Assembly of hybrids based on polyoxotungstates and Co-tris(imidazolyl) complexes with bifunctional electrocatalytic activities

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Electronic Supplementary Information

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

W(1)-O(12)		1.69(4)	W(4)-O(16)		1.90(2)
W(1)-O(1)		1.736(19)	W(4)-O(15)		1.92(3)
W(1)-O(11)		1.88(3)	W(4)-O(14)		1.93(4)
W(1)-O(8)		1.90(2)	W(4)-O(18)#1	W(4)-	2.32(3)
W(1)-O(7)	W(1)-	1.90(3)	O(19)#1		2.46(4)
O(21)#1		2.35(4)	W(5)-O(5)		1.64(2)
W(1)-O(20)#1		2.40(4)	W(5)-O(8)		1.86(2)
W(2)-O(2)		1.64(2)	W(5)-O(9)		1.88(3)
W(2)-O(13)		1.84(3)	W(5)-O(17)#1		1.89(2)
W(2)-O(17)		1.87(2)	W(5)-O(10)		1.90(3)
W(2)-O(16)#1		1.88(2)	W(5)-O(20)#1		2.32(3)
W(2)-O(12)		1.93(3)	W(5)-O(19)#1		2.45(4)
W(2)-O(21)#1		2.27(4)	W(6)-O(6)		1.73(2)
W(2)-O(19)		2.45(4)	W(6)-O(15)#1		1.85(3)
W(3)-O(3)		1.66(2)	W(6)-O(7)		1.85(3)
W(3)-O(13)		1.79(3)	W(6)-O(9)		1.89(3)
W(3)-O(11)		1.89(3)	W(6)-O(22)#1		1.90(4)
W(3)-O(14)		2.06(4)	W(6)-O(18)		2.38(3)
W(3)-O(22)		2.07(4)	W(6)-O(20)#1		2.45(4)
W(3)-O(18)#1		2.46(3)	Co(1)-O(1)		2.09(2)
W(3)-O(21)#1		2.48(4)	Co(1)-N(1)#2		2.11(3)
W(4)-O(4)		1.70(2)	Co(1)-N(5)		2.12(2)
W(4)-O(10)		1.87(3)	Co(1)-N(4)#3		2.12(3)
B(1)-O(19)		1.44(4)	Co(1)-O(2W)		2.15(2)
B(1)-O(21)		1.60(3)	Co(1)-O(1W)		2.17(2)
C(1)-C(2)		1.37(3)	C(1)-N(6)		1.46(3)
O(12)-W(1)-O(1)		109.3(15)	O(1)-Co(1)-O(1W)		84.9(8)
O(1)-W(1)-O(8)		97.3(11)	N(1)#2-Co(1)-O(1W)		94.0(9)
O(2)-W(2)-O(17)		100.0(12)	N(5)-Co(1)-O(1W)		174.6(9)
O(13)-W(2)-O(17)		84.9(13)	O(20)-B(1)-O(18)		106.9(17)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 -x+1,-y-1,-z+2; #3 x+1,y,z; #4 x-1,y,z.

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

W(1)-O(1)		1.677(16)	W(4)-O(16)		1.90(2)
W(1)-O(7)		1.82(3)	W(4)-O(15)		1.92(3)
W(1)-O(15)#1		1.88(3)	W(4)-O(14)		1.93(4)
W(1)-O(9)		1.93(3)	W(4)-O(18)#1	W(4)-	2.32(3)
W(1)-O(23)		2.44(3)	O(19)#1		2.46(4)
W(2)-O(2)		1.631(18)	W(5)-O(5)		1.64(2)
W(2)-O(13)		1.77(3)	W(5)-O(8)		1.86(2)
W(2)-O(11)		1.83(4)	W(5)-O(9)		1.88(3)

W(2)-O(7)#1	1.85(3)	W(5)-O(17)#1	1.89(2)
W(2)-O(12)	2.11(3)	W(4)-O(20)	2.43(3)
W(2)-O(21)#1	2.49(3)	W(5)-O(5)	1.68(2)
W(2)-O(22)#1	2.52(3)	W(5)-O(10)	1.85(2)
W(3)-O(3)	1.70(2)	W(5)-O(19)	1.868(19)
W(3)-O(15)	1.89(3)	W(5)-O(18)	1.87(2)
W(3)-O(17)	1.91(2)	W(5)-O(17)	1.89(2)
W(3)-O(14)	1.920(18)	W(5)-O(23)	2.36(3)
W(3)-O(12)	1.93(3)	W(6)-O(6)	1.682(19)
W(3)-O(22)#1	2.27(3)	W(6)-O(11)	1.82(4)
W(3)-O(20)	2.43(3)	W(6)-O(9)	1.83(3)
W(4)-O(4)	1.71(2)	W(6)-O(10)	1.88(2)
W(4)-O(16)	1.87(3)	W(6)-O(16)#1	1.91(3)
W(4)-O(13)#1	1.88(3)	W(6)-O(23)	2.44(3)
Si(1)-O(23)	1.58(3)	Co(1)-N(5)	2.09(2)
Si (1)-O(20)	1.59(3)	Co(1)-N(1)#2	2.09(2)
C(1)-C(2)	1.37(3)	Co(1)-N(4)#3	2.12(2)
C(1)-N(6)	1.44(3)	Co(1)-O(1)	2.129(17)
W(4)-O(18)	1.90(2)	Co(1)-O(1W)	2.21(2)
W(4)-O(21)	2.31(3)	Co(1)-O(2W)	2.15(2)
O(1)-W(1)-O(7)	111.2(13)	O(1)-Co(1)-O(2W)	84.0(7)
O(7)-W(1)-O(15)#1	91.8(13)	N(5)-Co(1)-O(1W)	174.1(8)
O(2)-W(2)-O(13)	112.7(14)	N(5)-Co(1)-O(1W)	174.1(8)
O(13)-W(2)-O(11)	112.5(13)	O(23)-Si(1)-O(20)	65.2(15)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z; #2 -x,-y-1,-z+1; #3 x+1,y,z; #4 x-1,y,z.

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

W(1)-O(1)	1.746(13)	W(4)-O(33)	1.967(14)
W(1)-O(35)	1.872(13)	W(4)-O(38)	2.373(13)
W(1)-O(15)	1.887(13)	W(5)-O(5)	1.699(14)
W(1)-O(14)	1.910(14)	W(5)-O(16)	1.884(14)
W(1)-O(13)	1.925(13)	W(5)-O(17)	1.904(14)
W(2)-O(2)	1.724(15)	W(5)-O(36)	1.920(13)
W(2)-O(18)	1.839(16)	W(4)-O(20)	2.43(3)
W(2)-O(17)	1.884(15)	W(5)-O(5)	1.68(2)
W(2)-O(19)	1.919(13)	W(6)-O(6)	1.686(17)
W(2)-O(14)	1.933(14)	W(6)-O(11)	1.868(19)
W(2)-O(40)	2.364(13)	W(6)-O(23)	1.926(17)
W(3)-O(3)	1.725(14)	W(6)-O(24)	1.917(13)
W(3)-O(20)	1.89(3)	W(6)-O(22)	1.933(15)
W(3)-O(13)	1.887(13)	W(6)-O(18)	1.964(16)
W(3)-O(19)	1.896(12)	Co(1)-N(1)	2.088(15)
W(3)-O(21)	1.948(13)	Co(1)-N(7)	2.139(18)

W(3)-O(40)	2.380(13)	Co(1)-O(1)	2.167(13)
W(4)-O(4)	1.733(15)	B(1)-O(40)	1.49(2)
W(4)-O(15)	1.892(13)	B(1)-O(39)	1.53(2)
W(4)-O(34)	1.913(12)	B(1)-O(37)	1.54(2)
W(4)-O(36)	1.919(13)	B(1)-O(38)	1.55(2)
C(1)-C(2)	1.36(3)	C(1)-N(2)	1.45(2)
O(1)-W(1)-O(35)	100.0(6)	N(1)-Co(1)-N(7)	93.3(6)
O(35)-W(1)-O(15)	85.6(6)	N(1)-Co(1)-O(1)	88.6(6)
O(2)-W(2)-O(14)	95.1(6)	N(1)-Co(1)-N(1)	180.0(2)
O(17)-W(2)-O(40)	86.1(5)	O(40)-B(1)-O(39)	109.9(15)

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

Table S4 Hydrogen bonds (Å and °) for compound **3**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N2– H2 ··· O (5a)	0.8607	2.5678	3.17(2)	128.33
N3 – H3 ··· O (18b)	0.8588	2.3843	3.19(3)	155.75
N4 – H4 ··· O (16c)	0.8599	1.7467	2.61(2)	177.89
C1 – H1 ··· O (19d)	0.9347	2.4654	3.25(3)	141.16
C1 – H3 ··· O36	0.9319	2.2151	3.05(3)	148.30
C5 – H5 ··· O(29e)	0.9296	2.3632	2.777(8)	122.51
C7 – H7 ··· O(11e)	0.9322	2.5460	3.43(3)	157.93
C8 – H8 ··· O(34f)	0.9342	2.3495	3.18(3)	148.47
C11 - H11 ··· O(1Wc)	0.9300	2.3715	3.27(3)	162.70
C12 – H12 ··· O(2Wg)	0.9296	2.3913	3.28(3)	161.13
C14 – H14 ··· O(38b)	0.9324	1.9083	2.78(2)	154.42
C14 – H14 ··· O(13b)	0.9324	2.5898	3.09(3)	114.07
C15 – H15 ··· O7	0.9297	2.4705	3.23(2)	139.16
C15 – H15 ··· O30	0.9297	2.3957	3.23(2)	150.06
C16 – H16 ··· O(1Wc)	0.9303	2.4694	3.40(3)	174.37
C18 – H18 ··· O31	0.9304	2.4338	3.23(3)	144.21
C22 – H22 ··· O(11e)	0.9275	2.5768	3.47(3)	160.98
C24- H24 ··· O(19d)	0.9297	2.3980	3.26(3)	153.97
C25 – H25 ··· O(2Wg)	0.9308	2.3587	3.28(3)	169.78
C29 – H29 ··· O(19d)	0.9290	2.3999	3.15(3)	137.41

Symmetry transformations used to generate equivalent atoms: a -1+x,y,z; b x,y,1+z; c 1+x,-1+y,z; d 1-x,-y,-z; e -x,1-y,1-z; f x,-1+y,z; g 1-x,-y,1-z.

Table S5 CAT% data of compounds **1-3** toward reduction of nitrite and oxidation of AA

substrate \ CAT%		Compound **1**	Compound **2**	Compound **3**
Nitrite	2×10^{-3}M	20	18	60
	4×10^{-3} M	80	45	300
	6×10^{-3} M	280	82	445
	8×10^{-3} M	550	100	580
AA	2×10^{-3} M	185	475	14
	4×10^{-3} M	257	675	28
	6×10^{-3} M	328	800	67
	8×10^{-3} M	386	1150	86

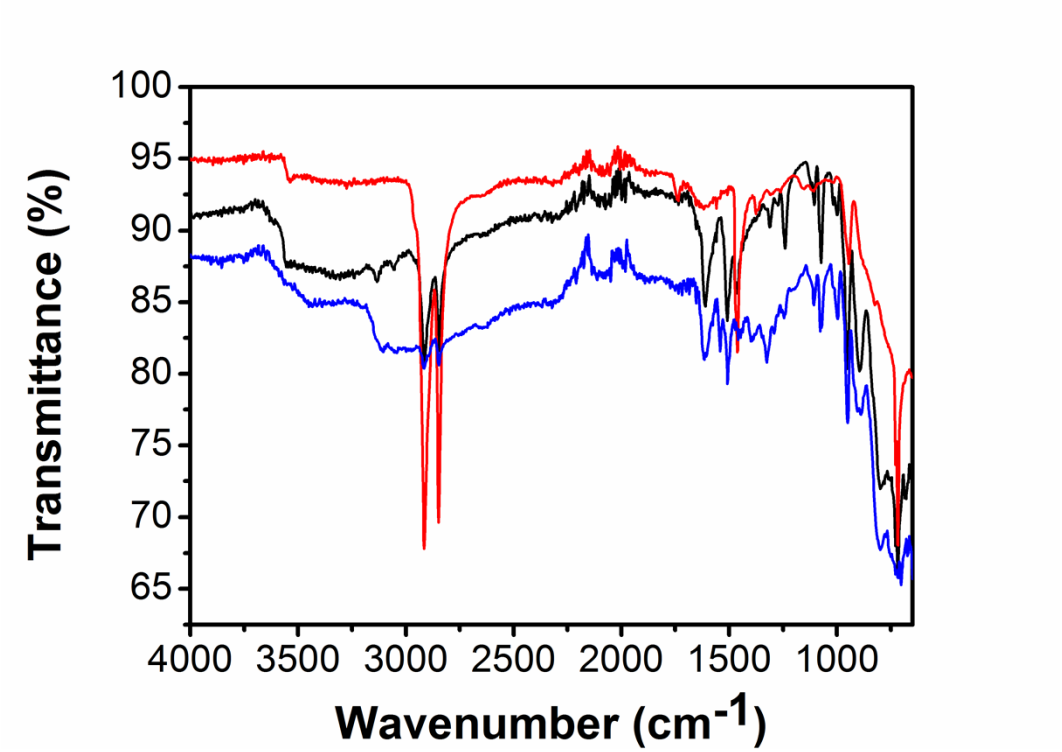

Fig. S1 IR spectra obtained from compounds **1** (black), **2** (red) and **3** (blue)

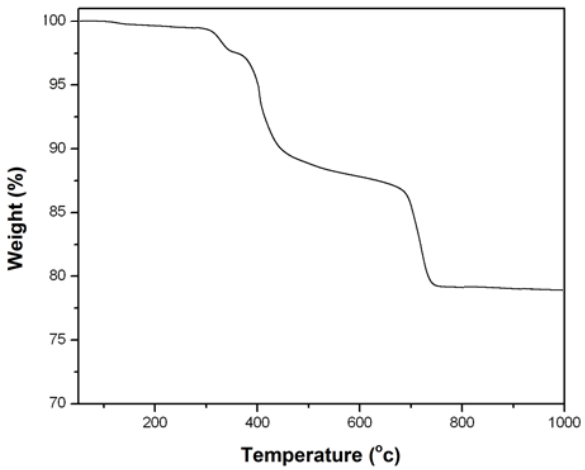

Fig. S2 TG curve obtained from compound **1**

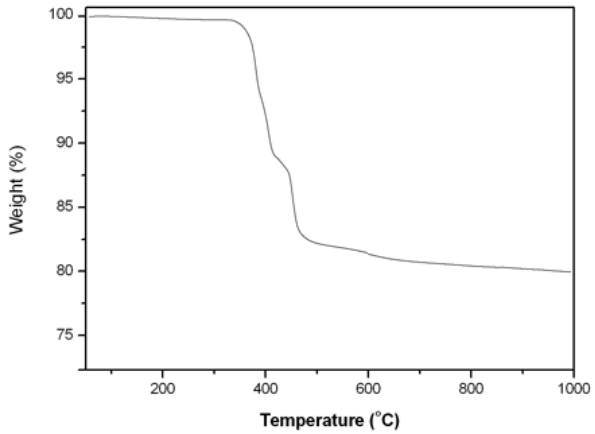

Fig. S3 TG curve obtained from compound **2**

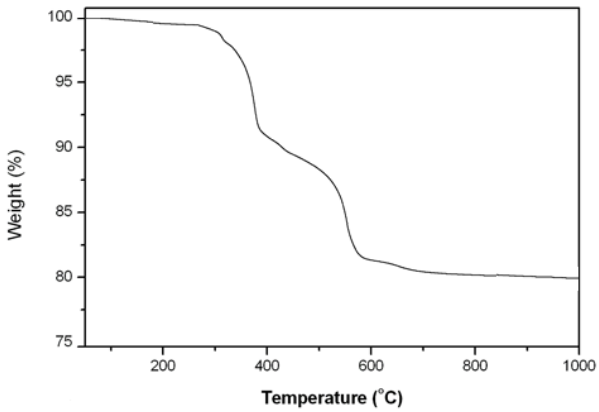

Fig. S4 TG curve obtained from compound **3**

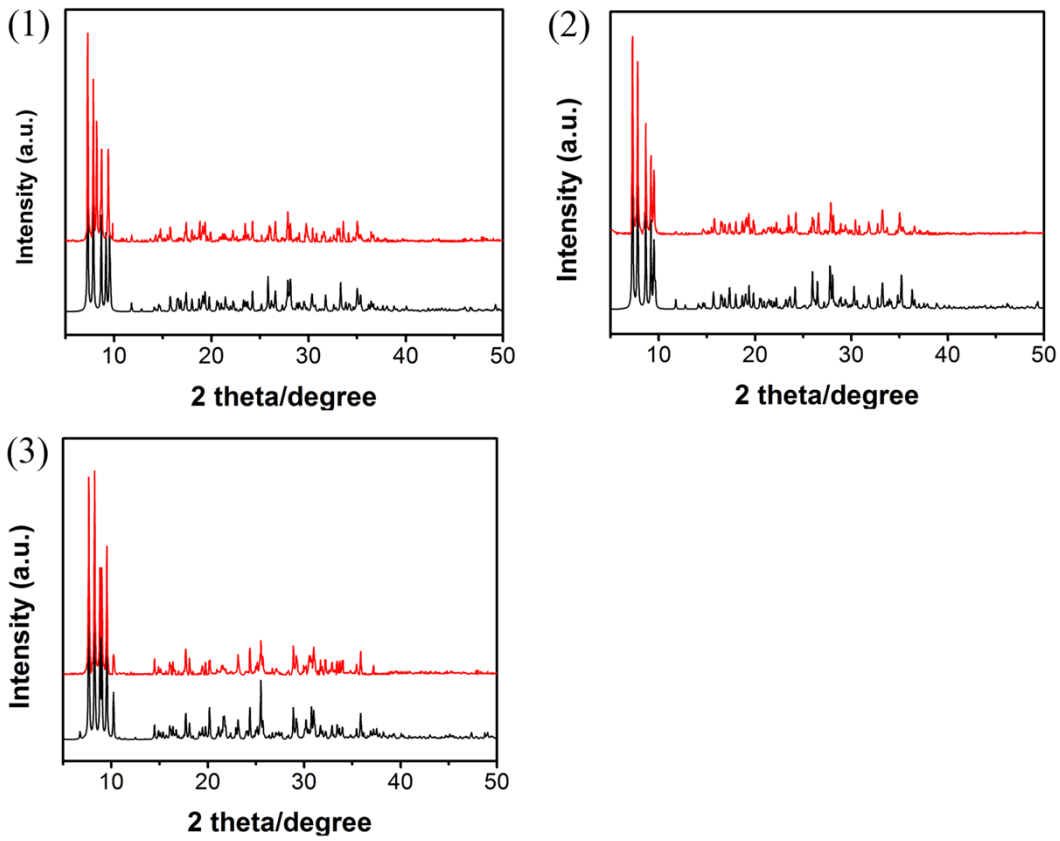

Fig. S5 The experimental (red line) and simulated (black line) PXRD patterns obtained from compounds **1**-**3**

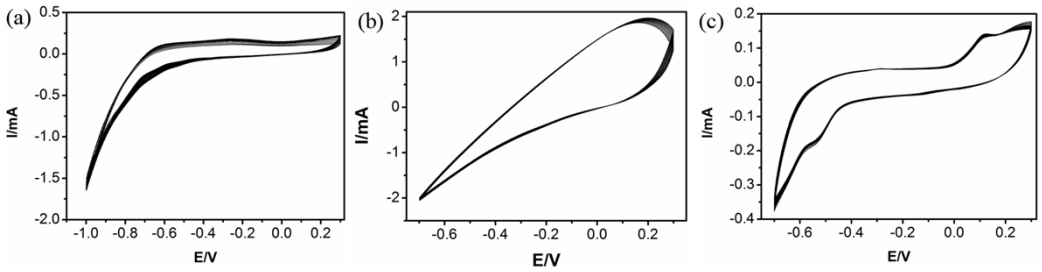

Fig. S6 Consecutive CVs (40 cycles) of (a) **1**-CPE, (b) **2**-CPE and (c) **3**-CPE for reduction of nitrite in 1M H_2SO_4 +Na_2SO_4 solutions (pH = 1) with concentration of 8 $\times 10^{-3}$ mol L^{-1} NO_2^- at the scan rate of 0.10 $V \cdot s^{-1}$.

Proposed mechanisms for electrocatalytic reduction of nitrite by compound **2**:

$$SiW^{VI}_{12-n}W^{V}_{n}O_{40}^{(4+n)-} + NO_2^- + xH^+ \rightarrow SiW^{VI}_{12}O_{40}^{4-} + \text{products (containing N)} \quad (1)$$

$$SiW^{VI}_{12-n}W^{V}_{n}O_{40}^{(4+n)-} + NO + yH^+ \rightarrow SiW^{VI}_{12}O_{40}^{4-} + \text{products (containing N)} \quad (2)$$

We deduce the oxidation mechanism as follows:

$$Co^{3+} + C_6H_8O_6 \rightarrow Co^{2+} + C_6H_6O_6 \quad (3)$$