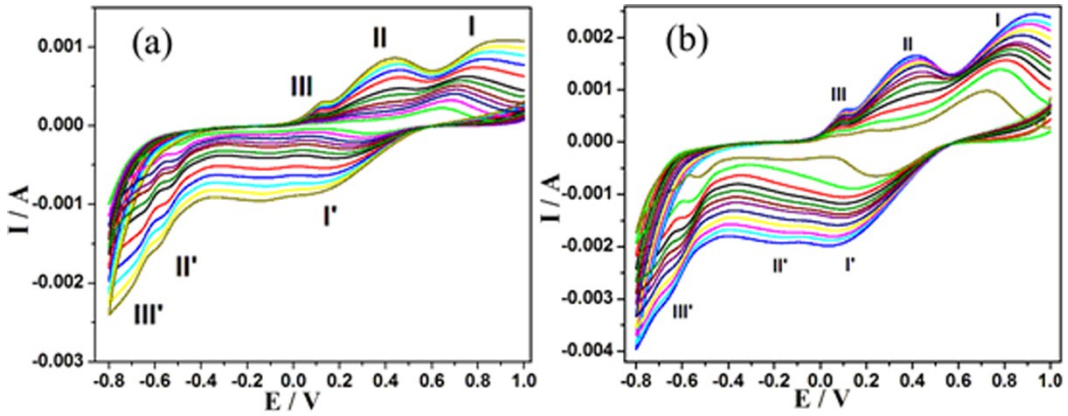

Figure S10 Cyclic voltammograms of **(a) 1**-CPE and **(b) 2**-CPE,, rates (from inner to outer: 20, 30, 40, 60, 80, 100, 120, 150, 200, 250, 300, 350 mV s^{-1}). Potentials vs. SCE. (Insert plots: The dependence of anodic peak II current on scan rates.)