Three polyoxometalates-based organic–inorganic hybrids decorated with Cu-terpyridine complexes exhibiting dual functional electro-catalytic behaviors

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Electronic Supplementary Information

Table S1 Crystal data and structure refinement for compounds **1-3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{45}H_{41}N_9O_{46}$ $Cu_3PMo_8V_6$	$C_{75}H_{59}N_{15}O_{82}$ $Cu_5P_2W_{24}$	$C_{45}H_{49}N_9O_{70}$ $Cu_3P_2W_{18}$
Formula weight	2738.62	7274.41	5397.79
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*P*2$_1$/c	*P***Error!**	*P*2$_1$/n
a(Å)	12.9312(6)	13.479(5)	16.5866(4)
b(Å)	29.6458(14)	21.683(5)	25.4564(5)
c(Å)	20.2652(10)	24.772(5)	22.0082(5)
α(°)	90	110.131(5)	90
β(°)	105.391(5)	103.113(5)	102.606(2)
γ(°)	90	98.596(5)	90
V(Å^{-3})	7490.2(6)	6412(3)	9068.6(4)
Z	4	2	4
μ (mm^{-1})	2.957	22.363	23.561
F(000)	5272	6442	9564
Limiting indices	-15<=*h*<=12 -35<=*k*<=35 -24<=*l*<=20	-16<=*h*<=13 - 25<=*k*<=22 -29<=*l*<=29	-19<=*h*<=19 -30<=*k*<=23 -18<=*l*<=26

Reflections collected unique	27347/13118	40633/22513	33512/15875
R(int)	0.0795	0.0668	0.0447
Data/restraints/parameters	13118/216 /1108	22513/186/ 1828	15875/102/1324
Goodness-of-fit on F^2	1.030	0.995	1.025
Final R indices [I>2sigma(I)]	R_1 = 0.1044 wR_2 = 0.2683	R_1 = 0.0490 wR_2 = 0.0781	R_1 = 0.0394 wR_2 = 0.0801
R indices (all data)	R_1 = 0.1759 wR_2= 0.3235	R_1 = 0.0842 wR_2 = 0.0913	R_1 = 0.0616 wR_2= 0.0884

[a]$R_1 = \sum\|F_o|-|F_c\|/\sum|F_o|$. [b]$wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°) for compound **1**

Mo(8)-O(34)	1.646(16)	Mo(4)-O(38)#1	1.910(8)
Mo(8)-O(24)	1.781(19)	Mo(4)-O(8)	1.900(8)
Mo(8)-O(13)	1.812(18)	Mo(4)-O(20)	2.452(9)
Mo(8)-O(43)	2.030(15)	Mo(4)-O(36)	2.513(10)
Mo(8)-O(31)	2.053(16)	Mo(5)-O(16)	1.667(7)
Mo(8)-O(7)	2.51(2)	Mo(5)-O(2)	1.892(7)
Mo(8)-O(38)	2.51(3)	Mo(5)-O(11)	1.886(8)
Mo(7)-O(25)	1.638(16)	Mo(5)-O(10)#1	1.899(7)
Mo(7)-O(19)	1.781(18)	Mo(5)-O(8)	1.902(8)
Mo(7)-O(33)	1.805(16)	Mo(5)-O(20)	2.446(10)
Mo(7)-O(44)	2.026(16)	Mo(5)-O(21)	2.492(11)
Mo(7)-O(41)	2.046(16)	Mo(6)-O(14)	1.668(7)
Mo(7)-O(36)	2.47(3)	Mo(6)-O(38)	1.887(7)
Mo(7)-O(5)	2.48(3)	Mo(6)-O(5)#1	1.869(8)
Mo(6)-O(39)	1.674(15)	Mo(6)-O(2)	1.901(7)
Mo(6)-O(18)	1.774(19)	Mo(6)-O(9)	1.949(8)
Mo(6)-O(20)	1.79(2)	Mo(6)-O(36)#1	2.449(11)
Mo(6)-O(31)	2.011(17)	Mo(6)-O(21)	2.483(11)
Mo(6)-O(44)	2.028(16)	V(1)-O(16)	1.603(16)
Mo(6)-O(7)	2.48(2)	V(1)-O(22)	1.903(17)
Mo(6)-O(5)	2.49(2)	V(1)-O(9)	1.906(19)
Mo(5)-O(3)	1.648(16)	V(1)-O(19)	1.907(19)
Mo(5)-O(17)	1.772(18)	V(1)-O(14)	1.92(2)
Mo(5)-O(22)	1.791(17)	V(2)-O(28)	1.589(16)
Mo(5)-O(41)	2.044(15)	V(2)-O(15)	1.862(17)
Mo(5)-O(43)	2.051(15)	V(2)-O(29)	1.903(18)
Mo(5)-O(4)	2.45(3)	V(2)-O(20)	1.91(2)
Mo(5)-O(36)	2.47(3)	V(2)-O(13)	1.918(18)

Mo(4)-O(26)	1.633(14)	V(3)-O(35)	1.614(16)
Mo(4)-O(8)	1.795(19)	V(3)-O(21)	1.90(2)
Mo(4)-O(9)	1.827(19)	V(3)-O(18)	1.897(19)
Mo(4)-O(37)	2.026(15)	V(3)-O(8)	1.924(19)
Mo(4)-O(45)	2.029(16)	V(3)-O(33)	1.938(17)
Mo(4)-O(12)	2.48(3)	V(4)-O(46)	1.604(17)
Mo(4)-O(6)	2.49(3)	V(4)-O(17)	1.902(18)
Mo(3)-O(27)	1.657(15)	V(4)-O(24)	1.91(2)
Mo(3)-O(30)	1.776(19)	V(4)-O(30)	1.917(17)
Mo(3)-O(15)	1.847(17)	V(4)-O(23)	1.920(16)
Mo(3)-O(40)	2.025(16)	V(5)-O(1)	1.670(15)
Mo(3)-O(42)	2.049(16)	V(5)-O(37)	1.894(17)
Mo(3)-O(11) Mo(3)-	2.44(3)	V(5)-O(42)	1.899(15)
O(10)	2.46(3)	V(5)-O(45)	1.920(16)
Mo(2)-O(32)	1.692(16)	V(5)-O(40)	1.921(16)
Mo(2)-O(14)	1.77(2)	V(6)-O(2)	1.660(16)
Mo(2)-O(23)	1.781(17)	V(6)-O(44)	1.892(16)
Mo(2)-O(40)	2.036(15)	V(6)-O(41)	1.906(15)
Mo(2)-O(37)	2.050(16)	V(6)-O(31)	1.908(15)
Mo(2)-O(6)	2.39(3)	V(6)-O(43)	1.924(16)
Mo(2)-O(11)	2.42(2)	Cu(1)-O(1)	1.868(15)
Mo(1)-O(38)	1.714(15)	Cu(1)-N(5)	1.89(2)
Mo(1)-O(21)	1.754(19)	Cu(1)-N(4)	2.00(2)
Mo(1)-O(29)	1.792(18)	Cu(1)-N(6)	2.03(2)
Mo(1)-O(45)	2.023(16)	Cu(2)-O(2)	1.887(16)
Mo(1)-O(42)	2.037(15)	Cu(2)-N(2)	1.93(2)
Mo(1)-O(12)	2.43(3)	Cu(2)-N(1)	1.95(2)
P(1)-O(7)	1.49(2)	Cu(2)-N(3)	1.97(2)
P(1)-O(5)	1.50(2)	Cu(2)-O(4)#1	2.421(15)
P(1)-O(36)	1.52(3)	Cu(3)-N(8)	1.95(2)
P(1)-O(38)	1.53(3)	Cu(3)-O(2W)	1.98(2)
P(1)-O(6)	1.55(3)	Cu(3)-N(9)	2.00(2)
C(1)-N(1)	1.37(4)	Cu(3)-N(7)	2.01(2)
C(1)-C(2)	1.41(4)	C(3)-C(4)	1.29(5)
C(2)-C(3)	1.46(4)	C(4)-C(5)	1.42(4)

O(16)-V(1)-O(22)	102.2(10)	O(37)-V(5)-Mo(4)	40.0(5)
O(22)-V(1)-O(9)	158.4(9)	O(42)-V(5)-Mo(4)	110.3(5)
O(15)-V(2)-O(20)	159.3(10)	O(40)-V(5)-Mo(4)	110.2(5)
O(1)-Cu(1)-N(4)	98.0(8)	O(34)-Mo(8)-O(24)	103.9(10)
N(5)-Cu(1)-N(4)	81.1(9)	O(34)-Mo(8)-O(13)	103.4(9)
O(10)-P(1)-O(38)	109.3(16)	O(24)-Mo(8)-O(13)	96.4(9)
O(5)-P(1)-O(36)	109.4(14)	N(2)-C(6)-C(7)	120(3)
O(3)-P(1)-O(11)	110.9(14)	N(2)-C(6)-C(5)	113(3)

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

Table S3 Selected bond lengths (Å) and angles (°) for compound **2**

W(1)-O(41)	1.722(12)	W(6)-O(19)	1.705(12)
W(1)-O(31)	1.861(10)	W(6)-O(43)	1.875(9)
W(1)-O(47)	1.885(11)	W(6)-O(40)	1.879(10)
W(1)-O(64)	1.923(12)	W(6)-O(34)	1.908(11)
W(1)-O(61)	1.943(11)	W(6)-O(63)	1.948(10)
W(1)-O(66)	2.321(10)	W(6)-O(68)	2.350(11)
W(2)-O(2)	1.741(11)	W(7)-O(54)	1.677(12)
W(2)-O(33)	1.875(11)	W(7)-O(65)	1.852(11)
W(2)-O(46)	1.893(11)	W(7)-O(32)	1.888(10)
W(2)-O(20)	1.900(11)	W(7)-O(47)	1.915(10)
W(2)-O(16)	1.903(10)	W(7)-O(7)	1.933(9)
W(2)-O(69)	2.276(10)	W(7)-O(66)	2.397(11)
W(3)-O(51)	1.723(11)	W(8)-O(55)	1.722(11)
W(3)-O(72)	1.893(11)	W(8)-O(61)	1.871(12)
W(3)-O(62)	1.898(10)	W(8)-O(46)	1.882(11)
W(3)-O(40)	1.931(9)	W(8)-O(32)	1.912(12)
W(3)-O(20)	1.937(11)	W(8)-O(17)	1.935(12)
W(3)-O(69)	2.360(11)	W(8)-O(66)	2.380(9)
W(4)-O(6)	1.677(11)	W(9)-O(59)	1.740(11)
W(4)-O(60)	1.899(10)	W(9)-O(7)	1.848(10)
W(4)-O(34)	1.905(12)	W(9)-O(9)	1.886(9)
W(4)-O(65)	1.935(12)	W(9)-O(60)	1.903(10)
W(4)-O(24)	1.948(11)	W(9)-O(15)	1.948(10)
W(4)-O(68)	2.384(10)	W(9)-O(67)	2.297(11)
W(5)-O(49)	1.695(10)	W(10)-O(3)	1.755(10)
W(5)-O(25)	1.870(11)	W(10)-O(63)	1.834(9)
W(5)-O(29)	1.880(12)	W(10)-O(15)	1.879(11)
W(5)-O(31)	1.904(11)	W(10)-O(62)	1.888(10)
W(5)-O(9)	1.940(10)	W(10)-O(25)	1.964(10)
W(5)-O(65)	2.457(9)	W(10)-O(67)	2.273(10)
W(11)-O(36)	1.692(10)	W(18)-O(28)	1.881(11)
W(11)-O(64)	1.876(12)	W(18)-O(8)	1.882(11)
W(11)-O(29)	1.900(11)	W(18)-O(30)	1.944(11)
W(11)-O(16)	1.924(11)	W(18)-O(21)	2.282(12)
W(11)-O(72)	1.932(12)	W(19)-O(56)	1.719(12)
W(11)-O(69)	2.415(10)	W(19)-O(23)	1.872(11)
W(12)-O(50)	1.710(10)	W(19)-O(35)	1.879(11)
W(12)-O(17)	1.847(12)	W(19)-O(27)	1.912(10)
W(12)-O(24)	1.884(11)	W(19)-O(13)	1.934(13)
W(12)-O(33)	1.909(11)	W(19)-O(57)	2.375(12)
W(12)-O(43)	1.939(11)	W(20)-O(48)	1.697(11)
W(12)-O(68)	2.329(10)	W(20)-O(23)	1.890(12)
W(13)-O(11)	1.701(11)	W(20)-O(75)	1.904(12)

W(13)-O(14)	1.895(11)	W(20)-O(73)	1.924(11)
W(13)-O(75)	1.899(12)	W(20)-O(70)	1.926(11)
W(13)-O(28)	1.904(11)	W(20)-O(76)	2.397(12)
W(13)-O(38)	1.912(12)	W(21)-O(52)	1.689(11)
W(13)-O(76)	2.389(12)	W(21)-O(30)	1.882(11)
W(14)-O(4)	1.723(12)	W(21)-O(12)	1.903(10)
W(14)-O(80)	1.865(11)	W(21)-O(22)	1.915(10)
W(14)-O(18)	1.889(10)	W(21)-O(37)	1.930(11)
W(14)-O(79)	1.897(13)	W(21)-O(21)	2.392(11)
W(14)-O(35)	1.921(11)	W(22)-O(39)	1.697(10)
W(14)-O(57)	2.394(12)	W(22)-O(37)	1.844(12)
W(15)-O(53)	1.685(10)	W(22)-O(71)	1.890(12)
W(15)-O(10)	1.854(12)	W(22)-O(26)	1.921(10)
W(15)-O(79)	1.881(12)	W(22)-O(74)	1.943(12)
W(15)-O(22)	1.929(11)	W(22)-O(77)	2.393(11)
W(15)-O(8)	1.949(11)	W(23)-O(1)	1.743(12)
W(15)-O(21)	2.406(11)	W(23)-O(73)	1.832(11)
W(16)-O(45)	1.706(11)	W(23)-O(27)	1.865(11)
W(16)-O(80)	1.901(10)	W(23)-O(74)	1.903(11)
W(16)-O(44)	1.904(12)	W(23)-O(44)	1.932(10)
W(16)-O(10)	1.914(12)	W(23)-O(77)	2.324(14)
W(16)-O(71)	1.961(12)	W(24)-O(58)	1.741(10)
W(16)-O(77)	2.410(11)	W(24)-O(26)	1.861(11)
W(17)-O(42)	1.681(12)	W(24)-O(12)	1.871(11)
W(17)-O(14)	1.870(11)	W(24)-O(70)	1.906(11)
W(17)-O(13)	1.887(14)	W(24)-O(38)	1.916(11)
W(17)-O(78)	1.914(12)	W(24)-O(76)	2.318(12)
W(17)-O(18)	1.922(11)	Cu(1)-N(5)	1.915(16)
W(17)-O(57)	2.392(12)	Cu(1)-O(1)	1.930(12)
W(18)-O(5)	1.764(12)	Cu(1)-N(15)	2.036(14)
W(18)-O(78)	1.854(12)	Cu(1)-N(13)	2.039(13)
Cu(1)-O(41)#1	2.213(11)	Cu(5)-O(5)	1.908(12)
Cu(2)-O(2)	1.925(11)	Cu(5)-N(3)	2.005(15)
Cu(2)-N(6)	1.925(16)	Cu(5)-N(2)	2.017(13)
Cu(2)-N(4)	1.997(16)	Cu(5)-N(1)	1.906(16)
Cu(2)-N(7)	2.022(17)	Cu(5)-O(2W)	2.274(13)
Cu(2)-O(58)	2.268(11)	P(1)-O(21)	1.550(17)
Cu(3)-N(9)	1.922(12)	P(1)-O(57)	1.490(16)
Cu(3)-O(3)	1.927(9)	P(1)-O(76)	1.527(17)
Cu(3)-N(10)	2.022(15)	P(1)-O(77)	1.504(17)
Cu(3)-N(8)	2.036(17)	P(2)-O(66)	1.37(3)
Cu(3)-O(1W)	2.241(13)	P(2)-O(67)	1.50(2)
Cu(4)-O(59)#2	1.891(11)	P(2)-O(68)	1.572(17)
Cu(4)-N(12)	1.94(2)	P(2)-O(69)	1.504(19)

Cu(4)-N(14)	1.98(2)	C(1)-C(15)	1.573(18)
Cu(4)-N(11)	2.048(16)	C(6)-C(7)	1.40(3)
Cu(4)-O(4)	2.330(13)	C(7)-N(13)	1.34(3)
C(9)-N(8)	1.36(2)	C(8)-C(62)	1.37(3)
O(41)-W(1)-O(31)	101.2(5)	O(68)-P(2)-O(67)	108.7(11)
O(41)-W(1)-O(47)	98.0(6)	O(66)-P(2)-O(69)	108.0(11)
O(31)-W(1)-O(47)	93.2(5)	O(57)-P(1)-O(21)	108.9(10)
O(2)-Cu(2)-N(4)	100.4(6)	O(77)-P(1)-O(21)	109.9(10)
N(6)-Cu(2)-N(4)	79.8(7)	N(11)-C(54)-C(49)	125(2)

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

Table S4 Selected bond lengths (Å) and angles (°) for compound **3**

W(1)-O(6)	1.722(9)	W(12)-O(22)	1.702(9)
W(1)-O(47)	1.877(9)	W(12)-O(4)	1.890(9)
W(1)-O(12)	1.902(9)	W(12)-O(8)	1.910(9)
W(1)-O(10)	1.915(9)	W(12)-O(23)	1.912(9)
W(1)-O(37)	1.930(9)	W(12)-O(43)	1.926(9)
W(1)-O(39)	2.378(9)	W(12)-O(26)	2.378(9)
W(2)-O(3)	1.708(9)	W(13)-O(58)	1.722(9)
W(2)-O(30)	1.889(8)	W(13)-O(18)	1.875(9)
W(2)-O(41)	1.891(9)	W(13)-O(51)	1.884(9)
W(2)-O(29)	1.896(9)	W(13)-O(35)	1.921(9)
W(2)-O(18)	1.944(9)	W(13)-O(17)	1.925(9)
W(2)-O(32)	2.374(9)	W(13)-O(40)	2.409(8)
W(3)-O(5)	1.694(9)	W(14)-O(14)	1.701(9)
W(3)-O(38)	1.866(9)	W(14)-O(25)	1.869(9)
W(3)-O(53)	1.894(9)	W(14)-O(9)	1.889(9)
W(3)-O(34)	1.923(9)	W(14)-O(47)	1.907(8)
W(3)-O(9)	1.928(9)	W(14)-O(20)	1.926(9)
W(3)-O(54)	2.379(8)	W(14)-O(54)	2.350(9)
W(4)-O(52)	1.708(9)	W(15)-O(61)	1.700(9)
W(4)-O(24)	1.861(9)	W(15)-O(13)	1.895(9)
W(4)-O(45)	1.890(9)	W(15)-O(56)	1.911(9)
W(4)-O(50)	1.924(9)	W(15)-O(4)	1.910(9)
W(4)-O(36)	1.954(9)	W(15)-O(21)	1.912(8)
W(4)-O(48)	2.363(8)	W(15)-O(19)	2.364(9)
W(5)-O(44)	1.710(9)	W(16)-O(2)	1.743(8)
W(5)-O(13)	1.862(9)	W(16)-O(31)	1.852(9)
W(5)-O(45)	1.902(8)	W(16)-O(36)	1.884(9)
W(5)-O(30)	1.915(9)	W(16)-O(17)	1.916(8)
W(5)-O(31)	1.976(9)	W(16)-O(16)	1.939(9)

W(5)-O(32)	2.377(8)	W(16)-O(40)	2.300(8)
W(6)-O(59)	1.695(10)	W(17)-O(60)	1.704(9)
W(6)-O(56)	1.899(9)	W(17)-O(28)	1.876(8)
W(6)-O(10)	1.901(9)	W(17)-O(34)	1.895(9)
W(6)-O(23)	1.905(9)	W(17)-O(46)	1.936(8)
W(6)-O(24)	1.935(9)	W(17)-O(43)	1.943(9)
W(6)-O(39)	2.369(9)	W(17)-O(26)	2.399(9)
W(7)-O(42)	1.721(9)	W(18)-O(33)	1.696(10)
W(7)-O(41)	1.894(9)	W(18)-O(57)	1.895(9)
W(7)-O(53)	1.894(9)	W(18)-O(7)	1.910(9)
W(7)-O(55)	1.914(9)	W(18)-O(16)	1.936(9)
W(7)-O(51)	1.927(9)	W(18)-O(35)	1.950(9)
W(7)-O(49)	2.386(8)	W(18)-O(40)	2.407(9)
W(8)-O(62)	1.709(9)	P(1)-O(39)	1.510(9)
W(8)-O(25)	1.913(9)	P(1)-O(19)	1.516(9)
W(8)-O(15)	1.922(9)	P(1)-O(54)	1.535(9)
W(8)-O(57)	1.922(9)	P(1)-O(26)	1.574(9)
W(8)-O(55)	1.929(9)	P(2)-O(32)	1.504(10)
W(8)-O(49)	2.352(9)	P(2)-O(48)	1.526(8)
W(9)-O(1)	1.717(9)	P(2)-O(49)	1.529(9)
W(9)-O(46)	1.869(9)	P(2)-O(40)	1.581(9)
W(9)-O(20)	1.891(9)	Cu(1)-N(7)	1.940(13)
W(9)-O(8)	1.920(9)	Cu(1)-O(1W)	1.986(10)
W(9)-O(12)	1.922(9)	Cu(1)-N(9)	2.020(12)
W(9)-O(26)	2.364(9)	Cu(1)-N(8)	2.026(13)
W(10)-O(3)	1.690(9)	Cu(1)-O(3)#1	2.342(9)
W(10)-O(29)	1.891(9)	Cu(1)-O(1)	2.362(9)
W(10)-O(21)	1.906(9)	Cu(2)-N(1)	1.917(12)
W(10)-O(38)	1.925(9)	Cu(2)-O(2)	1.931(9)
W(10)-O(28)	1.931(9)	Cu(2)-N(5)	1.994(12)
W(10)-O(19)	2.391(8)	Cu(2)-N(6)	2.016(11)
W(11)-O(11)	1.701(10	Cu(2)-O(2W)	2.188(11)
W(11)-O(37)	1.877(9)	Cu(3)-N(4)	1.915(12)
W(11)-O(15)	1.877(9)	Cu(3)-O(4W)	1.960(10)
W(11)-O(50)	1.898(8)	Cu(3)-N(3)	2.021(13)
W(11)-O(7)	1.934(9)	Cu(3)-N(2)	2.027(13)
W(11)-O(48)	2.371(8)	Cu(3)-O(3W)	2.200(10)
C(7)-N(8)	1.362(18)	C(6)-C(26)	1.49(2)
O(6)-W(1)-O(47)	102.3(4)	C(17)-N(1)-C(1)	124.7(12)
N(1)-Cu(2)-O(2)	163.0(5)	O(39)-P(1)-O(19)	111.8(5)
N(1)-Cu(2)-N(5)	81.3(5)	O(32)-P(2)-O(48)	111.6(5)

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

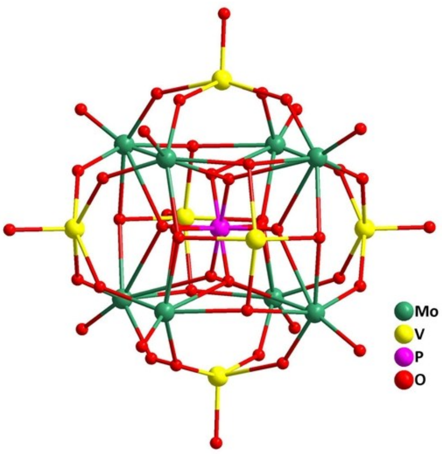


Fig. S1 The $[HPMo^{VI}_8V^{IV}_4O_{40}(V^{IV}O)_2]^{6-}$ unit in compound **1**.

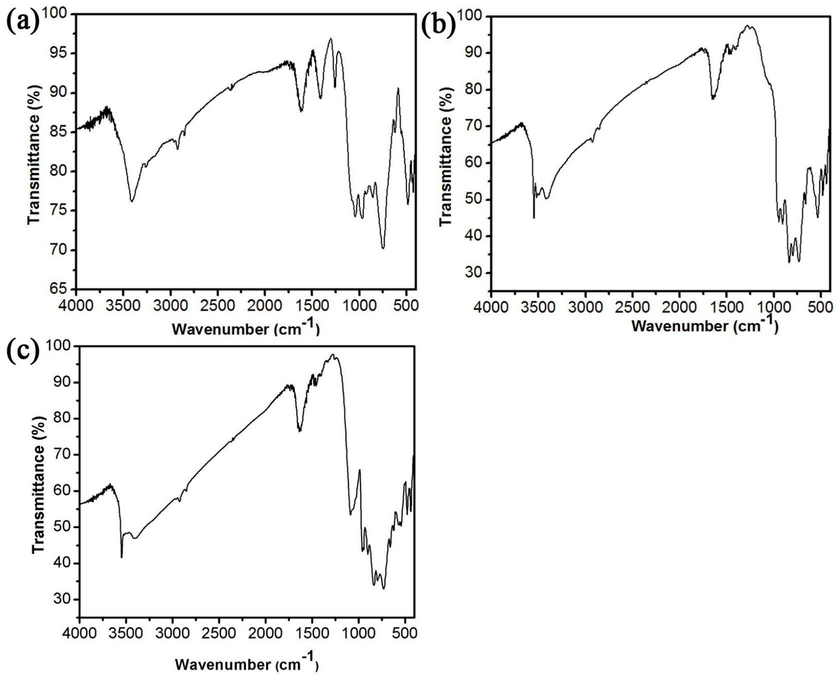


Fig. S2 IR spectra obtained from compound **1-3**.

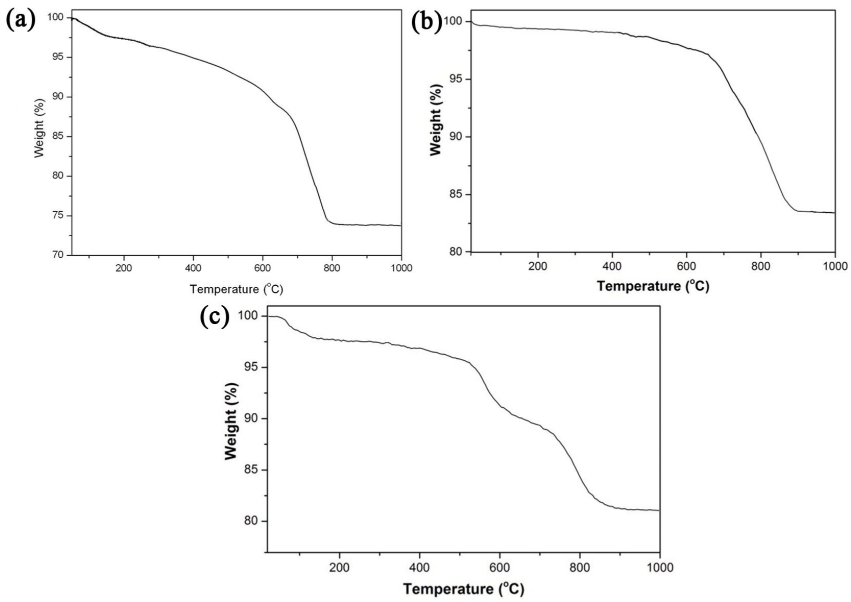


Fig. S3 TG curve obtained from compounds **1-3**.

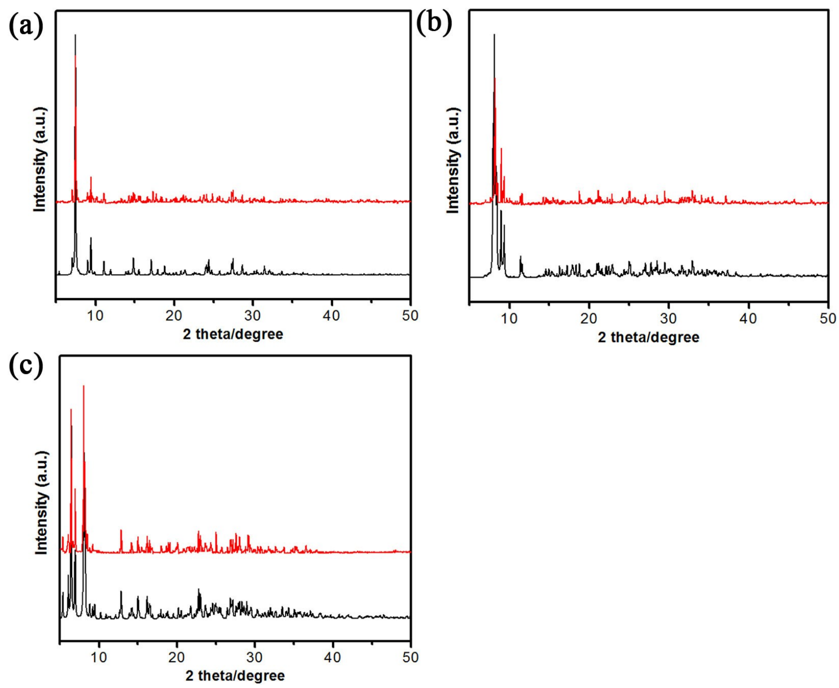


Fig. S4 The experimental (red line) and simulated (black line) PXRD patterns obtained from compounds **1-3**.

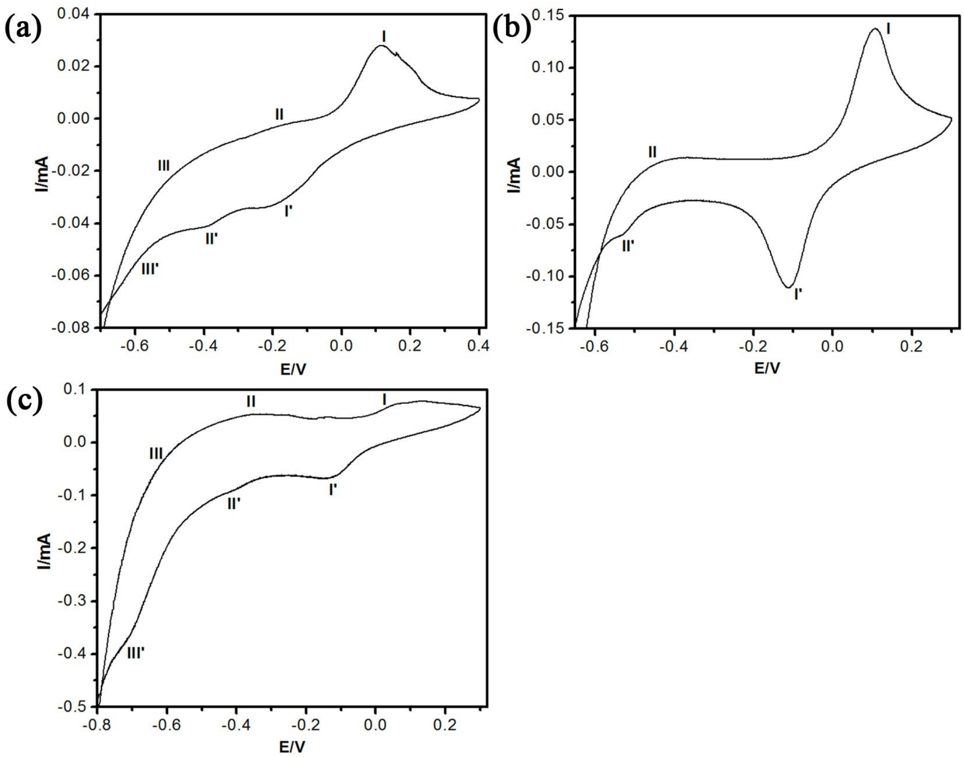


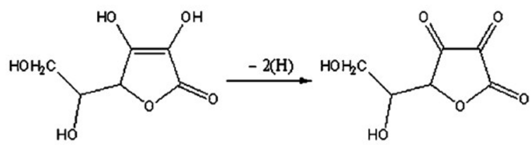
Fig. S5 The cyclic voltammograms of n-CPE (n = **1-3**) in H_2SO_4 + Na_2SO_4 solutions at a scan rate of 0.1 V s^{-1}.

Proposed mechanisms for electrocatalytic reduction of nitrite by **1-3**-CPE:

$PM^{VI}_{12-n}M^{V}_{n}O_{40}^{(4+n)-}/P_2W^{VI}_{18-n}W^{V}_{n}O_{62}^{(6+n)-} + NO_2^- + xH^+ \rightarrow PM^{VI}_{12}O_{40}^{4-}/P_2W^{VI}_{18}O_{62}^{6-}$ + products (containing N) (1)

$PM^{VI}_{12-n}M^{V}_{n}O_{40}^{(4+n)-}/P_2W^{VI}_{18-n}W^{V}_{n}O_{62}^{(6+n)-} + NO + yH^+ \rightarrow PM^{VI}_{12}O_{40}^{4-}/P_2W^{VI}_{18}O_{62}^{6-}$ + products (containing N) (2) (M = W, Mo)

It is known that oxidation of ascorbic acid undergoes a two-proton dehydrogenation process:



We deduce the oxidation mechanism as follows:

$$Cu^{II} + C_6H_8O_6 \rightarrow Cu + C_6H_6O_6 \quad (3)$$

Table S6 CAT% data of **1-3**-CPE toward reduction of nitrite

substrate	CAT%	Compound **1**	Compound **2**	Compound **3**
Nitrite	2mM	333	2443	423

	4 mM	719	3809	907
	6 mM	1962	5540	2413
	8 mM	4041	6994	2765

Table S7 CAT% data of **1**-**3**-CPE toward oxidation of AA

substrate \ CAT%		Compound **1**	Compound **2**	Compound **3**
AA	2 mM	20	52	28
	4 mM	42	152	46
	6 mM	54	310	67
	8 mM	65	655	96

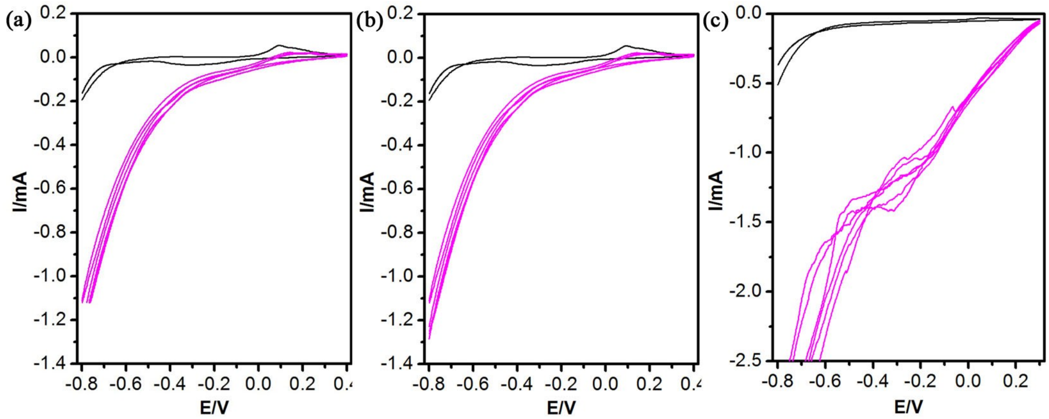


Fig. S6 The parallel experiments showing the steady electrocatalytic activities of **1**-**3**-CPE towards reduction of NO_2^- (8 mM for **1**, **3**; 6 mM for **2**).

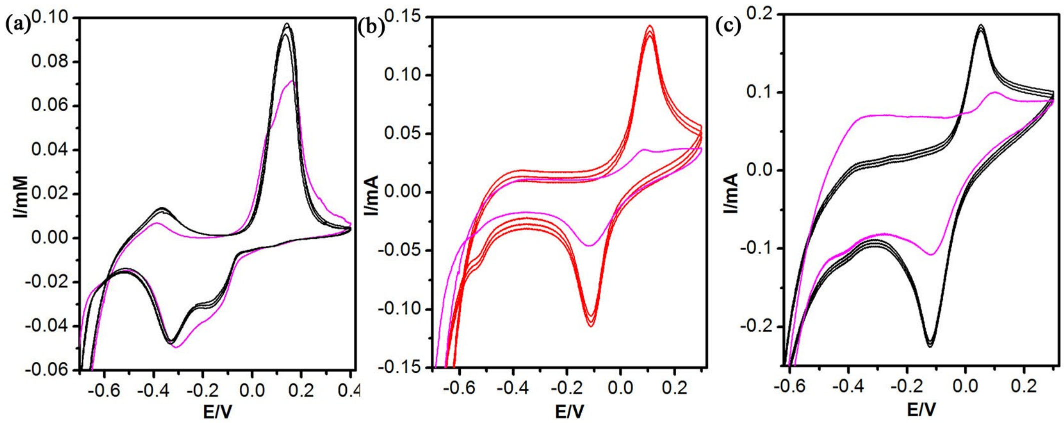


Fig. S7 The parallel experiments showing the steady electrocatalytic activities of **1**-**3**-CPE towards oxidations of AA (8 mM for **1**, **3**; 6 mM for **2**).