

Supplementary Material

Synthesis, crystal structure and properties of sandwich type compounds based on {AsW₉} and hexa-nuclear unit with three supporting M–triazole complexes

Jia-min Liu¹, Lu Wang², Kai Yu^{1,*}, Zhan-hua Su¹, Chun-xiao Wang¹, Chun-mei Wang¹, Bai-bin Zhou^{1,*}

1.Key Laboratory of synthesis of functional materials and green catalysis Colleges of Heilongjiang Province, Harbin Normal University, Harbin, 150080, P. R. China

2.Department of Biochemical Engineering, Harbin Institute of Technology, Harbin, 150090, P R China

1. Structural figures

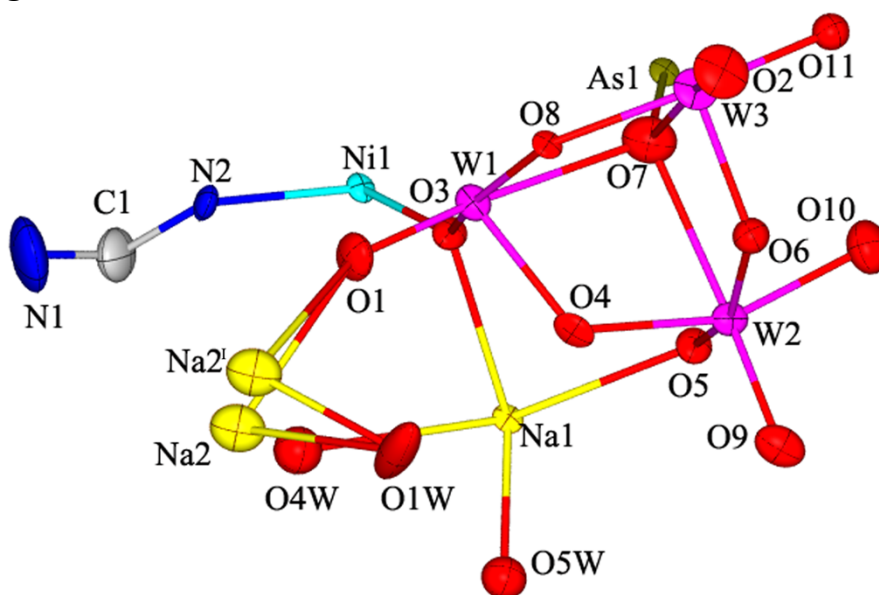


Figure S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoid.

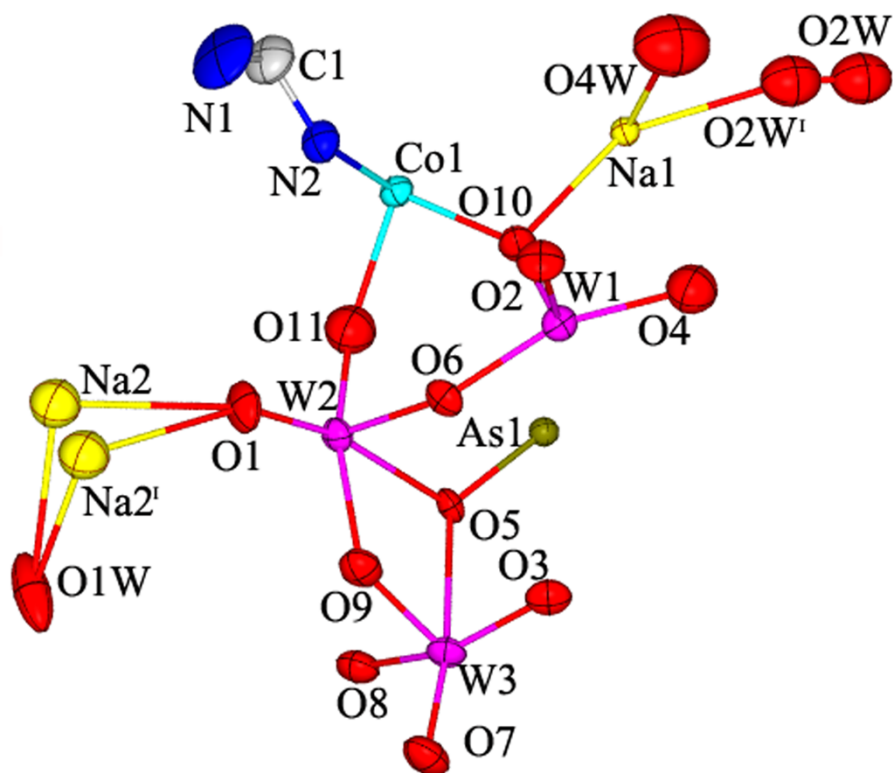


Figure S2 ORTEP view of the basic units in compound **2** with 50% thermal ellipsoid.

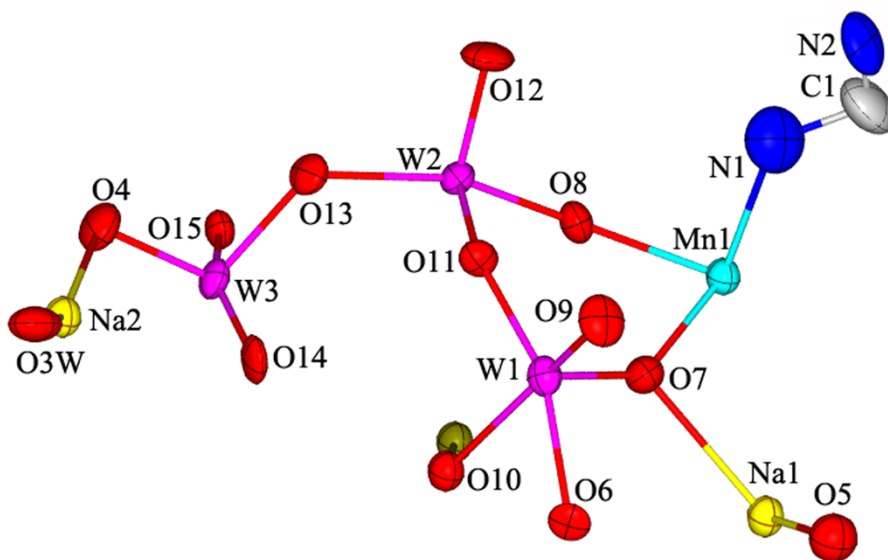


Figure S3 ORTEP view of the basic units in compound **3** with 50% thermal ellipsoid.

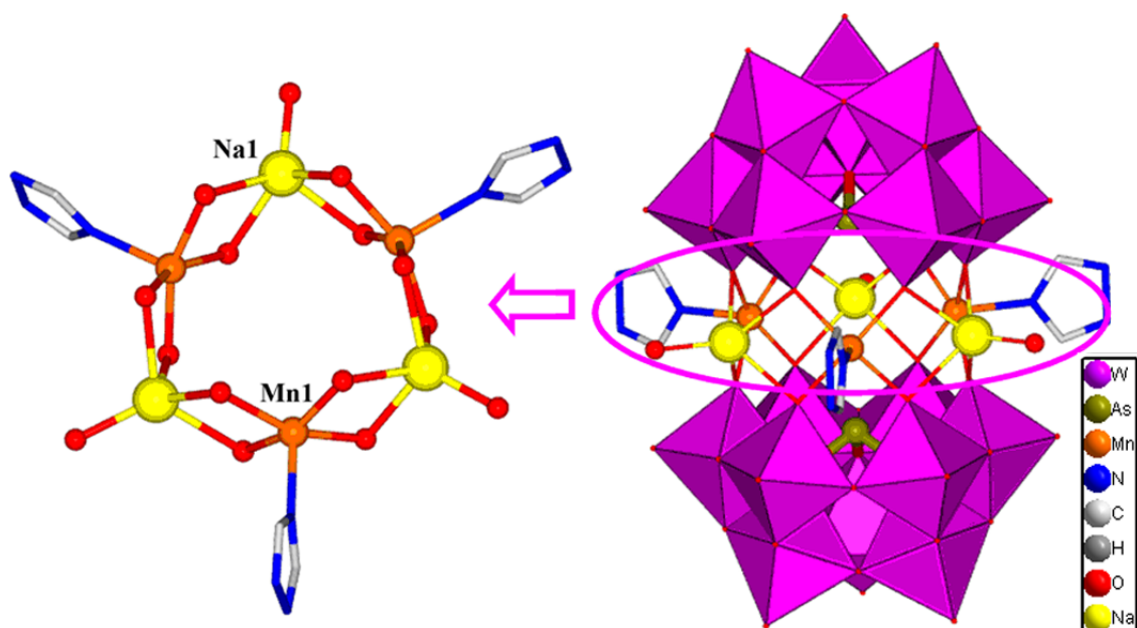


Figure S4 ORTEP view of the basic units in compound **3** with 50% thermal ellipsoid.

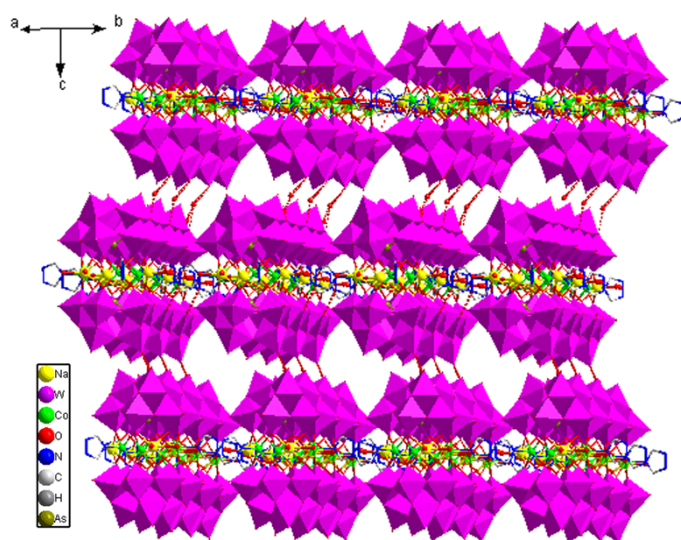


Figure S4 The packing arrangement of compound **2** viewed along *b* axis.

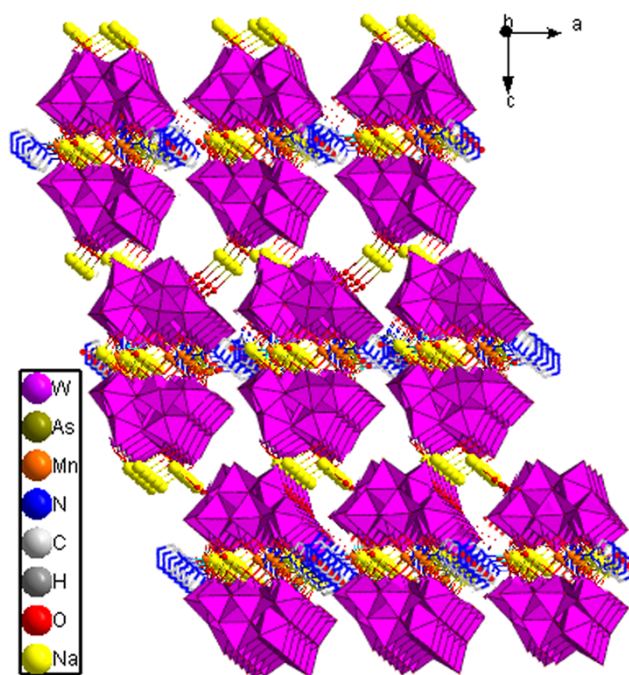


Figure S5 The packing arrangement of compound **3** viewed along *b* axis.

2. Structural data

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

W(1)-O(1)	1.738(11)	W(1)-O(3)	1.785(10)	W(1)-O(4)	1.950(10)
W(1)-O(7)	2.311(13)	W(1)-O(8)	2.026(8)	W(1)-O(10)	1.928(13)
W(2)-O(4)	1.945(10)	W(2)-O(5)	1.793(10)	W(2)-O(6)	2.030(10)
W(2)-O(7)	2.353(12)	W(2)-O(9)	1.722(11)	W(2)-O(10) #1	1.925(12)
W(3)-O(2)	1.927(10)	W(3)-O(2) #1	1.906(10)	W(3)-O(6)	1.884(10)
W(3)-O(7)	2.388(12)	W(3)-O(8)	1.888(9)	W(3)-O(11)	1.732(11)
As(1)-O(7)	1.796(12)	As(1)-O(7) #1	1.796(12)	As(1)-O(7)#2	1.796(12)
Ni(1)-O(3)	2.008(10)	Ni(1)-O(3)#4	2.008(10)	Ni(1)-O(5) #2	1.996(10)
Ni(1)-O(5) #3	1.996(10)	Ni(1)-N(1)	2.012(16)	Na(1)-O(5)	2.414(11)
Na(1)-O(3)	2.424(11)	Na(1)-O(3)#4	2.424(11)	Na(1)-O(5)#4	2.414(11)
Na(1)-O(4)	2.960(10)	Na(1)-O(4)#4	2.960(10)	Na(1)-O(4W)	2.77(4)
Na(1)-O(5W)	2.18(3)	Na(2)-O(4)#7	2.776(17)	Na(2')-O(4)#7	2.795(17)
Na(2')-O(5W)#9	2.96(2)				
O(1)-W(1)-O(3)	103.4(5)	O(1)-W(1)-O(10)	99.6(5)	O(1)-W(1)-O(4)	99.3(5)
O(1)-W(1)-O(8)	96.1(5)	O(1)-W(1)-O(7)	167.5(5)	O(5)-W(2)-O(7)	87.7(4)
O(5)-W(2)-O(10)#1	91.7(5)	O(5)-W(2)-O(4)	91.9(4)	O(5)-W(2)-O(6)	160.3(4)
O(6)-W(3)-O(8)	90.4(4)	O(6)-W(3)-O(2)#1	89.3(4)	O(6)-W(3)-O(2)	158.5(4)
O(6)-W(3)-O(7)	74.4(4)	O(5)#3-Ni(1)-O(5)#2	89.0(6)	O(5)#3-Ni(1)-O(3)	159.8(4)
O(5)#3-Ni(1)-O(3)#4	87.2(4)	O(5)#3-Ni(1)-N(1)	101.6(5)	O(5W)-Na(1)-O(4)	82.6(2)
O(5W)-Na(1)-O(4)#4	82.6(2)	O(5W)-Na(1)-O(5)#4	104.7(7)	O(5W)-Na(1)-O(5)	104.7(8)
O(5W)-Na(1)-O(3)#4	129.7(6)	O(5W)-Na(1)-O(3)	129.7(6)	O(5W)-Na(1)-O(4W)	70.1(11)
O(7)#1-As(1)-O(7)	97.6(5)	O(7)#1-As(1)-O(7)#2	97.6(5)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 x,y-1,z #3 x,y+1,z

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

As(1)-O(5)#1	1.789(9)	As(1)-O(5)	1.789(9)	As(1)-O(5)#2	1.789(9)
W(1)-O(2)	1.730(10)	W(1)-O(10)	1.789(10)	W(1)-O(6)	1.924(10)
W(1)-O(4)	1.940(14)	W(1)-O(8)#1	2.021(11)	W(1)-O(5)#1	2.357(9)
W(2)-O(1)	1.734(10)	W(2)-O(11)	1.785(14)	W(2)-O(6)	1.915(10)
W(2)-O(4)#2	1.953(14)	W(2)-O(9)	2.019(11)	W(2)-O(5)	2.318(9)
W(3)-O(7)	1.725(11)	W(3)-O(8)	1.883(11)	W(3)-O(9)	1.892(11)
W(3)-O(3)#1	1.916(11)	W(3)-O(3)	1.919(11)	W(3)-O(5)	2.389(9)
Co(1)-O(10)	2.027(10)	Co(1)-O(10)#3	2.027(10)	Co(1)-O(11)#3	2.038(14)
Co(1)-O(11)	2.038(14)	Co(1)-N(1)	2.067(18)	Na(1)-O(4W)	2.18(3)
Na(1)-O(10)	2.362(11)	Na(1)-O(10)#3	2.362(11)	Na(1)-O(11)#4	2.380(15)
Na(1)-O(11)#1	2.380(15)	Na(1)-O(2W')	2.42(5)	O(1)-Na(2')	2.74(2)
Na(2)-O(1)	2.739(18)	W(3)#2-O(3)	1.916(11)	W(2)#1-O(4)	1.953(14)
Na(2)#5-O(4)	2.79(2)	W(1)#2O(5)	2.357(9)	W(1)#2-O(8)	2.021(11)
Na(2')#5-O(4)	2.78(2)	Na(1)#2-O(11)	2.380(15)	Na(2')#6-O(1W)	2.28(2)
Na(2')#7-O(1W)	2.28(2)	Na(2')-O(1W)	2.28(2)	Na(2)#7-O(1W)	2.68(3)
Na(2)#6-O(1W)	2.68(3)	Na(2)-O(1W)	2.68(3)	Na(2)-O(4)#8	2.79(2)
Na(2')-O(4)#8	2.78(2)				
O(5)#1-As(1)-O(5)	97.5(4)	O(5)#1-As(1)-O(5)#2	97.5(4)	O(2)-W(1)-O(10)	103.9(5)
O(2)-W(1)-O(6)	101.1(5)	O(2)-W(1)-O(4)	99.8(6)	O(2)-W(1)-O(8)#1	95.7(5)
O(2)-W(1)-O(5)#1	166.7(4)	O(1)-W(2)-O(11)	103.8(6)	O(1)-W(2)-O(6)	100.4(5)
O(1)-W(2)-O(4)#2	99.2(6)	O(1)-W(2)-O(9)	96.3(5)	O(1)-W(2)-O(5)	167.6(5)
O(7)-W(3)-O(8)	100.7(5)	O(7)-W(3)-O(9)	100.5(5)	O(7)-W(3)-O(3)#1	100.5(5)
O(7)-W(3)-O(3)	101.0(5)	O(7)-W(3)-O(5)	171.8(5)	O(10)-Co(1)-O(10)#3	89.2(6)
O(10)-Co(1)-O(11)#3	157.4(5)	O(10)-Co(1)-O(11)	86.3(5)	O(10)-Co(1)-N(1)	102.4(5)
O(4W)-Na(1)-O(10)	104.7(7)	O(4W)-Na(1)-O(10)#3	104.7(7)	O(4W)-Na(1)-O(11)#4	125.0(7)
O(4W)-Na(1)-O(11)#1	125.0(7)	O(4W)-Na(1)-O(2W')	61.0(13)	O(1W)-Na(2)-O(1)	93.8(5)
O(1W)-Na(2)-O(4)#8	112.4(7)	O(1W)-Na(2')-O(1)	103.6(7)	O(1W)-Na(2')-O(4)#8	127.6(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 x,y-1,z #3 x,y+1,z

Table S3 Selected bond lengths (Å) and bond angles (°) of compound 3

W(1)-O(9)	1.726(16)	W(1)-O(7)	1.782(17)	W(1)-O(11)	1.929(14)
W(1)-O(6)	1.954(14)	W(1)-O(15)#1	2.006(15)	W(1)-O(10)	2.325(15)
W(2)-O(12)	1.729(16)	W(2)-O(8)	1.790(15)	W(2)-O(11)	1.906(14)
W(2)-O(6)#2	1.940(15)	W(2)-O(13)	2.008(15)	W(2)-O(10)#2	2.315(15)
W(3)-O(4)	1.720(17)	W(3)-O(15)	1.888(16)	W(3)-O(14)#2	1.888(17)
W(3)-O(13)	1.907(17)	W(3)-O(14)	1.945(17)	W(3)-O(10)#2	2.411(15)
As(1)-O(10)#1	1.798(16)	As(1)-O(10)	1.798(16)	As(1)-O(10)#2	1.798(16)
Mn(1)-O(7)#3	2.098(16)	Mn(1)-O(7)	2.098(16)	Mn(1)-O(8)	2.100(16)
Mn(1)-O(8)#3	2.100(16)	Mn(1)-N(1)	2.31(3)	W(2)#1-O(10)	2.315(15)
W(3)#1-O(10)	2.411(15)	W(2)#1-O(6)	1.940(14)	Na(1)#2-O(8)	2.392(19)
W(1)#2-O(15)	2.006(15)	W(3)#1-O(14)	1.888(17)	Na(1)-O(7)	2.415(18)
Na(2)-O(4)	3.00(2)	O(5)-Na(1)	2.21(6)	Na(1)-O(8)#1	2.392(19)
Na(1)-O(8)#4	2.392(19)	Na(1)-O(7)#3	2.415(18)	Na(2)-O(3W)	2.88(4)

O(9)-W(1)-O(7)	103.6(8)	O(9)-W(1)-O(11)	101.4(8)	O(9)-W(1)-O(6)	99.9(8)
O(9)-W(1)-O(15)#1	96.1(7)	O(9)-W(1)-O(10)	167.0(7)	O(12)-W(2)-O(8)	103.8(8)
O(12)-W(2)-O(11)	100.1(8)	O(12)-W(2)-O(6)#2	99.0(8)	O(12)-W(2)-O(13)	95.4(8)
O(12)-W(2)-O(10)#2	167.0(8)	O(4)-W(3)-O(15)	101.5(8)	O(4)-W(3)-O(14)#2	101.2(8)
O(4)-W(3)-O(13)	100.4(8)	O(4)-W(3)-O(14)	100.4(8)	O(4)-W(3)-O(10)#2	170.8(8)
O(10)#1-As(1)-O(10)	98.5(7)	O(10)#1-As(1)- O(10)#2	98.5(7)	O(7)#3-Mn(1)-O(7)	89.6(9)
O(7)#3-Mn(1)-O(8)	156.6(7)	O(7)#3-Mn(1)-O(8)#3	86.1(6)	O(7)#3-Mn(1)-N(1)	104.3(9)
O(5)-Na(1)-O(8)#1	121.7(12)	O(5)-Na(1)-O(8)#4	121.7(12)	O(5)-Na(1)-O(7)#3	110.1(13)
O(5)-Na(1)-O(7)	110.1(13)	O(3W)-Na(2)-O(4)	158.7(8)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 x,y-1,z #3 x,y+1,z

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+2 #2 x,y-1,z #3 x,y+1,z

Table S3: hydrogen bonds lengths (Å) for compound **1-3**

Table S4 Selected Hydrogen Bond Lengths () and Bond Angles (°) of complexes **1-3**

D-H...A	d(D-H)	d(H...A)	<D-H...A	d(D...A)	Symmetry
1 N(2) H(2A)...O(9)	0.86	2.34	148.85	3.107(16)	
O(2W)-H(2WA)...O(4W)	0.85	2.48	108.3	2.86(3)	
O(4W)-H(4WA)...O(1)	0.84	2.56	132.8	3.188(16)	[x, y, -z+1/2]
2 N2 H2... O2	0.86	2.32	149.08	3.090(12)	[-x+y+1, -x, z]
3 O3W H3WB... O13	0.85	1.99	2.66(4)	134.8	[-x, -y+1, -z+1]
O3W H3WB... O14	0.85	1.93	2.61(4)	136.4	[-x, -y+1, -z+1]
N2 H2A... O9	0.86	2.40	3.15(4)	147.1	[-y, x-y+1, z]
O2W H2WA... O1W	0.85	2.39	2.59(7)	93.9	[x-1, y-1, z]
O5 H5A... O2W	0.85	2.61	3.28(7)	137.0	[-y, x-y, z]
O3W H3WA... O15	0.85	2.10	2.66(4)	122.6	[y-1, -x+y, -z+1]
O1W H1WA... O2W	0.85	2.05	2.59(7)	120.4	[-x+y+1, -x+1, z]
O5 H5A... O6	0.85	3.16	3.42(3)	100.7	

3. Physical characterization

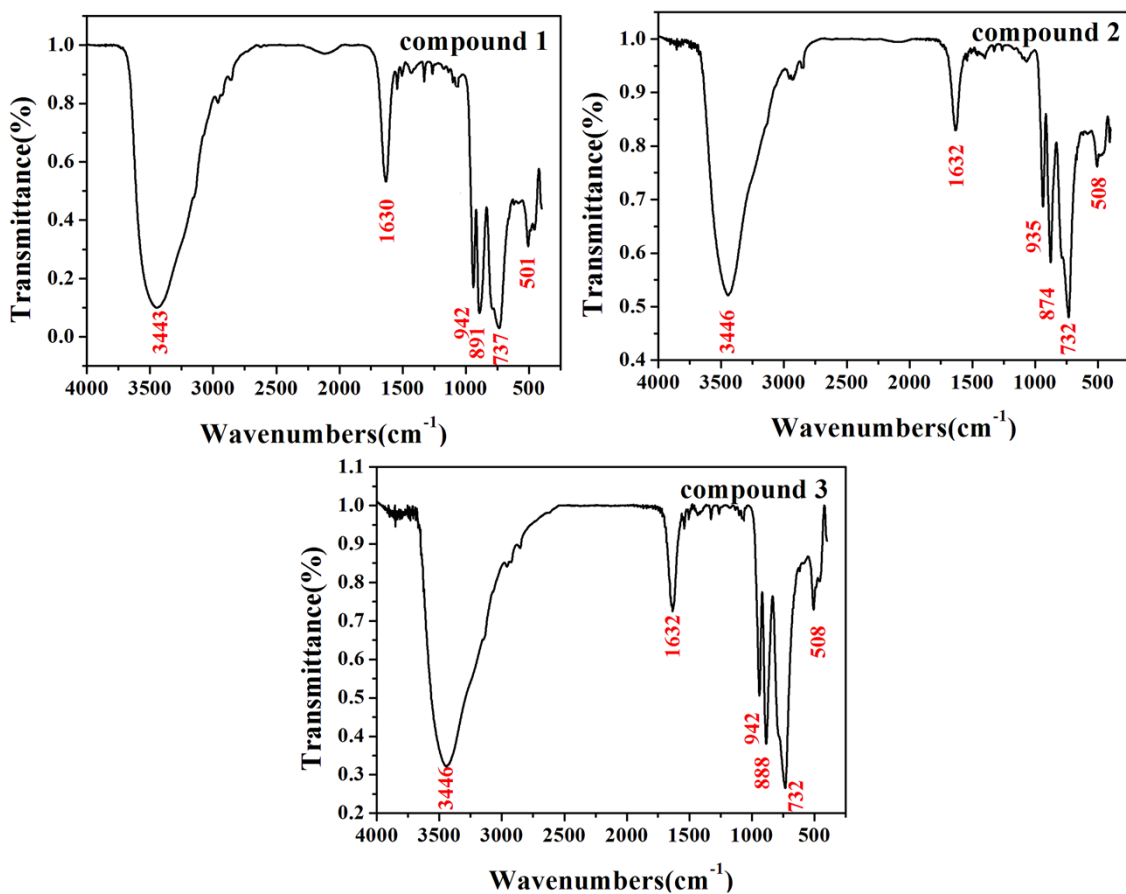


Fig.S6 IR spectras of compounds 1-3

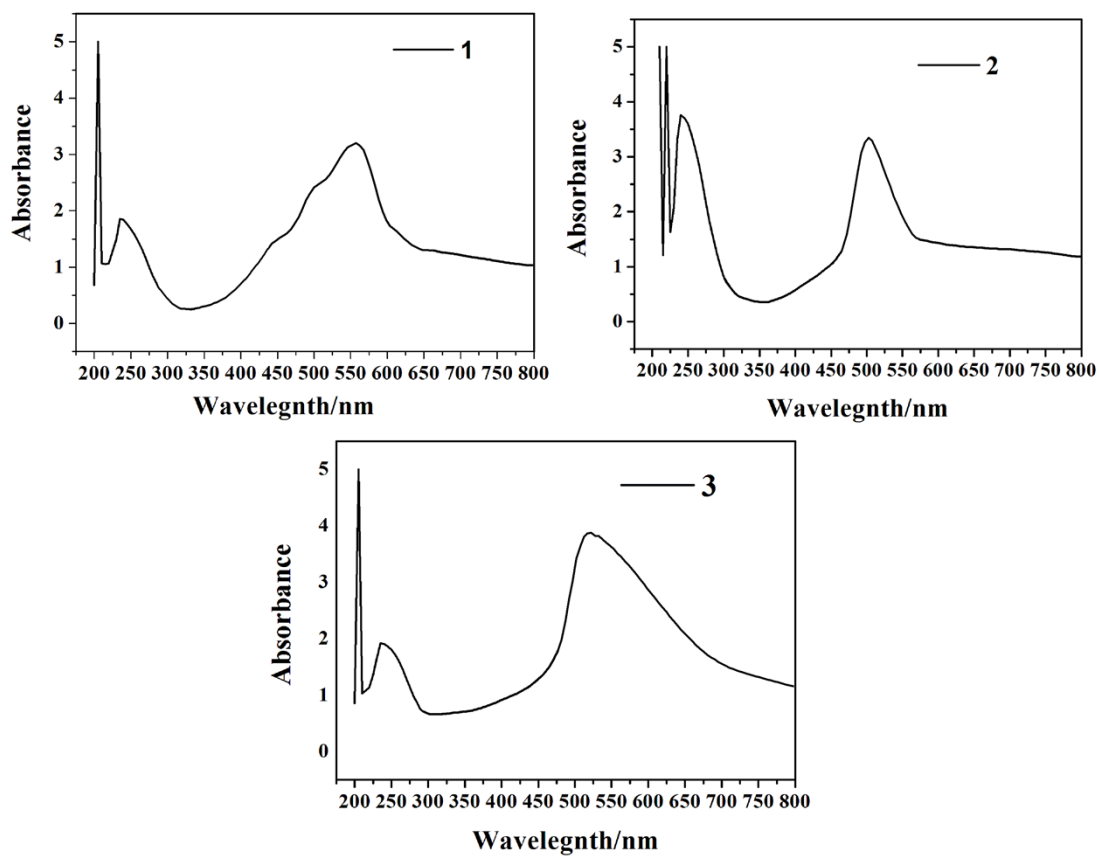


Fig.S7 UV--vis spectras of compounds 1-3

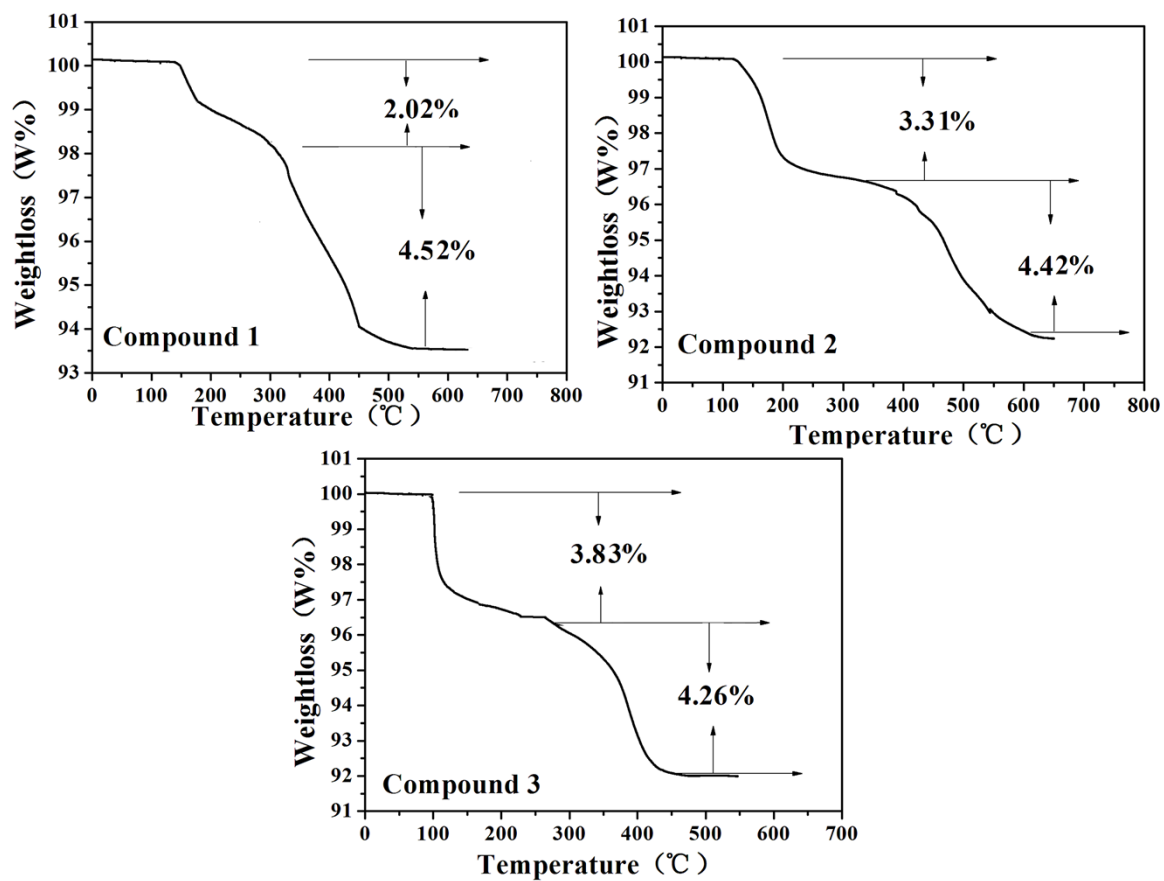


Fig.S8 TG curves of compounds 1-3

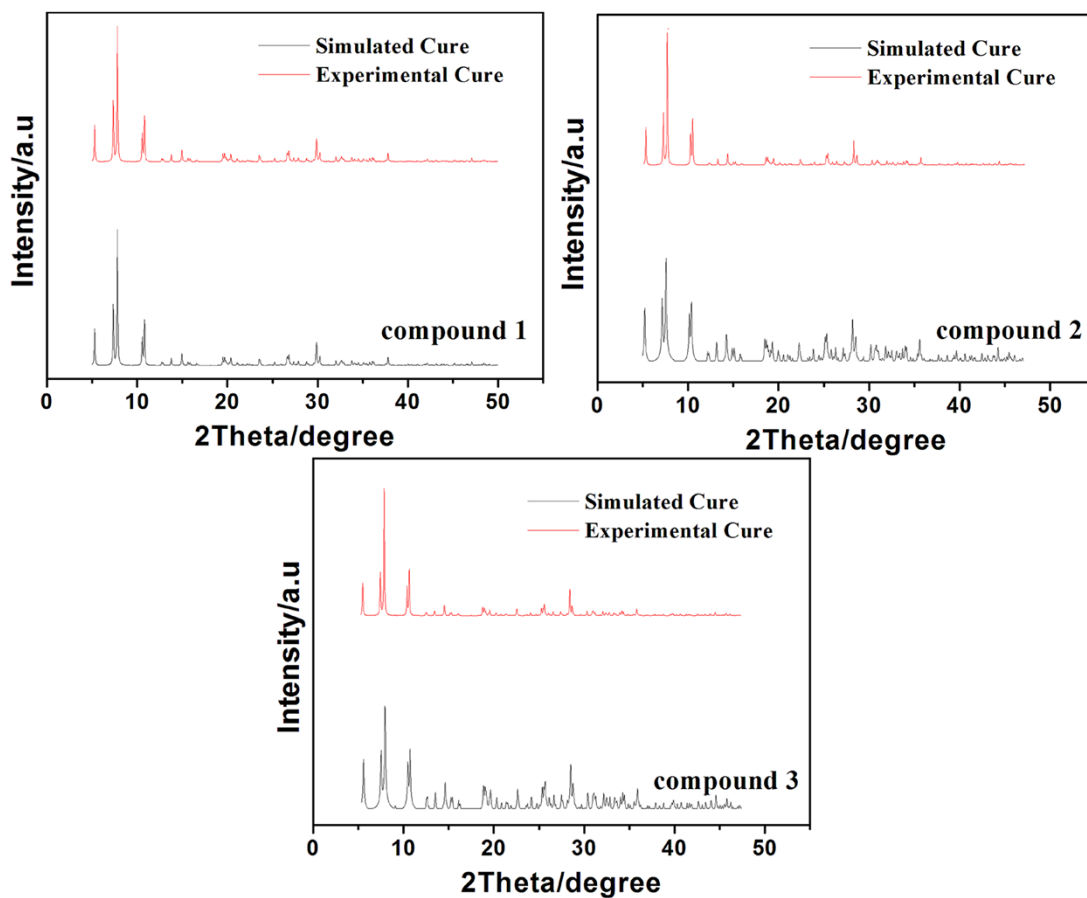


Fig.S9 Simulated and experimental XRD spectras of 1-3

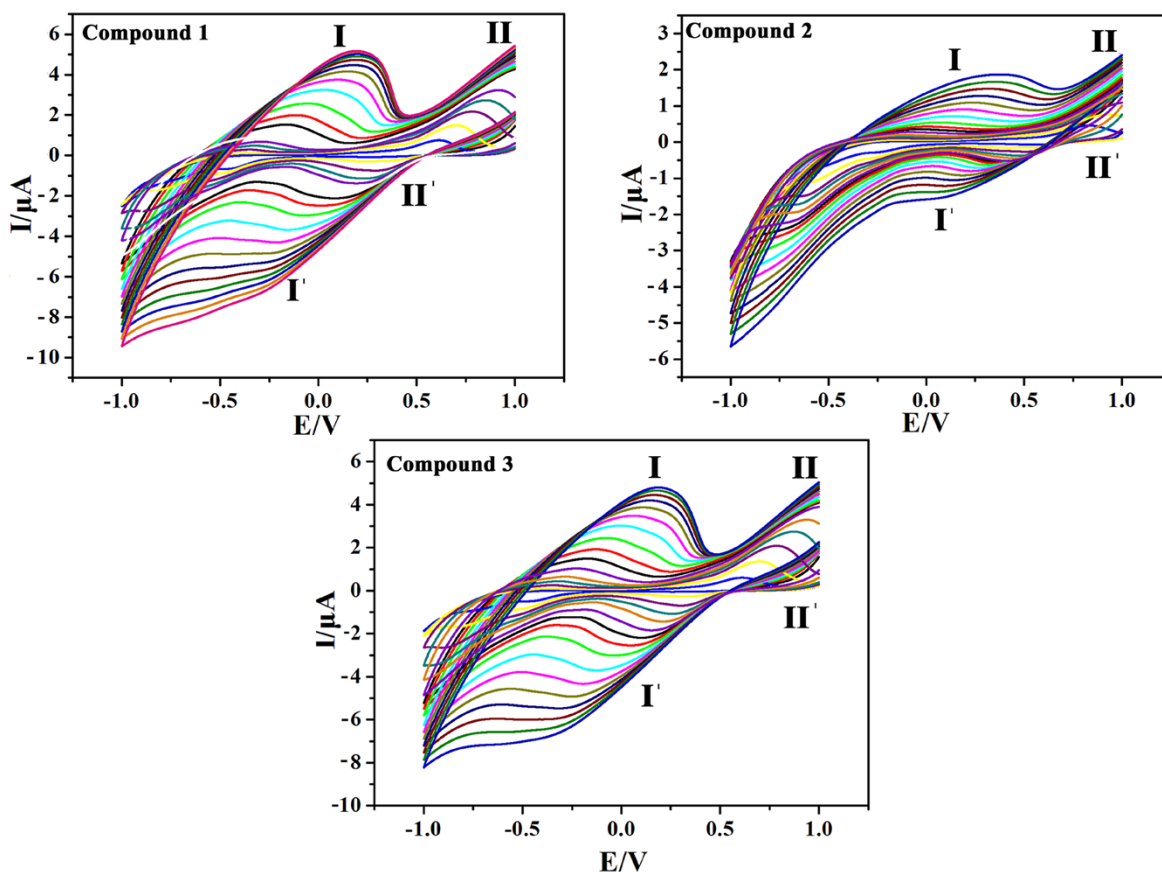


Fig. S10 Cyclic voltammograms of 1-CPE, 2-CPE, and (c) 3-CPE in the 1.0 M H_2SO_4 solution at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240 mV s^{-1}).

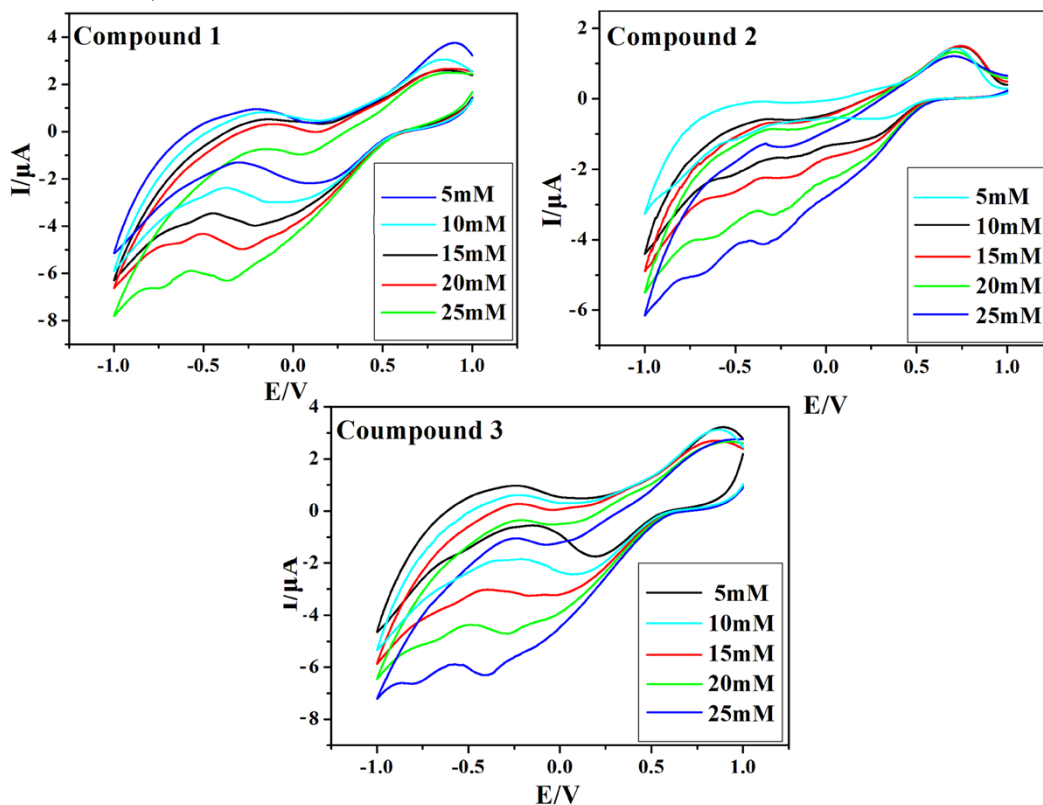


Fig. S11 Cyclic voltammograms of (a) 1, (b) 2, and (c) 3-CPE in 1 M H_2SO_4 solution containing nitrite at different concentrations (Potentials vs. SCE. Scan rate: 40 $\text{mV}\cdot\text{s}^{-1}$).