Three Novel and Various Isopolymolybdate-based Hybrids Built from the Carboxyl Oxygen Atoms of *In-situ* Ligands: Substituents-tuned Assembly, Architectures and Properties

Xiu-Li Wang,* Rui Zhang, Xiang Wang, Hong-Yan Lin, Guo-Cheng Liu and Hui-Xiu Zhang

Table S1. Selected bond lengths (Å) and angles (°) of compounds **1-3**.

Compound **1**			
Cu(1)-N1	1.978(4)	Cu(1)-N1#5	1.977(4)
Cu(1)-O(1)#4	2.017(4)	Cu(1)-O(1)#6	2.017(4)
Cu(1)-O(5)	2.372(4)	Cu(1)-O(5)#5	2.372(4)
N(1)#5-Cu(1)-N(1)	95.1(2)	N(1)#5-Cu(1)-O(1)#6	99.72(15)
N(1)-Cu(1)-O(1)#6	165.19(16)	N(1)#5-Cu(1)-O(1)#4	165.19(16)
N(1)-Cu(1)-O(1)#4	99.72(16)	O(1)#6-Cu(1)-O(1)#4	65.5(2)
N(1)#5-Cu(1)-O(5)	94.43(16)	N(1)-Cu(1)-O(5)	92.35(16)
O(1)#6-Cu(1)-O(5)	87.32(15)	O(1)#4-Cu(1)-O(5)	84.24(15)
C(1)#4-Cu(1)-O(5)	84.98(10)	N(1)#5-Cu(1)-O(5)#5	92.35(16)
N(1)-Cu(1)-O(5)#5	94.42(16)	O(1)#6-Cu(1)-O(5)#5	84.24(15)
O(1)#4-Cu(1)-O(5)#5	87.32(15)	C(1)#4-Cu(1)-O(5)#5	84.98(9)
O(5)-Cu(1)-O(5)#5	169.96(19)	Mo(1)-O(5)-Cu(1)	151.5(2)
Symmetry transformations used to generate equivalent atoms for 1: #1 x-y+2/3, x+1/3, -z+4/3; #2 y-1/3, -x+y+1/3, -z+4/3; #3 –y+1, x-y+1, z; #4 –x+y, –x+1, z; #5 y, x, –z+3/2; #6 –x+1, –x+y, –z+3/2.			
Compound **2**			
Cu(1)-O(30)	1.946(8)	Cu(1)-O(27)	1.89(4)
Cu(1)-N(1)	2.015(10)	Cu(1)-O(1W)	1.989(13)
Cu(1)-O(5)	1.994(8)	Cu(2)-O(26)	1.943(8)
Cu(2)-O(25)#2	1.946(7)	Cu(2)-N(2)#3	1.962(9)
Cu(2)-N(4)	1.973(9)	Cu(2)-O(4)#4	2.369(8)
N(2)-Cu(2)#5	1.962(9)	O(4)-Cu(2)#6	2.369(8)
O(25)-Cu(2)#2	1.946(9)	O(30)-Cu(1)-O(27)	95.0(11)
O(30)-Cu(1)-N(1)	91.8 (4)	O(27)-Cu(1)-N(1)	164.5(9)
O(30)-Cu(1)-O(1W)	131.7(6)	O(27)-Cu(1)-O(1W)	87.5(7)
N(1)-Cu(1)-O(1W)	90.5(5)	O(30)-Cu(1)-O(5)	141.1(4)
O(27)-Cu(1)-O(5)	82.4(10)	N(1)-Cu(1)-O(5)	100.9(4)
O(1W)-Cu(1)-O(30)	148.7(5)	C(14)-N(1)-Cu(1)	120.8(8)
C(12)-N(1)-Cu(1)	132.7(7)	O(26)-Cu(2)-O(25)#2	91.8(3)
O(26)-Cu(2)-N(2)#3	167.4(4)	O(25)#2-Cu(2)-N(2)#3	90.0(3)

O(26)-Cu(2)-N(4)	89.0(3)	O(25)#2-Cu(2)-N(4)	178.3(4)
N(2)#3-Cu(2)-N(4)	89.5(4)	O(26)-Cu(2)-O(4)#4	103.5(3)
O(25)#2-Cu(2)-O(4)#4	84.8(3)	N(2)#3-Cu(2)-O(4)#4	89.0(4)
N(4)-Cu(2)-O(4)#4	93.6(3)	C(15)-N(2)-Cu(2)#5	127.9(7)
C(9)-N(2)-Cu(2)#5	123.8(7)	Mo(3)-O(4)-Cu(2)#6	152.0(4)
C(16)-N(4)-Cu(2)	123.0(7)	C(4)-N(4)-Cu(2)	129.3(7)
C(7)-O(25)-Cu(2)#2	131.9(7)	Mo(8)-O(26)-Cu(2)	146.1(6)
Mo(6)-O(30)-Cu(1)	141.4(5)	Mo(2)-O(5)-Cu(1)	146.5(5)
C(8)-O(27)-Cu(1)	131(3)		

Symmetry transformations used to generate equivalent atoms for 2: #1 –x+1, -y+1, -z; #2 -x+2,-y,-z+1; #3 x,y+1,z+1; #4 x,y,z+1; #5 x,y-1,z-1; #6 x,y,z-1; #7 –x+1, -y+1, -z+1.

Compound **3**

Cu(1)-N(1)#3	1.867(3)	Cu(1)-N(1)	1.867(3)
N(1)#3-Cu(1)-N(1)	180.0	C(6)-N(1)-Cu(1)	123.2(2)
C(7)-N(1)-Cu(1)	126.8(2)		

Symmetry transformations used to generate equivalent atoms for 2: #1 x, -y-2, z-1/2; #2 –x+1, -y-2, -z+1; #3 -x+1/2,-y-1/2; #4 x, -y-2, z+1/2; #5 –x+1, y, -z+1/2.

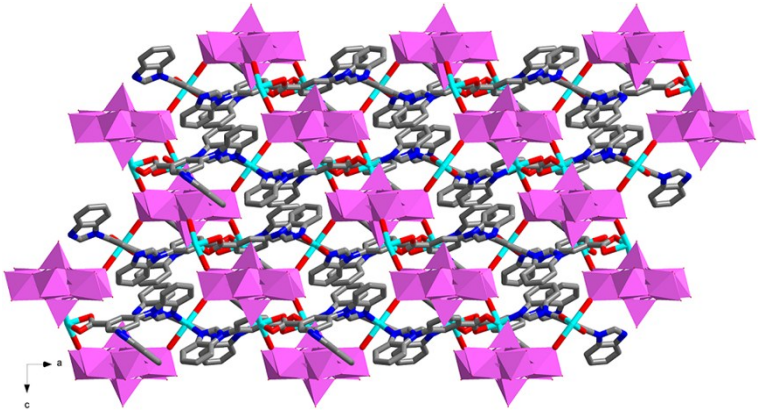

Fig. S1 The 3D framework structure of compound **1**.

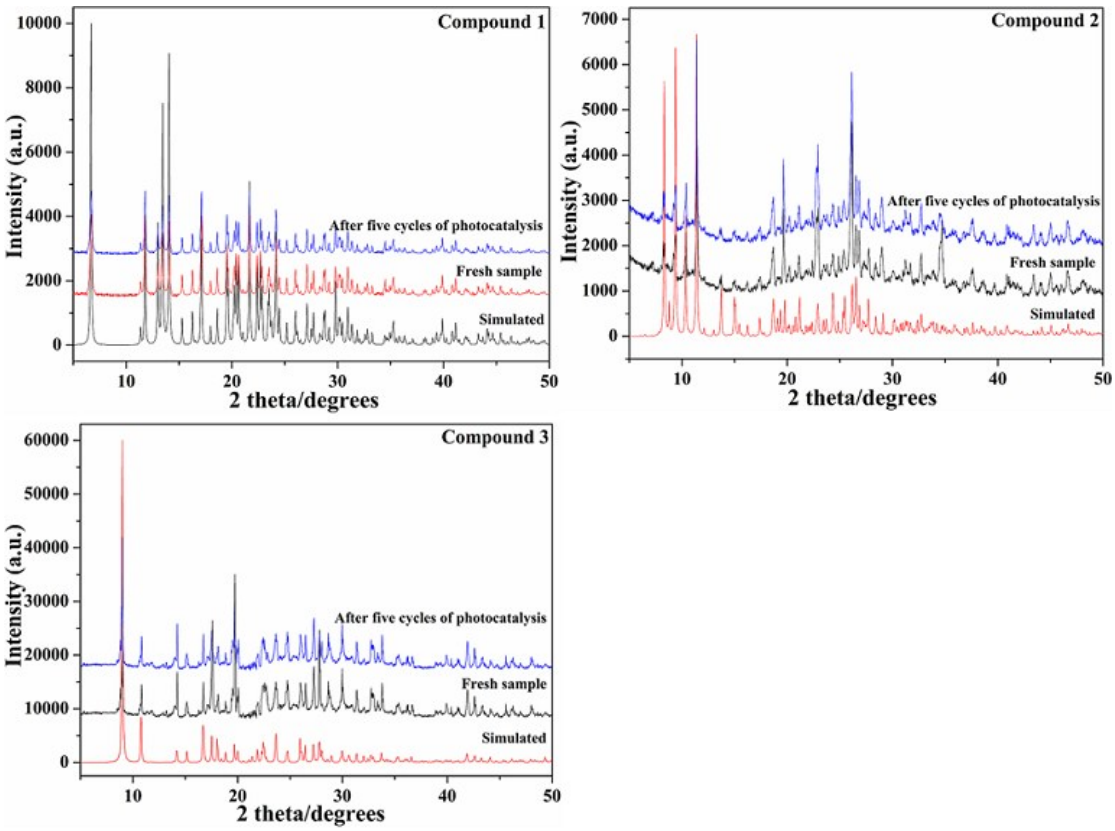

Fig. S2 The PXRD patterns of compounds **1**-**3**.

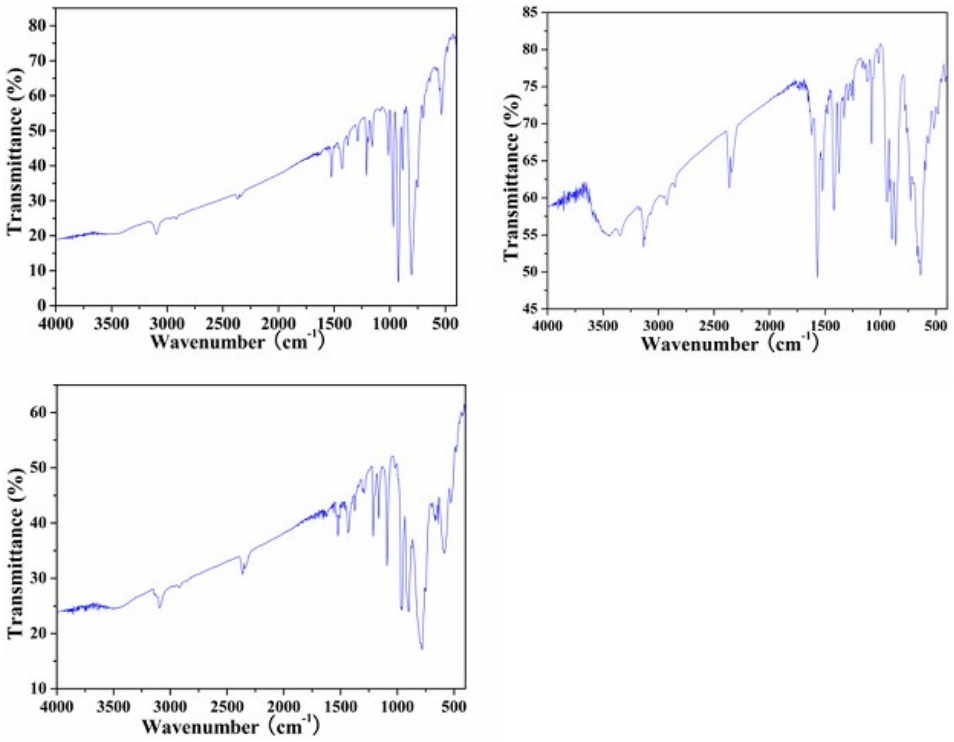

Fig. S3 The IR spectra of compounds **1**-**3**.

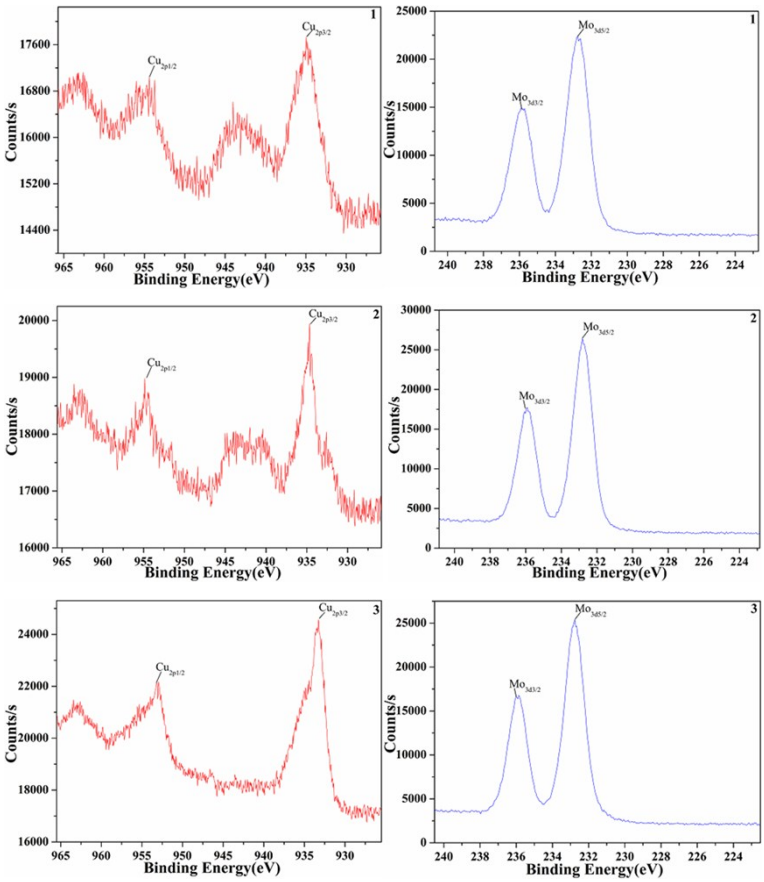

Fig. S4 The XPS spectra of compounds **1**-**3**.

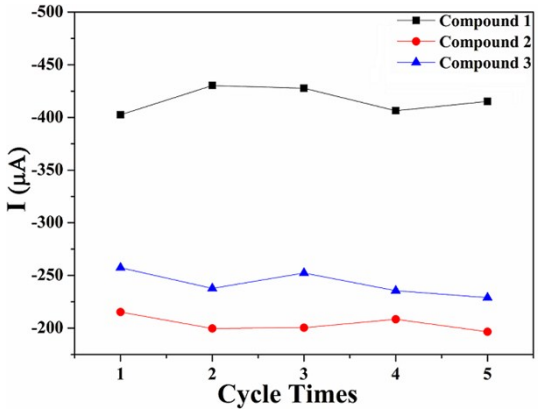

Fig. S5 The electracatalytic reduction of hydrogen peroxide with **1**-CPE, **2**-CPE and **3**-CPE after five cycles.

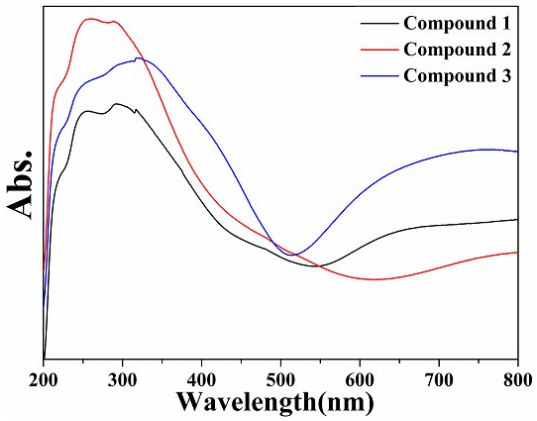

Fig. S6 The diffuse reflection spectra of compounds **1-3** in the crystalline state.

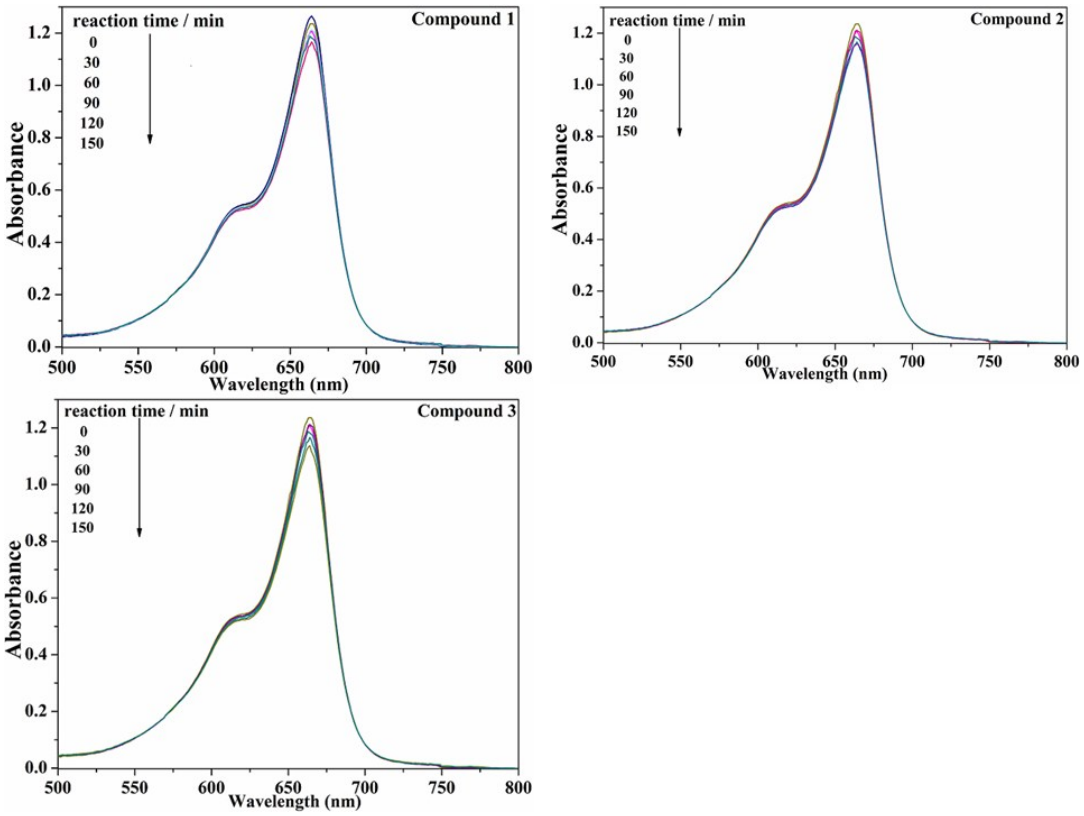

Fig. S7 The absorption spectra of the MB solution at the presence of compounds **1-3** in the darkness.