Supporting Information

Syntheses, Structures, Magnetism and Electrocatalytic Oxygen Evolution for Four Cobalt, Manganese and Copper Complexes with Dinuclear, 1D and 3D Structures

Li Zhong, Shang-Fang Xie, Jian-Qiang He, Qi-Sui Zhong, Meng Yang, Wen-Bin Chen* and Wen Dong*

Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R.China.

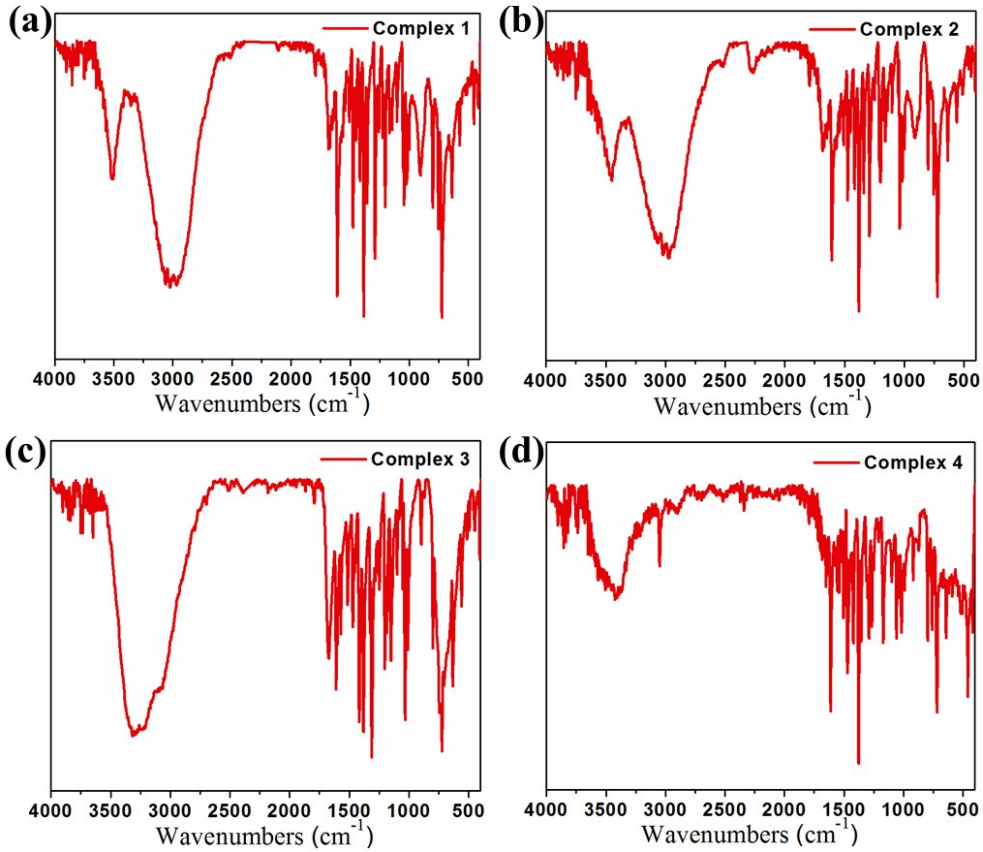

Fig. S1 IR spectra plots of complexes **1**-**4**.

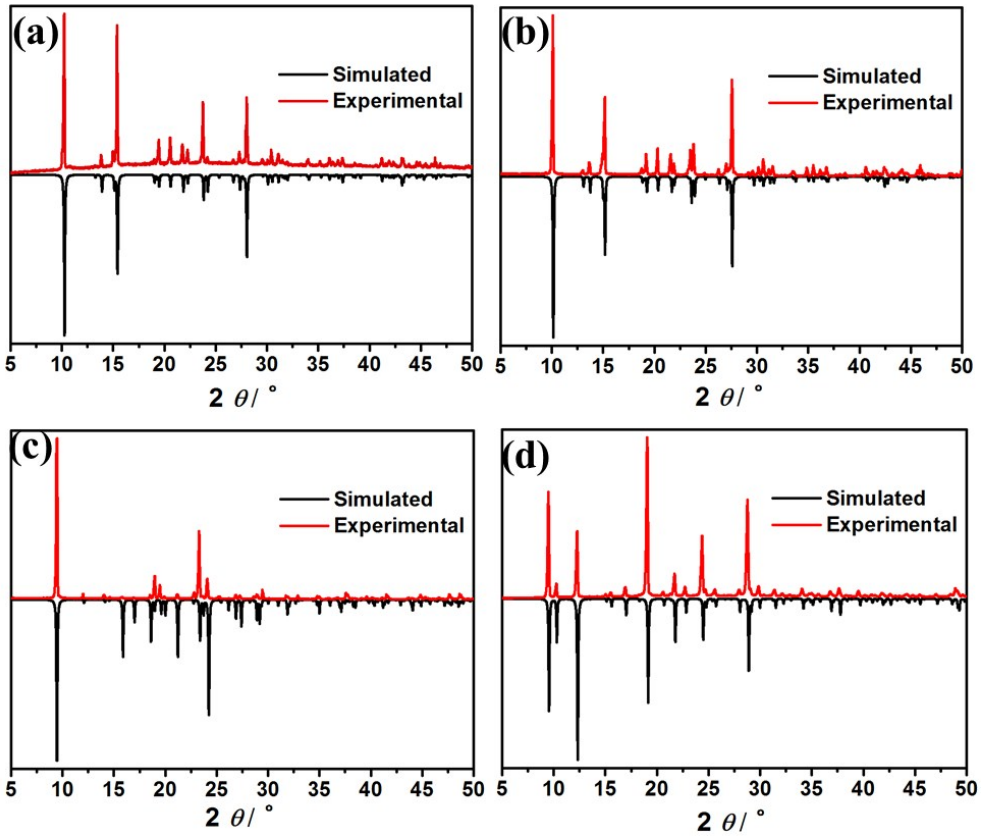

Fig. S2 Powder X-ray diffraction (PXRD) patterns for complexes **1** **4**.

Table S1 Selected bond distances (Å) and angles (°) for **1** and **2**.

1		**2**	
Mn1-O2	2.267(3)	Co1-O1	2.116(2)
Mn1-O1	2.190(3)	Co1-O2	2.172(2)
Mn1-N1	2.305(2)	Co1- N1	2.1954(17)
Mn1-N3A	2.233(2)	Co1- N2	2.0477(18)
Mn1-N5A	2.270(2)	Co1- N3A	2.0994(17)
Mn1-N2	2.181(2)	Co1- N5A	2.1767(18)
N3-Mn1A	2.233(2)	Co1A- N3	2.0995(17)
N5-Mn1A	2.270(2)	Co1A- N5	2.1766(18)
O2-Mn1-N1	88.41(11)	O1-Co1-O2	171.37(8)
O2-Mn1-N5A	88.50(10)	O1-Co1-N1	89.02(8)
O1-Mn1-O2	173.72(10)	O1-Co1-N5A	87.42(8)
O1-Mn1-N1	90.40(12)	O2-Co1-N1	86.99(8)
O1-Mn1-N3A	91.63(11)	O2-Co1-N5A	87.65(7)
O1-Mn1-N5A	87.17(10)	N2-Co1-O1	95.34(8)
N3A-Mn1-O2	91.48(11)	N2-Co1-O2	91.08(8)
N3A-Mn1-N1	161.17(9)	N2-Co1-N1	75.68(7)
N3A-Mn1-N5A	73.31(9)	N2-Co1-N3A	91.29(7)
N5A-Mn1-N1	125.50(9)	N2-Co1-N5A	166.59(7)

N2-Mn1-O2	89.07(10)	N3A-Co1-O1	92.10(9)
N2-Mn1-O1	96.47(11)	N3A-Co1-O2	93.51(8)
N2-Mn1-N1	72.87(8)	N3A-Co1-N1	166.98(6)
N2-Mn1-N3A	88.31(9)	N3A-Co1-N5A	75.47(7)
N2-Mn1-N5A	161.38(9)	N5A-Co1-N1	117.55(7)
Symmetry code: A= -x, 1-y, z.			

Table S2 Selected bond distances (Å) and angles (°) for **3** and **4**.

3		**4**	
Mn1-O1	2.2555(16)	Cu1-N1	2.060(3)
Mn1-O2	2.1389(16)	Cu1-N2	1.932(4)
Mn1-N1	2.3375(19)	Cu1-N3A	1.967(3)
Mn1-N2	2.1751(18)	Cu1-N5A	2.008(4)
Mn1-N3A	2.2624(18)	Cu1-N7B	2.217(4)
Mn1-N5A	2.3067(18)	N1-Cu1-N7B	90.51(13)
O1-Mn1-N1	84.13(6)	N2-Cu1-N1	78.82(14)
O1-Mn1-N3A	153.44(6)	N2-Cu1-N3A	91.43(14)
O1-Mn1- N5A	82.82(6)	N2-Cu1-N5A	165.16(15)
O2-Mn1-O1	87.71(6)	N2-Cu1-N7B	92.93(15)
O2-Mn1-N1	85.98(6)	N3A-Cu1-N1	164.61(15)
O2-Mn1-N2	159.26(7)	N3A-Cu1-N5A	78.41(14)
O2-Mn1-N3A	84.70(6)	N3A-Cu1-N7B	101.96(15)
O2-Mn1-N5A	100.12(6)	N5A-Cu1-N1	108.62(14)
N2-Mn1-O1	93.56(6)	N5A-Cu1-N7B	99.71(16)
N2-Mn1-N1	73.59(6)	Symmetry code: A= x, y, 1-z; B = 3/2-x, 3/2+y, 5/4+z.	
N2-Mn1-N3A	102.44(6)		
N2-Mn1-N5A	100.57(7)		
N3A-Mn1-N1	120.55(6)		
N3A-Mn1-N5A	73.57(6)		
N5A-Mn1-N1	165.33(7)		
Symmetry code: A= 1-x, 1-y, -1/2+z.			

Table S3. Information of hydrogen bonds in complex **1**.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
O1—H1A...N4	2.7439(24)	169	1/4-x, 1/4+y, 1/4+z
O1—H1B...O2	2.9810(27)	142	1/2-x, 1-y, 1/2+z
O2—H2A...N7	2.7484(25)	177	-1/4-x, 1/4+y, -1/4+z
O2—H2B...N8	2.8275(24)	173	1/4+x, 3/4-y, -1/4+z

Table S4. Information of hydrogen bonds in complex **2**.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
O1—H1A...N4	2.7556(33)	168	3/4-x, 1/4+y, -1/4+z
O1—H1B...O2	2.8684(33)	141	1/2-x, 1-y, -1/2+z
O2—H2A...N7	2.7669(33)	178	5/4-x, 1/4+y, 1/4+z
O2—H2B...N8	2.8059(32)	175	-1/4+x, 3/4-y, 1/4+z

Table S5. Information of hydrogen bonds in complex **3**.

Hydrogen Bond	Bond Distances (Å)	Bond Angles (°)	Symmetry of the acceptor
O1—H1A...N7	2.8627(25)	172	1/2+x, 3/2-y, -1+z
O1—H1B...N4	2.9273(24)	138	1/2+x, 3/2-y, z
O2—H2A...N8	2.7606(24)	148	1/2+x, 3/2-y, -1+z
O2—H2B...N6	2.8298(26)	143	1-x, 1-y, -3/2+z

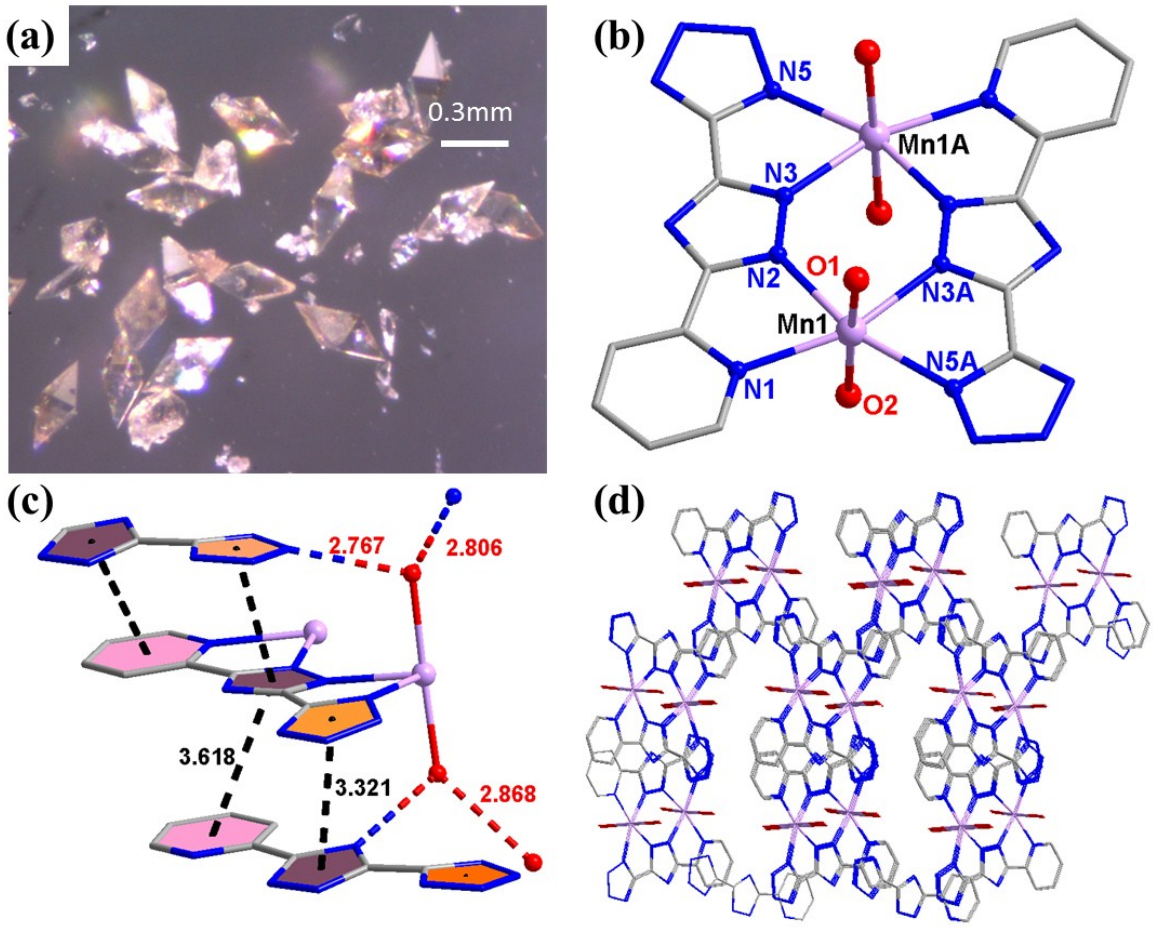

Fig. S3. (a) Photograph of single crystal of complex **2**. (b) Molecular structure of complex **2**, hydrogen atoms are omitted for clarity. Symmetry code: A= -x, 1-y, z. (c) O-H···O and O–H···N hydrogen bonds and π-π stacking interactions. (d) 3D supramolecular structure of **2**. Color code: Mn, bright blue; N, blue; O, red; C, gray.

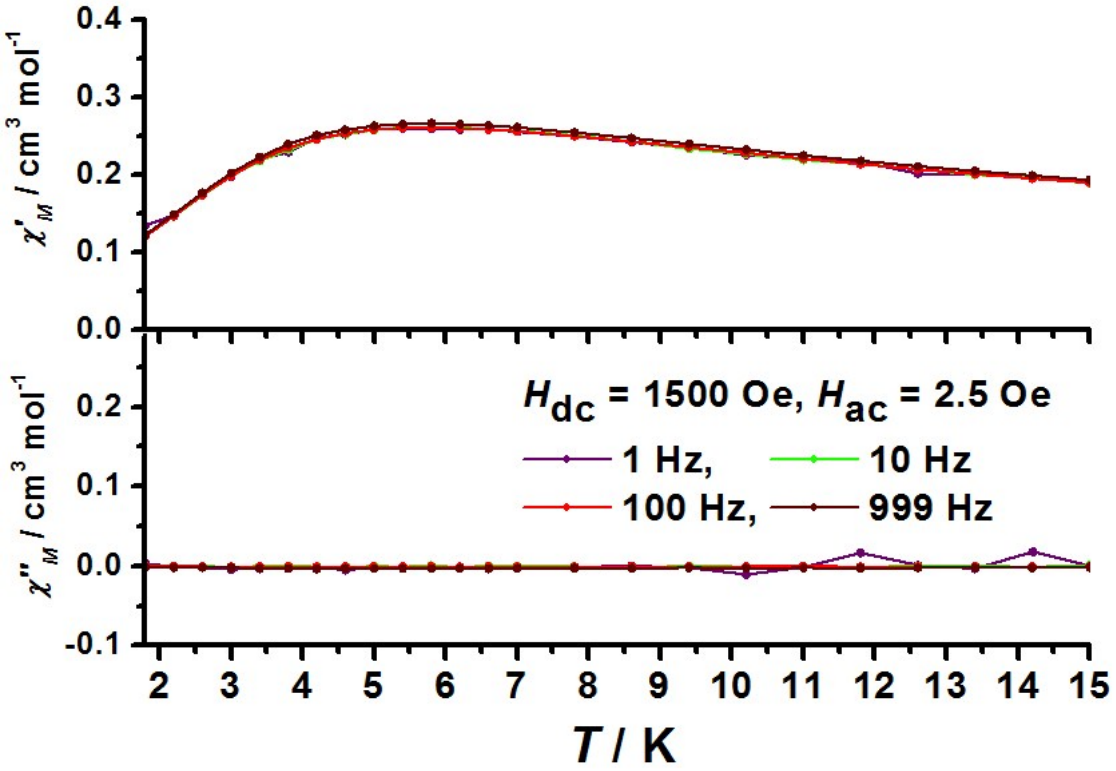

Fig. S4. Temperature dependence of the in-phase (χ'_M) and out-of-phase (χ''_M) AC magnetic susceptibilities at 1500 Oe dc field for **1**. Lines are to guide the eyes.

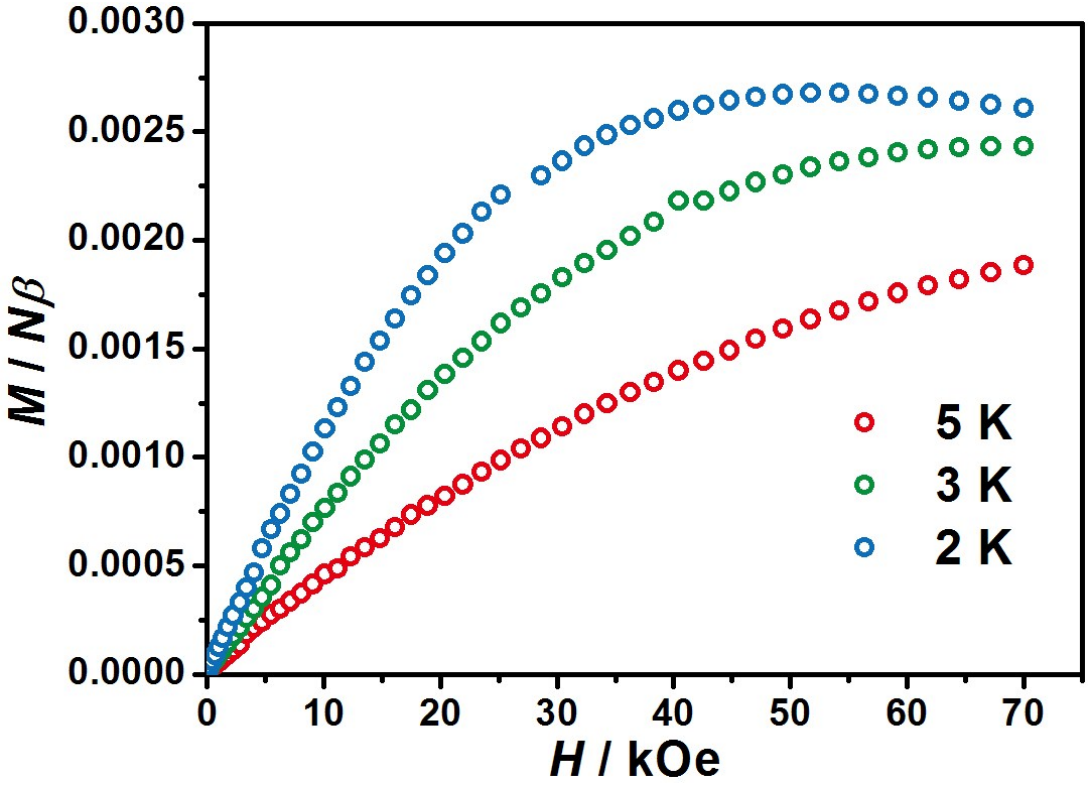

Fig. S5. Plots of M–H for **4** at 2, 3 and 5 K. The solid lines are guides to the eyes.

Table S6. Comparison of cobalt, manganese and copper-based OER catalytic performance in neutral condition.

Catalyst	potential at 2 mA cm^{-2} (mV vs.RHE)	potential at 10 mA cm^{-2} (mV vs.RHE)	*j* @1.8 V (mA cm^{-2})	Reference
$[Co_2(TPT)_2(H_2O)_2]$	1.86	2.00	0.67	This work
$[Mn_2(TPT)_2(H_2O)_2]$	NA	NA	0.14	This work
$[Mn(TPT)(H_2O)_2]_n$	2.09	NA	0.30	This work
$[Cu(TPT)]_n$	1.92	2.08	0.48	This work
Co_3O_4	1.89	NA	0.61	Adv. Funct. Mater. 2013, 23, 227-233
CoPi	1.90	NA	0.43	Science 2008, 321, 1072-1075
ZIF-67@GC	1.76	NA	3.65	J. Am. Chem. Soc. 2017, 139, 1778–1781
MAF-X27-Cl	NA	NA	0.028	J. Am. Chem. Soc. 2016,138, 8336−8339
RuO_2	1.65	NA	5.8	Angew. Chem. Int. Ed. 10.1002/anie.201809144
$Mn_3(PO_4)_2$	NA	NA	0.05	J. Am. Chem. Soc. 2014, 136, 7435−7443
Mn_2O_3	NA	NA	0.025	J. Am. Chem. Soc. 2014, 136, 7435−7443
$([Cu_2(TPMAN)(\mu\text{-}OH)(H_2O)]^{3+}$	NA	NA	0.025	Inorg. Chem. 2018, 57, 10481−10484
$[Cu2(BPMAN)(\mu\text{-}OH)]^{3+}$	NA	NA	0.05	Angew. Chem., 2015, 127, 4991–4996
$Na_2[Cu(opba)]$	1.96	NA	0. 75	RSC Adv., 2014,4, 53674-53680

BPMAN=2,7-[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine; opba = o-phenylenebis(oxamato).