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Support Information

Effective photocatalytic and bifunctional electrocatalytic materials based on Keggin arsenomolybdate and transition metal capped assemblies

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1. Structural figures

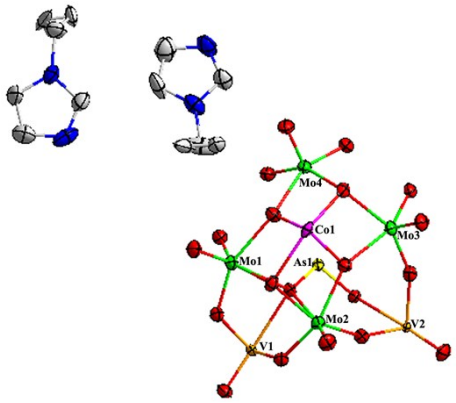

Fig. S1 ORTEP view of the basic units in compound **1** with 50% thermal ellipsoid.

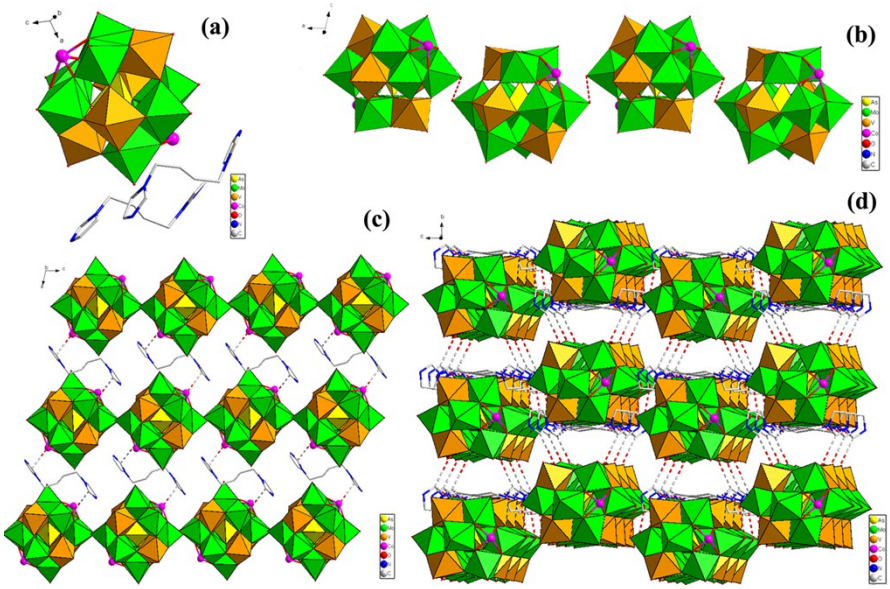

Fig. S2 (a) the Polyhedral representation of compound **1;** (b) The 1-D supramolecular chain of compound **1;** (c) The 2-D supramolecular layer of compound **1;**(d) The 3-D supramolecular network of compound **1.**

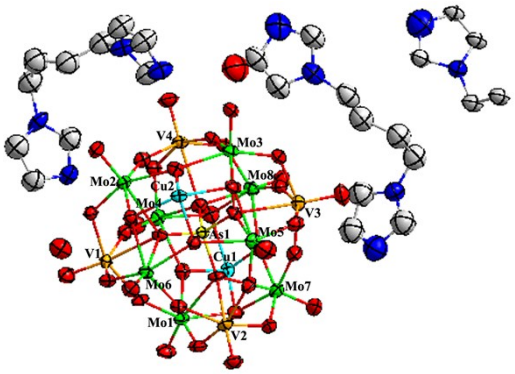

Fig. S3 ORTEP view of the basic units in compound **2** with 50% thermal ellipsoid.

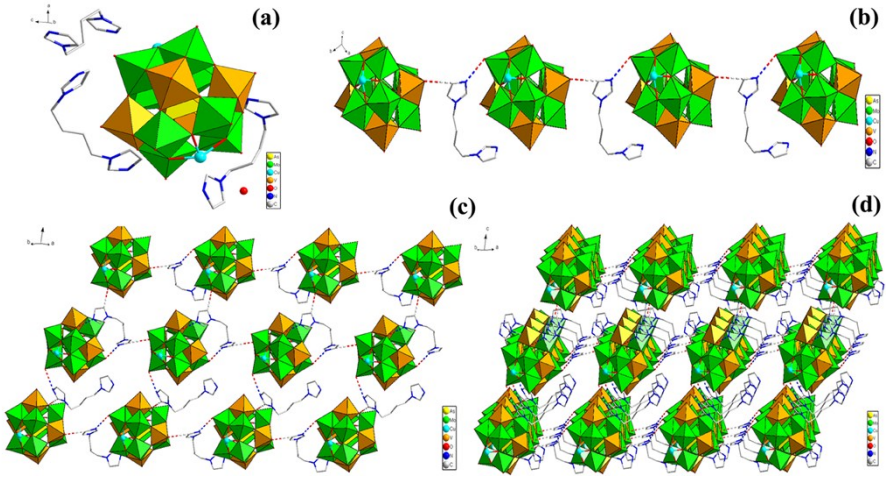

Figure S4 (a) the Polyhedral representation of compound **2;** (b) The 1-D supramolecular chain of compound **2;** (c) The 2-D supramolecular layer of compound **2;** (d) The 3-D supramolecular network of compound **2.**

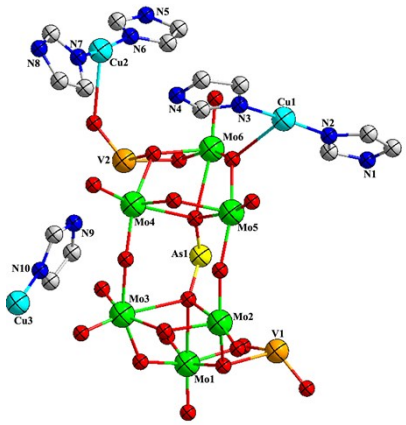

Figure S5 ORTEP view of the basic units in compound **3** with 50% thermal ellipsoid.

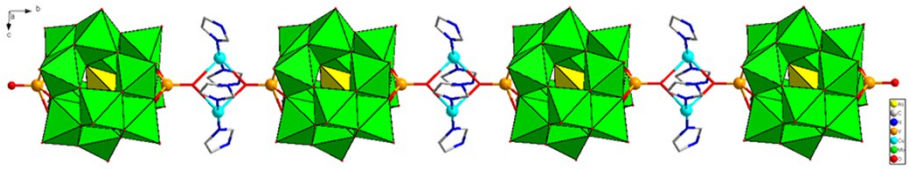

Figure S6 Polyhedral and ball-and-stick representation of the 1-D chain of 3.

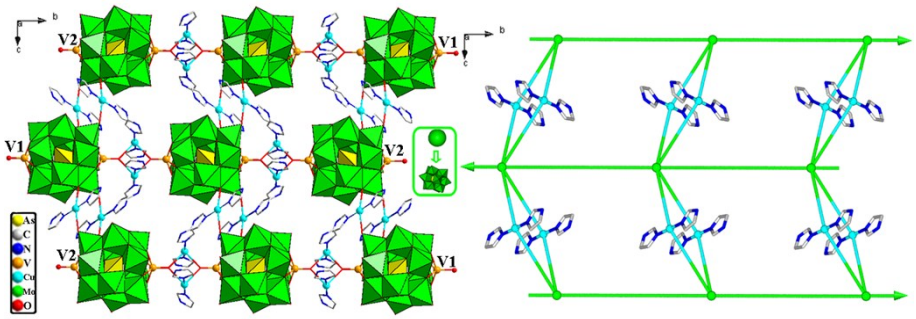

Figure S7 (a) Polyhedral and ball-and-stick representation 2-D layer of **3**; (b) Schematic view of the 2-D structural topology of **3** in A-B-A-B mode.

2. Structural data

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

As(1)-O(2)	1.674(4)	Mo(1)-O(2)	2.359(5)	Mo(2)-O(2)	2.351(5)
As(1)-O(13)	1.674(4)	Mo(1)-O(4)	1.799(5)	Mo(2)-O(5)	1.793(5)
As(1)-O(2)#1	1.674(4)	Mo(1)-O(8)	2.120(5)	Mo(2)-O(9)	2.079(5)
As(1)-O(13)#1	1.674(4)	Mo(1)-O(9)	2.060(5)	Mo(2)-O(10)	1.673(5)
Mo(3)-O(1)	2.095(5)	Mo(1)-O(11)	1.816(5)	Mo(2)-O(18)	2.093(5)
Mo(3)-O(3)	1.797(5)	Mo(1)-O(17)	1.680(5)	Mo(2)-O(19)	1.833(5)
Mo(3)-O(6)	1.677(5)	Mo(4)-O(1)	2.074(5)	V(1)-O(2)	2.386(4)
Mo(3)-O(14)	1.801(5)	Mo(4)-O(8)	2.114(5)	V(1)-O(7)	1.598(5)
Mo(3)-O(18)	2.106(5)	Mo(4)-O(12)	1.684(5)	V(1)-O(11)	1.945(5)
Mo(3)-O(13)#1	2.371(5)	Mo(4)-O(16)	1.803(5)	V(1)-O(19)	1.948(5)
V(2)-O(3)	1.935(5)	Mo(4)-O(20)	1.800(5)	V(1)-O(4)#1	1.940(5)
V(2)-O(5)	1.942(5)	Mo(4)-O(13)#1	2.374(4)	V(1)-O(16)#1	1.941(5)
V(2)-O(13)	2.409(5)	Co(1)-O(1)	1.951(5)	O(13)-As(1)-O(2)	108.5(2)
V(2)-O(15)	1.607(5)	Co(1)-O(8)	1.812(5)	O(13)-As(1)-O(2)#1	111.5(2)
V(2)-O(14)#1	1.965(5)	Co(1)-O(9)	2.129(5)	O(13)-As(1)-O(13)#1	108.6(3)
V(2)-O(20)#1	1.979(5)	Co(1)-O(18)	1.812(5)	O(6)-Mo(3)-O(1)	98.2(2)
O(17)-Mo(1)-O(2)	166.9(2)	O(10)-Mo(2)-O(2)	165.8(2)	O(6)-Mo(3)-O(3)	104.1(2)
O(17)-Mo(1)-O(4)	104.9(2)	O(10)-Mo(2)-O(5)	105.6(2)	O(6)-Mo(3)-O(14)	102.8(2)
O(17)-Mo(1)-O(8)	99.8(2)	O(10)-Mo(2)-O(9)	96.1(2)	O(6)-Mo(3)-O(18)	100.9(2)
O(17)-Mo(1)-O(9)	96.8(2)	O(10)-Mo(2)-O(18)	100.8(2)	O(6)-Mo(3)-O(13)#1	167.4(2)
O(17)-Mo(1)-O(11)	102.4(2)	O(10)-Mo(2)-O(19)	101.9(2)	O(15)-V(2)-O(3)	104.3(2)
O(12)-Mo(4)-O(1)	98.6(2)	O(7)-V(1)-O(2)	170.8(2)	O(15)-V(2)-O(5)	103.3(3)
O(12)-Mo(4)-O(8)	99.6(2)	O(7)-V(1)-O(11)	101.7(2)	O(15)-V(2)-O(13)	170.2(2)
O(12)-Mo(4)-O(16)	103.6(2)	O(7)-V(1)-O(19)	100.2(2)	O(15)-V(2)-O(14)#1	102.3(3)
O(12)-Mo(4)-O(20)	103.4(2)	O(7)-V(1)-O(4)#1	103.4(2)	O(15)-V(2)-O(20)#1	100.6(2)
O(12)-Mo(4)-O(13)#1	168.3(2)	O(7)-V(1)-O(16)#1	101.4(2)	O(8)-Co(1)-O(1)	81.8(2)
O(8)-Co(1)-O(9)	78.6(2)	O(8)-Co(1)-O(18)	108.4(2)		

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

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

As(1)-O(1)	1.698(13)	Mo(1)-O(5)	2.100(16)	Mo(2)-O(1)	2.353(14)
Mo(1)-O(10)	1.694(10)	Mo(2)-O(17)	1.711(11)	Mo(3)-O(16)	1.706(11)
Mo(1)-O(11)	1.775(10)	Mo(2)-O(2)	1.777(10)	Mo(3)-O(20)	1.781(11)
Mo(1)-O(22)	1.811(11)	Mo(2)-O(39)	1.783(10)	Mo(3)-O(9)	1.779(10)
Mo(1)-O(5)	2.094(11)	Mo(2)-O(4)	2.059(10)	Mo(3)-O(6)	2.101(11)
Mo(1)-O(12)	2.106(10)	Mo(2)-O(28)	2.122(10)	Mo(3)-O(28)	2.120(10)
Mo(1)-O(18)	2.384(9)	Mo(2)-O(1)	2.362(9)	Mo(3)-O(8)	2.362(10)
Mo(4)-O(25)	1.700(11)	Mo(5)-O(32)	1.681(12)	Mo(6)-O(37)	1.693(10)
Mo(4)-O(26)	1.790(10)	Mo(5)-O(36)	1.774(10)	Mo(6)-O(3)	1.793(10)
Mo(4)-O(24)	1.809(10)	Mo(5)-O(19)	1.811(11)	Mo(6)-O(7)	1.813(10)
Mo(4)-O(14)	2.027(10)	Mo(5)-O(6)	2.092(10)	Mo(6)-O(4)	2.072(10)
Mo(4)-O(12)	2.133(10)	Mo(5)-O(21)	2.108(10)	Mo(6)-O(21)	2.123(10)
Mo(4)-O(13)	2.365(10)	Mo(5)-O(8)	2.384(10)	Mo(6)-O(1)	2.379(9)
Mo(7)-O(35)	1.716(12)	Mo(8)-O(23)	1.683(11)	Cu(1)-O(33)	1.807(11)
Mo(7)-O(38)	1.783(11)	Mo(8)-O(15)	1.809(11)	Cu(1)-O(12)	1.816(10)
Mo(7)-O(34)	1.803(11)	Mo(8)-O(31)	1.827(11)	Cu(1)-O(5)	2.008(11)
Mo(7)-O(5)	2.062(10)	Mo(8)-O(14)	2.093(10)	Cu(1)-O(14)	2.089(11)
Mo(7)-O(33)	2.115(11)	Mo(8)-O(33)	2.139(10)	Cu(2)-O(28)	1.812(10)
Mo(7)-O(18)	2.373(10)	Mo(8)-O(13)	2.385(9)	Cu(2)-O(21)	1.824(10)
As(1)-O(13)	1.679(9)	As(1)-O(18)	1.689(9)	Cu(2)-O(6)	1.990(11)
As(1)-O(8)	1.684(9)	As(1)-O(1)	1.690(9)	Cu(2)-O(4)	2.063(10)
V(1)-O(29)	1.573(11)	V(2)-O(27)	1.599(10)	V(3)-O(40)	1.595(12)
V(1)-O(11)	1.965(9)	V(2)-O(3)	1.957(10)	V(3)-O(15)	1.922(11)
V(1)-O(7)	1.973(10)	V(2)-O(36)	1.961(11)	V(3)-O(38)	1.959(11)
V(1)-O(24)	1.995(10)	V(2)-O(22)	1.985(11)	V(3)-O(19)	1.983(11)
V(1)-O(39)	2.020(10)	V(2)-O(34)	2.014(12)	V(3)-O(9)	2.026(11)
V(1)-O(1)	2.400(10)	V(2)-O(18)	2.384(10)	V(3)-O(8)	2.385(10)
V(4)-O(30)	1.597(11)	V(4)-O(2)	1.977(10)	V(4)-O(26)	2.008(11)
V(4)-O(20)	1.970(11)	V(4)-O(31)	1.984(11)	V(4)-O(13)	2.363(10)
O(13)-As(1)-O(8)	107.9(5)	O(13)-As(1)-O(18)	112.6(5)	O(13)-As(1)-O(1)	108.2(5)
O(10)-Mo(1)-O(5)	97.5(5)	O(17)-Mo(2)-O(4)	98.0(5)	O(16)-Mo(3)-O(6)	96.8(5)
O(10)-Mo(1)-O(22)	103.5(5)	O(17)-Mo(2)-O(28)	99.2(5)	O(16)-Mo(3)-O(28)	99.5(4)
O(10)-Mo(1)-O(11)	104.5(5)	O(17)-Mo(2)-O(2)	104.4(5)	O(16)-Mo(3)-O(20)	104.1(5)
O(10)-Mo(1)-O(12)	100.1(5)	O(17)-Mo(2)-O(39)	103.4(5)	O(16)-Mo(3)-O(9)	101.3(5)
O(10)-Mo(1)-O(18)	166.8(5)	O(17)-Mo(2)-O(1)	167.7(5)	O(16)-Mo(3)-O(8)	167.1(5)
O(25)-Mo(4)-O(14)	98.2(5)	O(32)-Mo(5)-O(6)	96.8(5)	O(37)-Mo(6)-O(4)	96.5(5)
O(25)-Mo(4)-O(12)	98.3(5)	O(32)-Mo(5)-O(21)	101.3(5)	O(37)-Mo(6)-O(21)	100.0(5)
O(25)-Mo(4)-O(26)	103.8(5)	O(32)-Mo(5)-O(36)	106.1(6)	O(37)-Mo(6)-O(3)	105.7(5)
O(25)-Mo(4)-O(24)	103.4(5)	O(32)-Mo(5)-O(19)	102.8(6)	O(37)-Mo(6)-O(7)	104.2(5)
O(25)-Mo(4)-O(13)	169.7(5)	O(32)-Mo(5)-O(8)	166.6(5)	O(37)-Mo(6)-O(1)	O(37)-
O(35)-Mo(7)-O(5)	97.3(5)	O(23)-Mo(8)-O(14)	96.6(5)	O(29)-V(1)-O(11)	103.1(5)
O(35)-Mo(7)-O(33)	99.6(5)	O(23)-Mo(8)-O(33)	99.3(5)	O(29)-V(1)-O(7)	102.3(5)
O(35)-Mo(7)-O(38)	104.9(5)	O(23)-Mo(8)-O(15)	104.7(5)	O(29)-V(1)-O(24)	102.1(5)
O(35)-Mo(7)-O(34)	103.0(5)	O(23)-Mo(8)-O(31)	103.0(5)	O(29)-V(1)-O(39)	100.4(5)
O(35)-Mo(7)-O(18)	167.5(5)	O(23)-Mo(8)-O(13)	166.4(5)	O(29)-V(1)-O(1)	170.5(5)
O(27)-V(2)-O(3)	103.8(5)	O(40)-V(3)-O(15)	104.1(6)	O(30)-V(4)-O(20)	101.8(5)
O(27)-V(2)-O(36)	104.8(5)	O(40)-V(3)-O(38)	102.5(6)	O(30)-V(4)-O(2)	102.1(5)
O(27)-V(2)-O(22)	99.7(5)	O(40)-V(3)-O(19)	99.7(6)	O(30)-V(4)-O(31)	100.6(6)
O(27)-V(2)-O(34)	99.0(5)	O(40)-V(3)-O(9)	102.3(6)	O(30)-V(4)-O(26)	101.6(6)
O(27)-V(2)-O(18)	168.6(5)	O(40)-V(3)-O(8)	170.0(6)	O(30)-V(4)-O(13)	172.4(5)
O(33)-Cu(1)-O(14)	78.6(4)	O(33)-Cu(1)-O(5)	80.0(4)	O(33)-Cu(1)-O(12)	105.2(5)
O(28)-Cu(2)-O(4)	78.4(4)	O(28)-Cu(2)-O(6)	80.7(4)	O(28)-Cu(2)-O(21)	105.6(5)

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

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

As(1)-O(7)	1.664(6)	V(1)-O(1)	1.596(11)	V(2)-O(19)	2.002(6)
As(1)-O(13)	1.660(5)	V(1)-O(2)	1.998(6)	V(2)-O(19)#1	2.002(6)
As(1)-O(7)#1	1.664(6)	V(1)-O(2)#1	1.998(6)	V(2)-O(20)	1.899(6)
As(1)-O(13)#1	1.660(5)	V(1)-O(3)	1.909(6)	V(2)-O(20)#1	1.899(6)
Mo(1)-O(2)	2.041(6)	V(1)-O(3)#1	1.909(6)	V(2)-O(22)	1.598(11)
Mo(1)-O(3)	2.059(6)	Mo(2)-O(2)	2.052(6)	Mo(3)-O(6)	1.974(6)
Mo(1)-O(4)	1.684(6)	Mo(2)-O(3)#1	2.053(6)	Mo(3)-O(7)	2.426(6)
Mo(1)-O(5)	1.826(6)	Mo(2)-O(7)	2.392(5)	Mo(3)-O(9)	1.966(6)
Mo(1)-O(6)	1.837(6)	Mo(2)-O(8)	1.673(6)	Mo(3)-O(10)	1.648(7)
Mo(1)-O(7)	2.400(6)	Mo(2)-O(9)	1.860(6)	Mo(3)-O(11)	1.950(6)
Mo(4)-O(13)	2.395(5)	Mo(2)-O(12)	1.816(6)	Mo(3)-O(14)	1.953(6)
Mo(4)-O(14)	1.831(6)	Mo(5)-O(5)#1	1.945(6)	Mo(6)-O(11)#1	1.832(6)
Mo(4)-O(15)	1.836(6)	Mo(5)-O(12)	1.955(6)	Mo(6)-O(13)	2.401(5)
Mo(4)-O(19)	2.055(6)	Mo(5)-O(13)	2.396(5)	Mo(6)-O(16)	1.840(6)
Mo(4)-O(20)#1	2.060(6)	Mo(5)-O(15)	1.976(6)	Mo(6)-O(18)	1.684(6)
Mo(4)-O(21)	1.677(6)	Mo(5)-O(16)	1.968(6)	Mo(6)-O(19)	2.042(6)
Cu(1)-N(2)	1.878(9)	Mo(5)-O(17)	1.645(6)	Mo(6)-O(20)	2.040(6)
Cu(1)-N(3)	1.881(9)	Cu(2)-N(6)	1.882(11)	Cu(3)-N(10)	1.864(11)
Cu(1)-O(18)	2.747(6)	Cu(2)-N(7)	1.906(10)	Cu(3)-N(10)#2	1.864(11)
Cu(1)-O(16)	2.867(6)	Cu(2)-O(1)	2.467(7)	Cu(2)-O(22)	2.463(7)
O(13)-As(1)-O(13)#1	110.9(4)	O(1)-V(1)-O(3)#1	121.58(19)	O(22)-V(2)-O(20)#1	122.78(18)
O(13)-As(1)-O(7)#1	108.8(3)	O(1)-V(1)-O(3)	121.58(18)	O(22)-V(2)-O(20)	122.78(18)
O(13)-As(1)-O(7)	108.8(3)	O(1)-V(1)-O(2)#1	108.21(18)	O(22)-V(2)-O(19)#1	108.21(17)
O(4)-Mo(1)-O(5)	104.8(3)	O(1)-V(1)-O(2)	108.21(18)	O(22)-V(2)-O(19)	108.21(17)
O(4)-Mo(1)-O(6)	101.8(3)	O(8)-Mo(2)-O(12)	104.2(3)	O(10)-Mo(3)-O(11)	104.2(3)
O(4)-Mo(1)-O(2)	100.7(3)	O(8)-Mo(2)-O(9)	100.3(3)	O(10)-Mo(3)-O(14)	104.1(3)
O(4)-Mo(1)-O(3)	99.0(3)	O(8)-Mo(2)-O(2)	100.4(3)	O(10)-Mo(3)-O(9)	101.2(3)
O(4)-Mo(1)-O(7)	168.6(3)	O(8)-Mo(2)-O(3)#1	100.4(3)	O(10)-Mo(3)-O(6)	100.7(3)
O(21)-Mo(4)-O(14)	103.9(3)	O(8)-Mo(2)-O(7)	167.3(3)	O(10)-Mo(3)-O(7)	169.2(3)
O(21)-Mo(4)-O(15)	102.1(3)	O(17)-Mo(5)-O(5)#1	103.2(3)	O(18)-Mo(6)-O(11)#1	104.9(3)
O(21)-Mo(4)-O(19)	99.9(3)	O(17)-Mo(5)-O(12)	102.3(3)	O(18)-Mo(6)-O(16)	102.3(3)
O(21)-Mo(4)-O(20)#1	99.5(3)	O(17)-Mo(5)-O(16)	101.3(3)	O(18)-Mo(6)-O(20)	99.2(3)
O(21)-Mo(4)-O(13)	168.2(3)	O(17)-Mo(5)-O(15)	101.3(3)	O(18)-Mo(6)-O(19)	99.3(3)
O(22)-Cu(2)-N(6)	96.7(6)	O(17)-Mo(5)-O(13)	170.5(3)	O(18)-Mo(6)-O(13)	167.8(3)
O(22)-Cu(2)-N(7)	92.9(6)	O(18)-Cu(1)-N(3)	87.3(5)	O(18)-Cu(1)-O(16)	166.7(5)
O(22)-Cu(2)-O(1)	84.9(6)	O(18)-Cu(1)-N(2)	92.0(5)	N(10)-Cu(3)-N(10)#2	179.9(1)

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

Table S4 Selected Hydrogen Bond Lengths ( ) and Bond Angles (°) of complexes **1-2**

	D-H...A	d(D-H)	d(H...A)	<D-H...A	d(D...A)	Symmetry
1	N2-H2A...O9	0.86	1.99	154.3	2.788(9)	[x, y, z+1]
	N3-H3A...O19	0.86	2.01	160.9	2.839(9)	[-x+1/2, -y+1/2, -z]
2	N6-H6A...O16	0.86	2.19	140.1	2.898(19)	
	O1W-H1WA...O25	0.85	2.01	159.4	2.817(16)	
	N10-H10...O35	0.86	2.51	124.8	3.08(2)	
	N6-H6A...O25	0.86	2.19	127.5	2.793(19)	[x-1, y, z]
	N2-H2...O1W	0.86	2.60	157.0	3.41(3)	[-x+1, -y+1, -z+1]
	O1W-H1WB...O17	0.84	2.06	162.2	2.871(16)	[x+1, y, z]
	N10-H10...O40	0.86	2.60	144.5	3.34(2)	[-x+1, -y, -z+1]
	O2W-H2WA...O19	0.85	2.20	146.1	2.94(3)	[-x+1, -y+1, -z+1]

3. Physical characterization

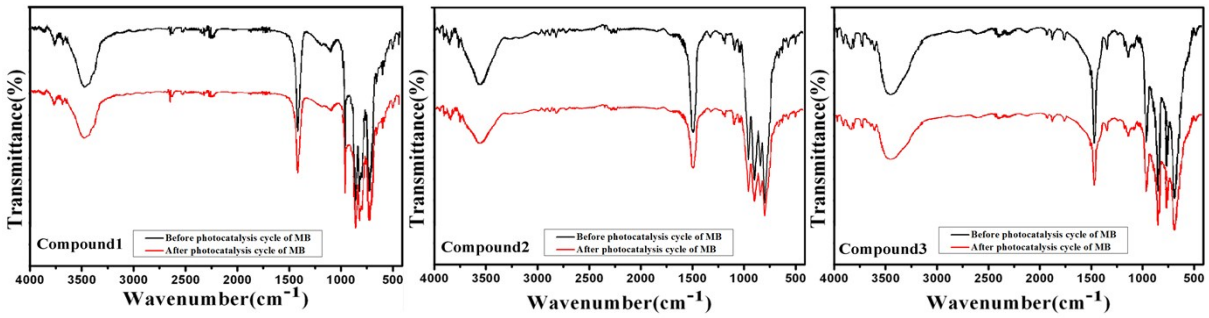

Fig. S8 IR spectra of compounds **1, 2, and 3** before and after photocatalysis cycle.

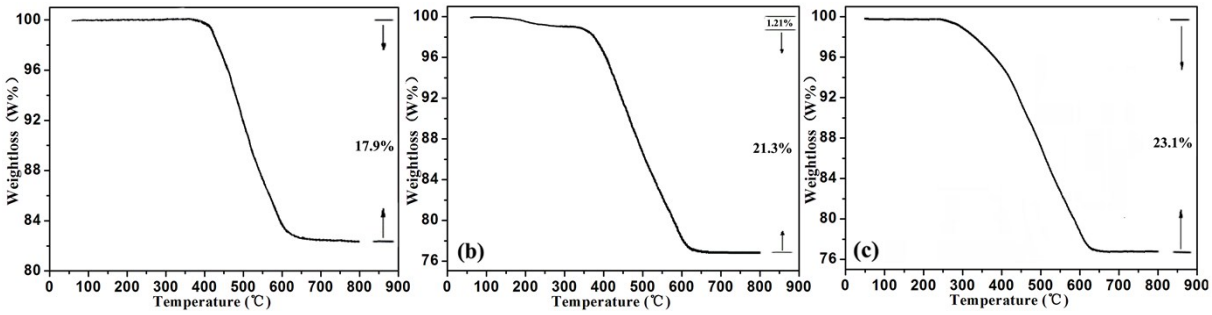

Fig. S9 TG curves of compounds **1, 2, and 3.**

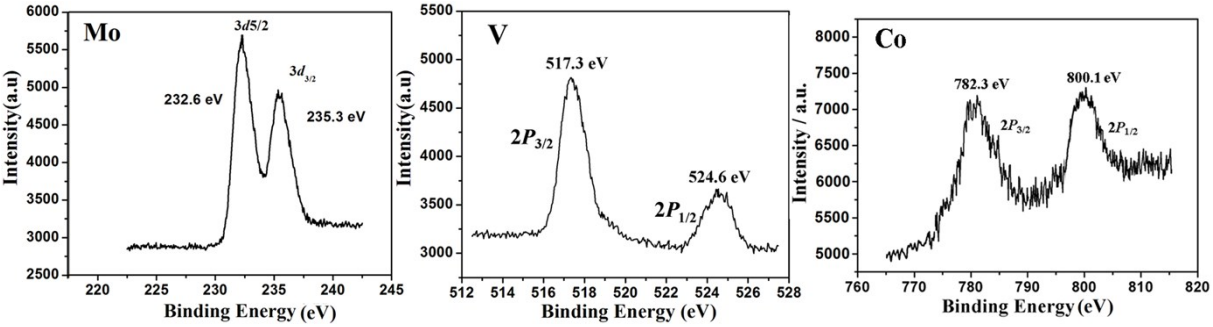

Fig.S10 The XPS spectrum of compound **1**.

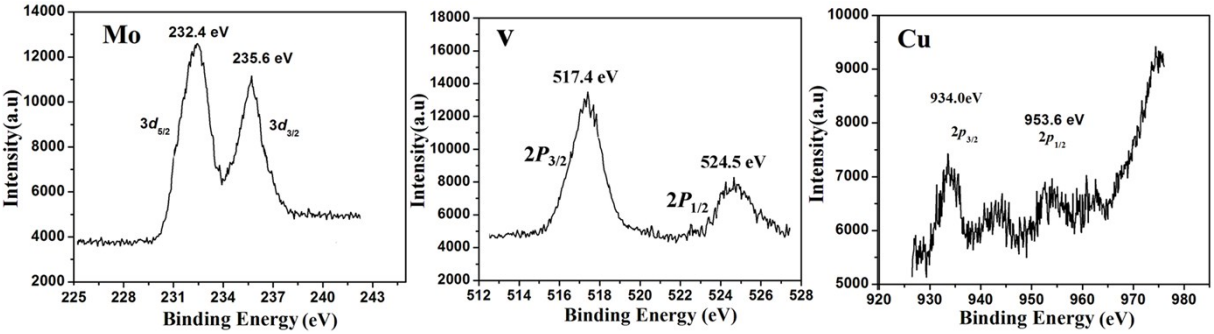

Fig.S11 The XPS spectrum of compound **2**.

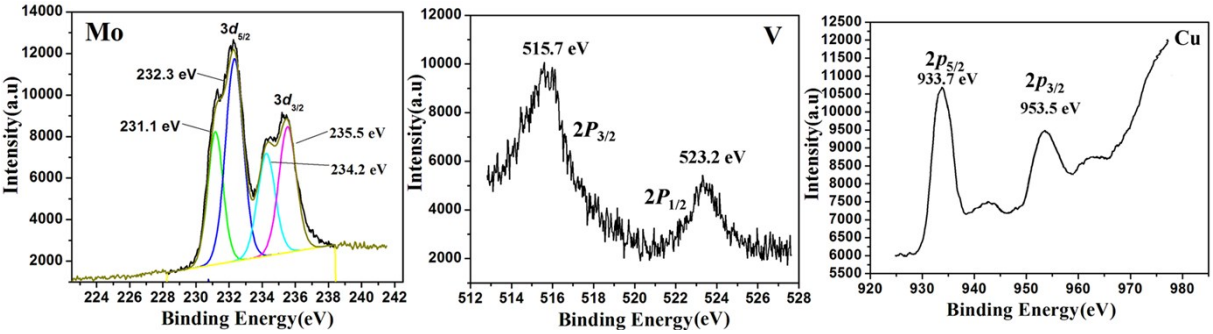

Fig.S12 The XPS spectrum of compound **3**.

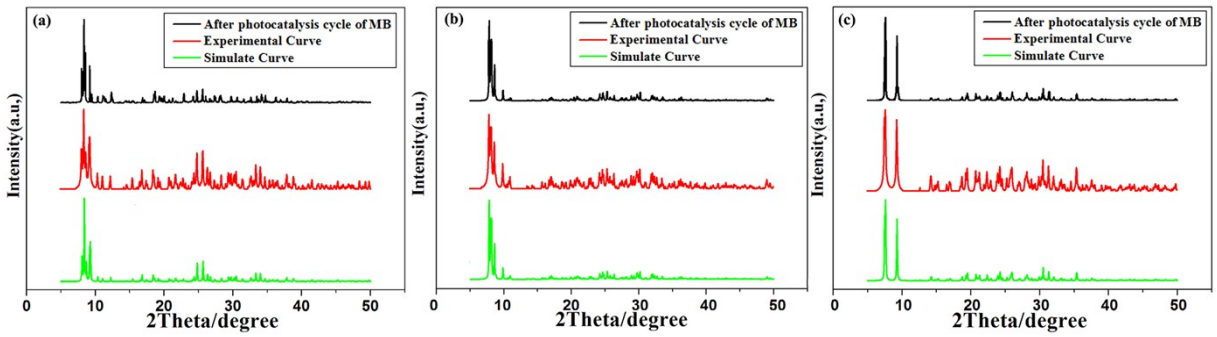

Figure S13 The PXRD contrast curves of compounds **1, 2, and 3.**

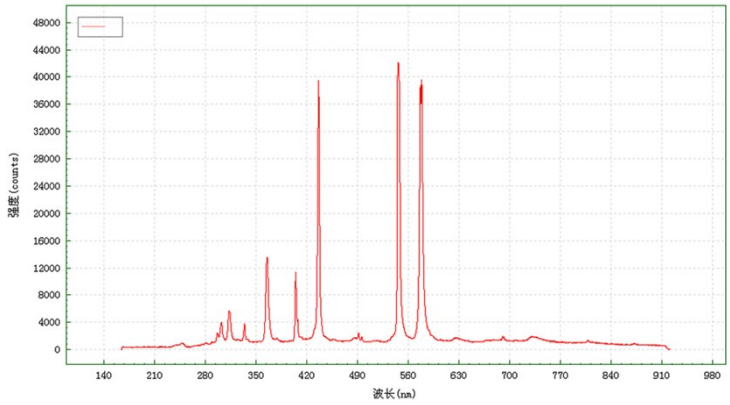

Figure S14 The light spectrum of for the photocatalytic reaction

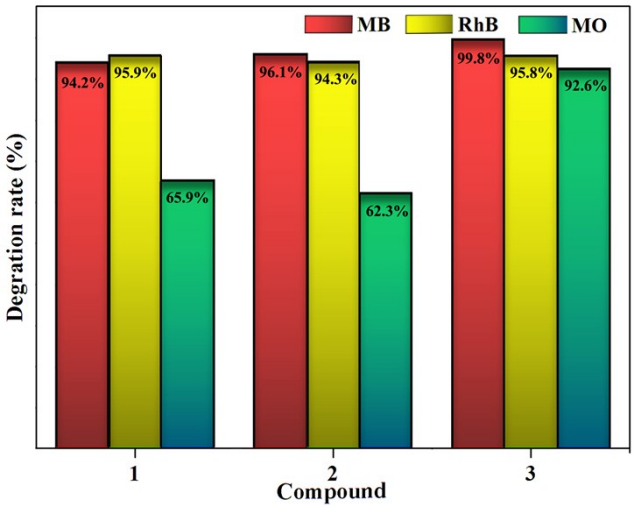

Fig. S15 Degradation rates of the MB, RhB and MO solutions in the presence of **1**–**3**

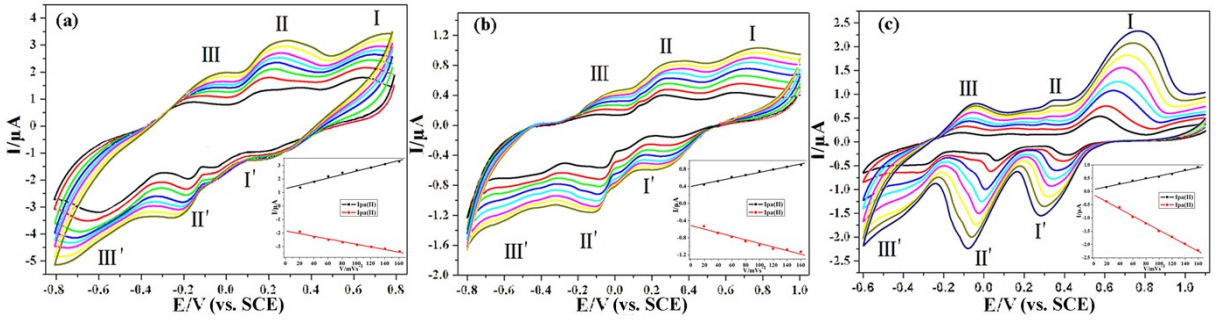

Fig. S16 Cyclic voltammograms of **(a) 1**-CPE**, (b) 2**-CPE and **(c) 3**-CPE in the 0.1 M H_2SO_4 solution at different scan rate. rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, and 160 mV s^{-1} for **1-3**

(Potentials vs. SCE).