**Supporting Information**

Polyoxometalates decorated with metal-organic moieties as new molecular photo- and electro-catalysts

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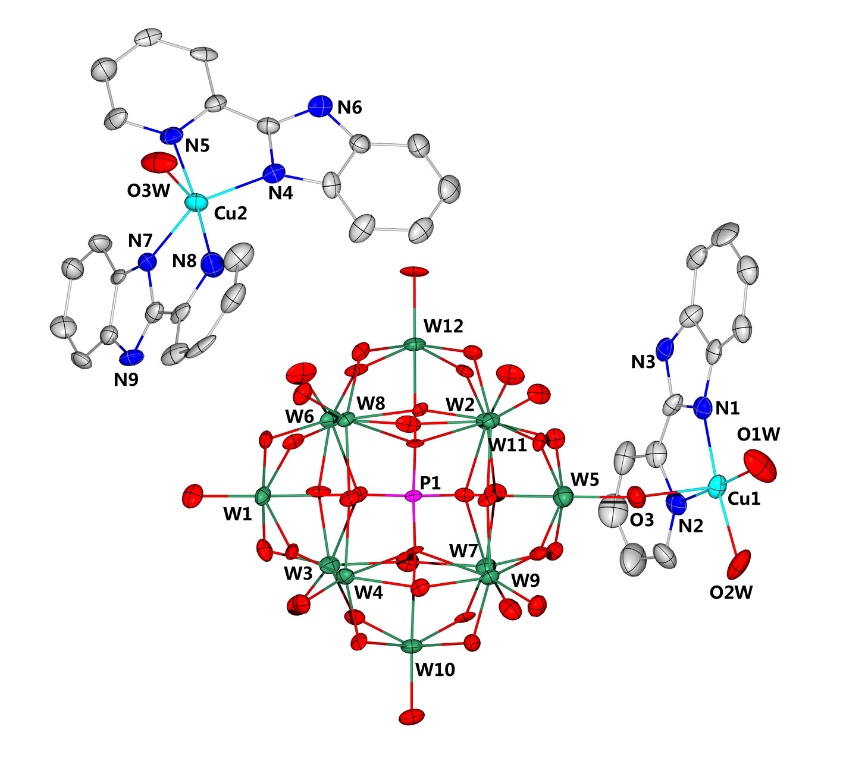


Figure S1. ORTEP view of the basic unit in compound **1** with thermal ellipsoids of 50%. H atoms and lattice water molecules are omitted for clarity.

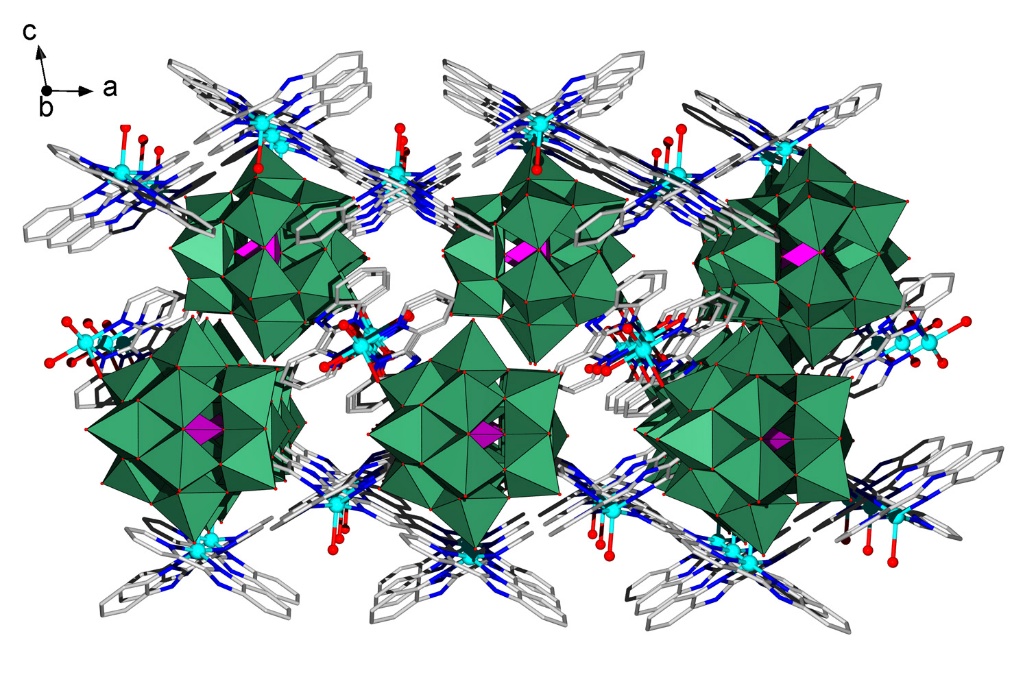


Figure S2. Ball-and-stick and polyhedral view of the packing arrangement of compound **1** viewed along *b* axis. H atoms and lattice water molecules are omitted for clarity.

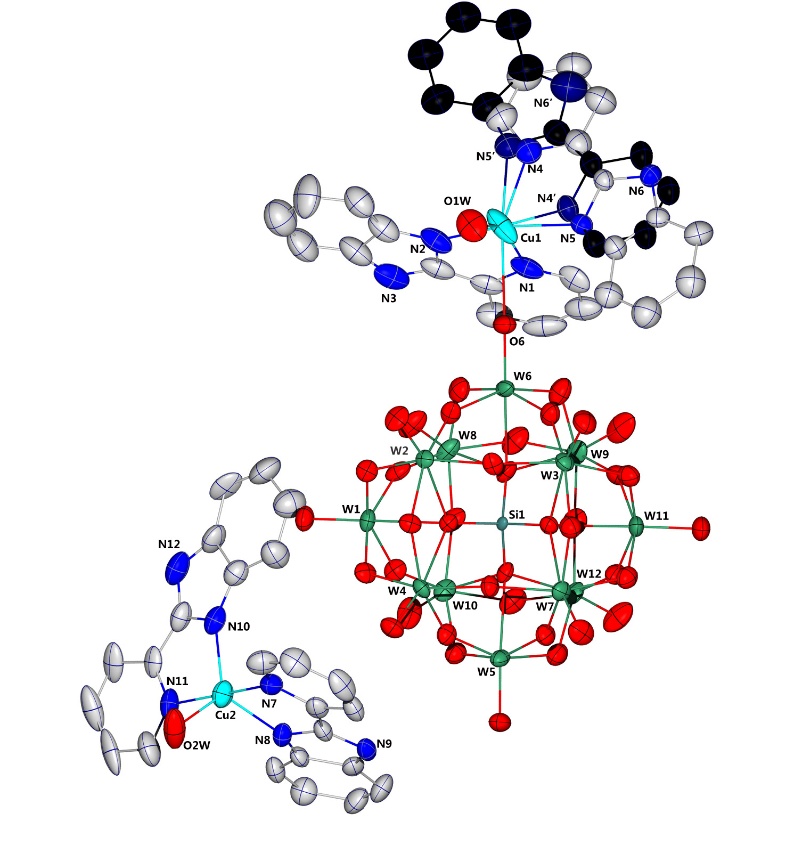


Figure S3. ORTEP view of the basic unit in compound **2** with thermal ellipsoids of 50%. H atoms and lattice water molecules are omitted for clarity. One of the PBI ligand one Cu(1) center is disordered into two possible positions.

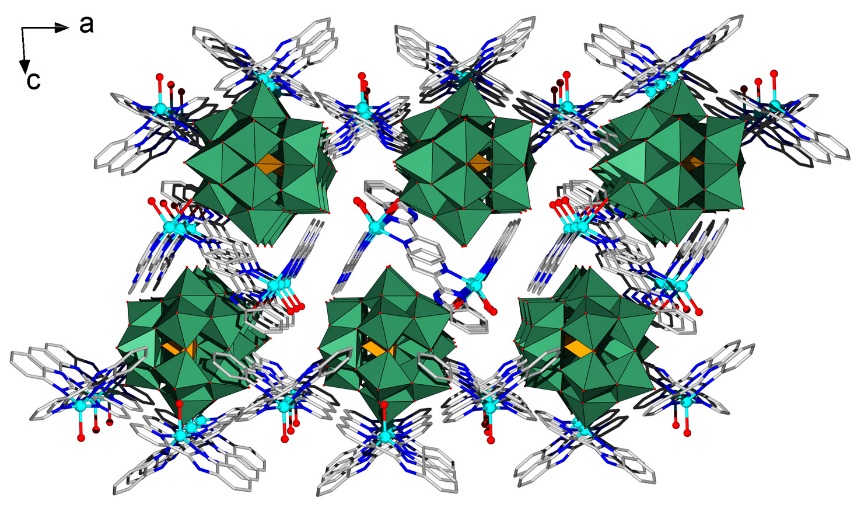


Figure S4. Ball-and-stick and polyhedral view of the packing arrangement of compound **2** viewed along *b* axis. H atoms and lattice water molecules are omitted for clarity.

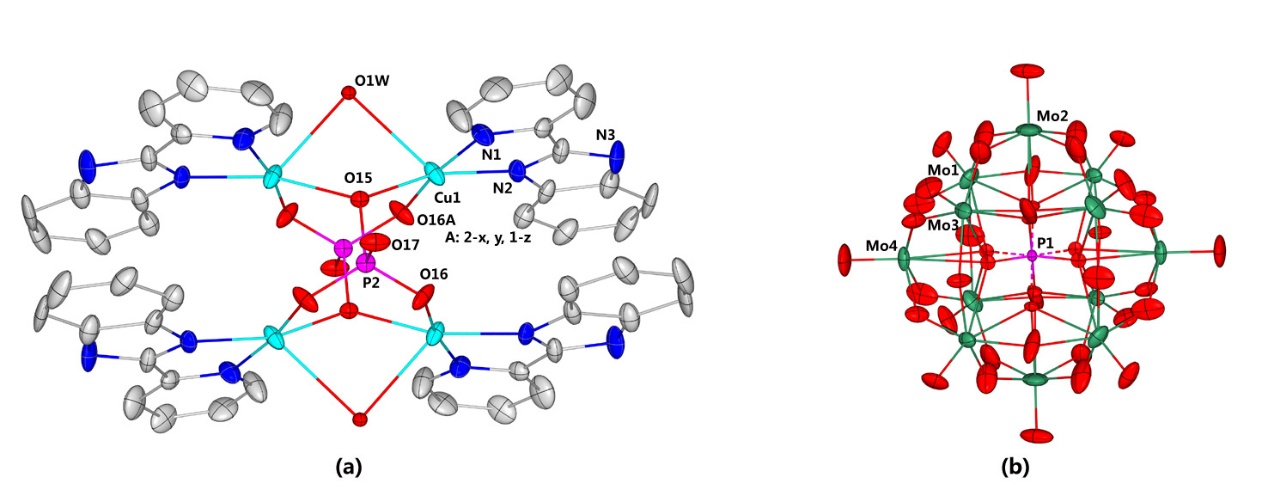


Figure S5. ORTEP view of cationic cluster **(a)** and polyoxoanion **(b)** in compound **3** with thermal ellipsoids of 30%. H atoms and lattice water molecules are omitted for clarity.

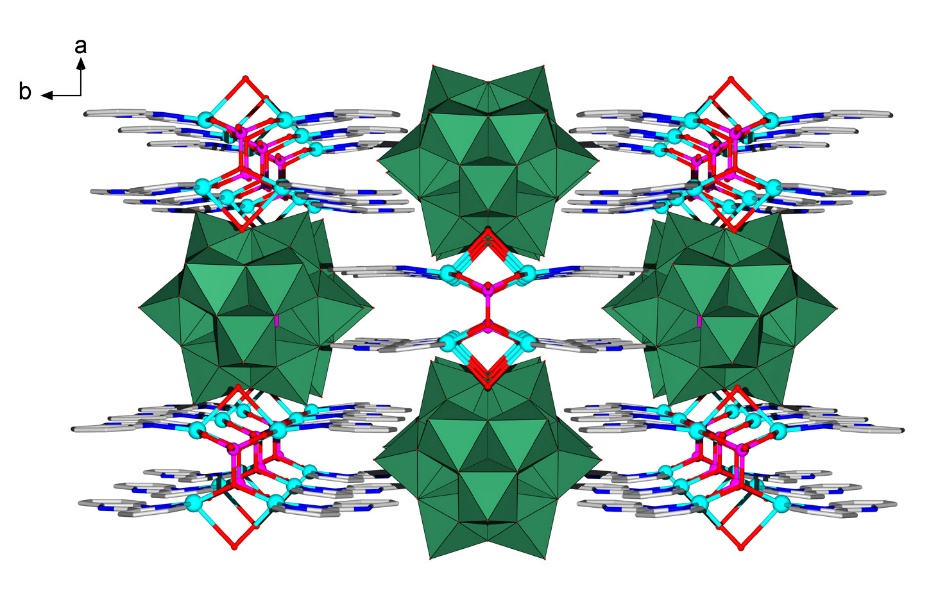


Figure S6. Ball-and-stick and polyhedral view of the packing arrangement of compound **3** viewed along *c* axis. H atoms and lattice water molecules are omitted for clarity.

1. **Selected bond lengths, bond angles and BVS calculations of compounds 1-3**

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

|  |  |  |  |
| --- | --- | --- | --- |
| W(1)**-**O(5) | 1.700(10) | W(2)-O(13) | 1.918(9) |
| W(1)**-**O(20) | 1.925(9) | W(2)-O(17) | 1.911(9) |
| W(1)-O(25) | 1.913(9) | W(2)-O(22) | 1.921(9) |
| W(1)-O(31) | 2.428(9) | W(2)-O(26) | 2.446(8) |
| W(1)-O(36) | 1.899(9) | W(2)-O(32) | 1.707(9) |
| W(1)-O(39) | 1.924(9) | W(2)-O(35) | 1.902(10) |
| W(3)-O(6) | 1.705(9) | W(4)-O(1) | 1.739(9) |
| W(3)-O(9) | 1.917(9) | W(4)-O(21) | 1.896(9) |
| W(3)-O(20) | 1.928(10) | W(4)-O(29) | 1.917(9) |
| W(3)-O(30) | 1.914(9) | W(4)-O(34) | 1.932(9) |
| W(3)-O(31) | 2.435(9) | W(4)-O(36) | 1.917(9) |
| W(3)-O(38) | 1.909(10) | W(4)-O(40) | 2.453(9) |
| W(0AA)-O(12) | 2.428(8) | W(6)-O(28) | 1.881(9) |
| W(0AA)-O(14) | 1.907(9) | W(6)-O(30) | 1.940(9) |
| W(0AA)-O(15) | 1.699(9) | W(6)-O(31) | 2.458(9) |
| W(0AA)-O(16) | 1.910(9) | W(6)-O(35) | 1.925(10) |
| W(0AA)-O(24) | 1.923(9) | W(6)-O(37) | 1.700(10) |
| W(0AA)-O(33) | 1.914(9) | W(6)-O(39) | 1.918(9) |
| W(7)-O(2) | 1.692(10) | W(8)-O(4) | 1.698(10) |
| W(7)-O(11) | 1.914(9) | W(8)-O(12) | 2.425(9) |
| W(7)-O(18) | 1.923(9) | W(8)-O(16) | 1.924(9) |
| W(7)-O(22) | 1.930(9) | W(8)-O(21) | 1.921(9) |
| W(7)-O(26) | 2.452(9) | W(8)-O(23) | 1.914(9) |
| W(7)-O(38) | 1.891(10) | W(8)-O(25) | 1.898(9) |
| W(9)-O(10) | 1.711(9) | W(10)-O(8) | 1.679(9) |
| W(9)-O(19) | 1.926(9) | W(10)-O(9) | 1.895(9) |
| W(9)-O(27) | 1.904(9) | W(10)-O(11) | 1.901(9) |
| W(9)-O(33) | 1.910(9) | W(10)-O(19) | 1.962(9) |
| W(9)-O(34) | 1.908(9) | W(10)-O(29) | 1.926(9) |
| W(9)-O(40) | 2.441(9) | W(10)-O(40) | 2.420(8) |
| W(11)-O(3) | 1.736(10) | W(12)-O(7) | 1.730(9) |
| W(11)-O(14) | 1.912(9) | W(12)-O(12) | 2.451(8) |
| W(11)-O(17) | 1.936(9) | W(12)-O(13) | 1.896(9) |
| W(11)-O(18) | 1.921(9) | W(12)-O(23) | 1.922(9) |
| W(11)-O(26) | 2.421(9) | W(12)-O(24) | 1.896(9) |
| W(11)-O(27) | 1.928(9) | W(12)-O(28) | 1.930(9) |
| P(1)-O(12) | 1.544(9) | P(1)-O(31) | 1.541(9) |
| P(1)-O(26) | 1.535(10) | P(1)-O(40) | 1.545(9) |
| Cu(1)-O(3) | 2.286(10) | Cu(2)-N(4) | 2.036(13) |
| Cu(1)- N(1) | 1.967(13) | Cu(2)-N(5) | 2.002(8) |
| Cu(1)-N(2) | 2.017(9) | Cu(2)-N(7) | 2.029(12) |
| Cu(1)-O(1W) | 1.948(12) | Cu(2)-N(8) | 2.011(9) |
| Cu(1)-O(2W) | 1.969(11) | Cu(2)-O(3W) | 2.146(12) |

Table S2. Bond valence sum (BVS) calculation result of W atoms in compound **1**.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| W | BVSa | W | BVSa | W | BVSa |
| W1 | 6.10 | WOAA | 5.77 | W9 | 6.04 |
| W2 | 6.04 | W6 | 6.07 | W10 | 6.02 |
| W3 | 6.02 | W7 | 6.11 | W11 | 6.07 |
| W4 | 5.84 | W8 | 6.09 | W12 | 5.95 |
| The average BVS value of each W: **6.01**, suggesting that all W centers are +6 oxidation state. | | | | | |
| Bond | Bond length | BVS | Bond | Bond length | BVS |
| Cu1-O2W | 1.969 | 0.43 | Cu2-O3W | 2.146 | 0.27 |
| Cu1-O1W | 1.948 | 0.46 | Cu2-N5 | 2.002 | 0.53 |
| Cu1-O3 | 2.286 | 0.18 | Cu2-N8 | 2.011 | 0.51 |
| Cu1-N1 | 1.967 | 0.59 | Cu2-N4 | 2.036 | 0.49 |
| Cu1-N2 | 2.017 | 0.51 | Cu2-N7 | 2.029 | 0.48 |
| Cu1 | | 2.16 | Cu2 | | 2.28 |
| BVS results suggest that both Cu centers are +2 oxidation state;  BVS value of O1W is quite close to 0.5, suggesting that O1W could be a OH- group;  BVS values of O2W and O3W are less than 0.5, representing the coordinated water molecules. | | | | | |

a: W-O, r0 = 1.917; Cu-O, r0 = 1.649; Cu-N, r0 = 1.751.1-2

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

|  |  |  |  |
| --- | --- | --- | --- |
| W(1)-O(33) | 1.708(8) | W(2)-O(5) | 1.710(8) |
| W(1)-O(25) | 1.899(8) | W(2)-O(31) | 1.893(8) |
| W(1)-O(13) | 1.908(8) | W(2)-O(24) | 1.893(8) |
| W(1)-O(38) | 1.921(8) | W(2)-O(4) | 1.912(8) |
| W(1)-O(36) | 1.917(8) | W(2)-O(13) | 1.934(8) |
| W(1)-O(15) | 2.357(7) | W(2)-O(15) | 2.349(7) |
| W(3)-O(17) | 1.707(9) | W(4)-O(3) | 1.683(8) |
| W(3)-O(19) | 1.905(8) | W(4)-O(10) | 1.908(8) |
| W(3)-O(24) | 1.900(8) | W(4)-O(38) | 1.918(8) |
| W(3)-O(21) | 1.919(9) | W(4)-O(4) | 1.927(8) |
| W(3)-O(14) | 1.927(9) | W(4)-O(8) | 1.924(8) |
| W(3)-O(2) | 2.353(8) | W(4)-O(15) | 2.368(7) |
| W(5)-O(1) | 1.693(9) | W(6)-O(6) | 1.709(8) |
| W(5)-O(8) | 1.881(8) | W(6)-O(31) | 1.891(8) |
| W(5)-O(12) | 1.905(8) | W(6)-O(27) | 1.922(9) |
| W(5)-O(11) | 1.936(9) | W(6)-O(19) | 1.902(8) |
| W(5)-O(30) | 1.963(9) | W(6)-O(39) | 1.931(9) |
| W(5)-O(35) | 2.386(8) | W(6)-O(34) | 2.338(8) |
| W(7)-O(22) | 1.713(9) | W(8)-O(7) | 1.698(9) |
| W(7)-O(12) | 1.883(8) | W(8)-O(16) | 1.889(9) |
| W(7)-O(10) | 1.888(8) | W(8)-O(25) | 1.888(8) |
| W(7)-O(14) | 1.924(8) | W(8)-O(28) | 1.918(10) |
| W(7)-O(29) | 1.951(9) | W(8)-O(39) | 1.932(9) |
| W(7)-O(2) | 2.353(8) | W(8)-O(34) | 2.360(8) |
| W(9)-O(37) | 1.698(9) | W(10)-O(32) | 1.694(9) |
| W(9)-O(26) | 1.883(9) | W(10)-O(36) | 1.871(8) |
| W(9)-O(18) | 1.914(9) | W(10)-O(16) | 1.903(9) |
| W(9)-O(28) | 1.931(10) | W(10)-O(11) | 1.933(9) |
| W(9)-O(27) | 1.930(9) | W(10)-O(23) | 1.958(9) |
| W(9)-O(34) | 2.345(8) | W(10)-O(35) | 2.364(8) |
| W(11)-O(40) | 1.708(9) | W(12)-O(9) | 1.704(9) |
| W(11)-O(20) | 1.886(9) | W(12)-O(26) | 1.913(9) |
| W(11)-O(18) | 1.900(9) | W(12)-O(30) | 1.911(9) |
| W(11)-O(29) | 1.911(9) | W(12)-O(20) | 1.913(9) |
| W(11)-O(21) | 1.936(9) | W(12)-O(23) | 1.930(9) |
| W(11)-O(2) | 2.357(7) | W(12)-O(35) | 2.330(7) |
| Si(1)-O(35) | 1.616(8) | Si(1)-O(2) | 1.628(8) |
| Si(1)-O(15) | 1.617(7) | Si(1)-O(34) | 1.633(7) |
| Cu(1)-N(4) | 2.17(3) | Cu(2)-N(7) | 1.982(11) |
| Cu(1)-N(2) | 1.932(13) | Cu(2)-N(11) | 1.991(12) |
| Cu(1)-O(1W) | 2.016(10) | Cu(2)-N(10) | 2.024(13) |
| Cu(1)-N(1) | 2.098(13) | Cu(2)-N(8) | 2.050(11) |
| Cu(1)-N(4) | 2.29(3) | Cu(2)-O(2W) | 2.054(11) |
| N(4)-Cu(1)-N(2) | 172.0(9) | N(7)-Cu(2)-N(11) | 175.5(5) |
| N(4)-Cu(1)-O(1W) | 111.3(10) | N(7)-Cu(2)-N(10) | 99.1(5) |
| N(4)-Cu(1)-N(1) | 98.7(10) | N(7)-Cu(2)-N(8) | 82.3(5) |
| N(4)-Cu(1)-N(5) | 78.0(11) | N(7)-Cu(2)-O(2W) | 87.2(5) |

Table S4. Bond valence sum (BVS) calculation result of W atoms in compound **2**.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **W** | **BVSa** | | **W** | **BVSa** | **W** | **BVSa** |
| W1 | 6.15 | | W5 | 6.11 | W9 | 6.08 |
| W2 | 6.20 | | W6 | 6.19 | W10 | 6.21 |
| W3 | 6.19 | | W7 | 6.12 | W11 | 6.18 |
| W4 | 6.17 | | W8 | 6.24 | W12 | 6.18 |
| The average BVS value of each W: **6.17**, suggesting that all W centers are +6 oxidation state. | | | | | | |
| Bond | | Bond length | BVS | Bond | Bond length | BVS |
| Cu(1)-N(4) | | 2.29 | 0.69 | Cu(2)-N(7) | 1.982 | 0.54 |
| Cu(1)-N(2) | | 1.932 | 0.6 | Cu(2)-N(11) | 1.991 | 0.51 |
| Cu(1)-O(1W) | | 2.016 | 0.37 | Cu(2)-N(10) | 2.024 | 0.48 |
| Cu(1)-N(1) | | 2.098 | 0.39 | Cu(2)-N(8) | 2.050 | 0.45 |
| Cu(1)-N(5) | | 2.24 | 0.27 | Cu(2)-O(2W) | 2.054 | 0.34 |
| Cu1 | | | 2.33 | Cu2 | | 2.33 |
| BVS results suggest that both Cu centers are +2 oxidation state;  BVS values of O1W and O2W are less than 0.5, representing the coordinated water molecules. | | | | | | |

a: W-O, *r0* = 1.917; Cu-O, *r0* = 1.649; Cu-N, *r0* = 1.751.1-2

Table S5. Selected bond lengths (Å) and angles (°) in compound **3**.

|  |  |  |  |
| --- | --- | --- | --- |
| Mo(1)-O(6) | 1.637(6) | Mo(2)-O(8) | 1.621(10) |
| Mo(1)-O(4) | 1.862(7) | Mo(2)-O(7) | 1.857(8) |
| Mo(1)-O(7) | 1.882(8) | Mo(2)-O(7)#1 | 1.857(8) |
| Mo(1)-O(5) | 1.910(4) | Mo(2)-O(9) | 1.881(8) |
| Mo(1)-O(10)#1 | 1.902(7) | Mo(2)-O(9)#1 | 1.881(8) |
| Mo(1)-O(2)#1 | 2.422(9) | Mo(2)-O(2)#1 | 2.493(10) |
| Mo(1)-O(1) | 2.508(9) | Mo(2)-O(2) | 2.493(10) |
| Mo(3)-O(12) | 1.668(6) | Mo(4)-O(13) | 1.644(9) |
| Mo(3)-O(10) | 1.866(7) | Mo(4)-O(11) | 1.858(6) |
| Mo(3)-O(9) | 1.887(7) | Mo(4)-O(11)#2 | 1.858(6) |
| Mo(3)-O(14) | 1.896(3) | Mo(4)-O(4) | 1.917(7) |
| Mo(3)-O(11) | 1.916(6) | Mo(4)-O(4)#2 | 1.917(7) |
| Mo(3)-O(2) | 2.377(9) | Mo(4)-O(1) | 2.412(14) |
| Cu(1)-O(16) | 1.896(6) | Mo(4)-O(3)#3 | 2.476(13) |
| Cu(1)-O(15)#4 | 2.034(4) | Cu(1)-O(15) | 2.034(4) |
| Cu(1)-N(2) | 1.974(7) | Cu(1)-O(1AW)#5 | 2.034(4) |
| Cu(1)-N(1) | 2.014(7) |  |  |
| P(1)-O(3) | 1.448(12) | P(1)-O(2) | 1.568(10) |
| P(1)-O(3)#3 | 1.448(12) | P(1)-O(2)#3 | 1.568(10) |
| P(1)-O(1) | 1.505(13) | P(1)-O(2)#1 | 1.568(10) |
| P(1)-O(1)#3 | 1.505(13) | P(1)-O(2)#2 | 1.568(10) |
| P(2)-O(16) | 1.509(6) | P(2)-O(15) | 1.544(7) |
| P(2)-O(16)#6 | 1.509(6) | P(2)-O(17) | 1.557(7) |
| O(16)#4-Cu(1)-N(2) | 91.3(3) | O(16)#4-Cu(1)-O(15) | 92.2(2) |
| O(16)#4-Cu(1)-N(1) | 171.7(3) |  |  |

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

Table S6. Bond valence sum (BVS) calculation result of Mo atoms in compound **3**.

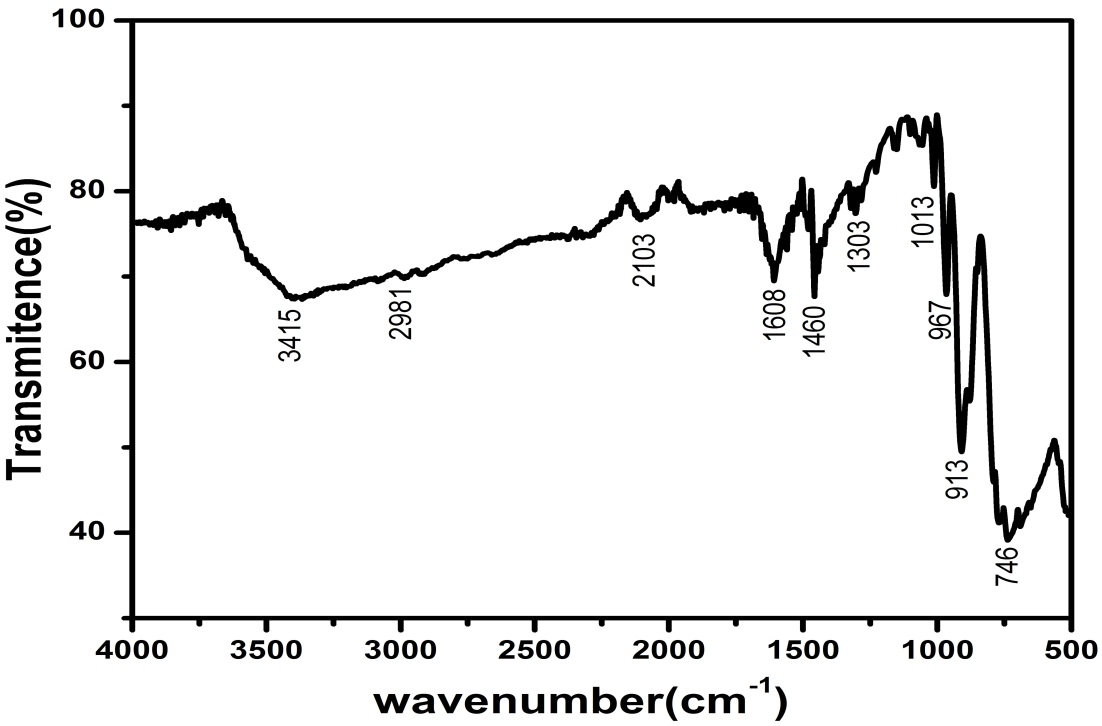
|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Mo | | BVSa | | | Mo | | BVSa | |
| Mo1 | | 6.22 | | | Mo3 | | 6.11 | |
| Mo2 | | 6.46 | | | Mo4 | | 6.21 | |
| The average BVS value of each Mo: **6.25**, suggesting that all Mo centers are +6 oxidation state. | | | | | | | | |
| Bond | Bond length | | BVS | Bond | | Bond length | | BVS |
| Cu(1)-O(16) | 1.896 | | 0.50 | P(2)-O(16) | | 1.509 | | 1.36 |
| Cu(1)-N(2) | 1.974 | | 0.55 | P(2)-O(16)#6 | | 1.509 | | 1.36 |
| Cu(1)-N(1) | 2.014 | | 0.49 | P(2)-O(15) | | 1.544 | | 1.24 |
| Cu(1)-O(15) | 2.034 | | 0.35 | P(2)-O(17) | | 1.557 | | 1.16 |
| Cu(1)-O(1AW) | 2.034 | | 0.13 |  | |  | |  |
| Cu1 | | | 2.03 | P2 | | | | 5.12 |
| BVS results suggest that Cu1 is +2 oxidation state; P2 is +5 oxidation state  BVS values of O1AW is less than 0.5, representing the coordinated water molecule. The terminal O17 atom of {PO4} is close to 1.0, suggesting that such O atom could be easy to be protonated. | | | | | | | | |

a:  *r0* = 1.89 for Mo-O; *r0* = 1.649 for Cu-O and *r0* = 1.751 for Cu-N; *r0* = 1.617 for P-O; 1-2

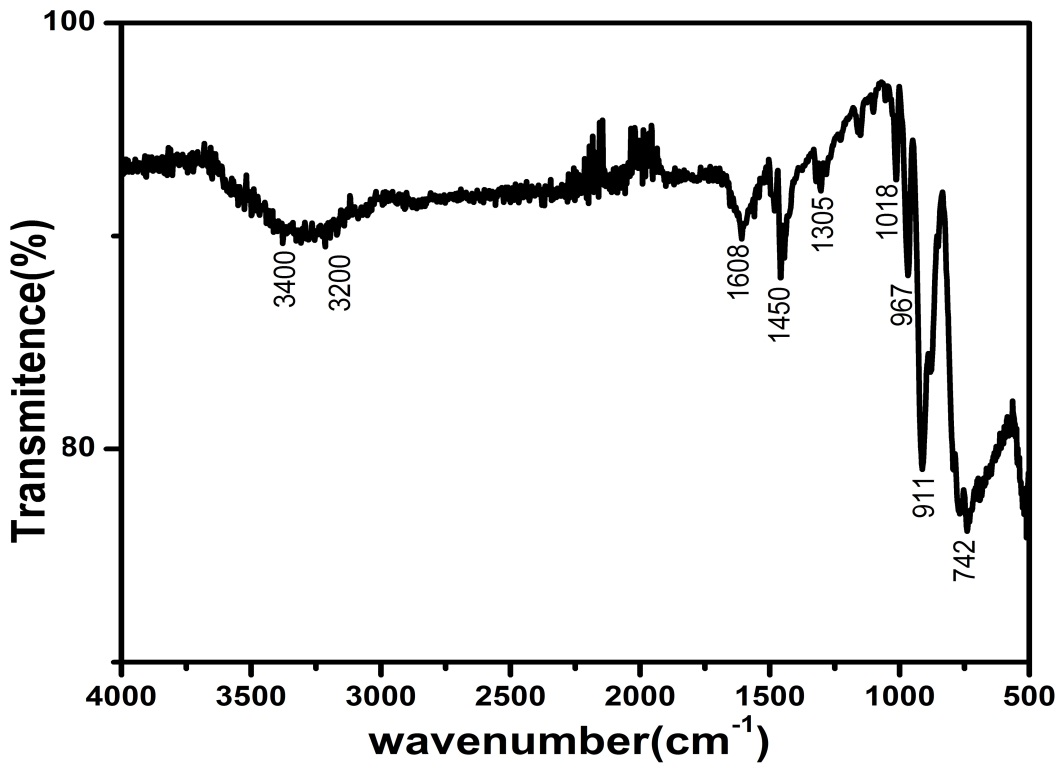
**3. Additional physical measurements of compounds 1-3**

* 1. **IR spectra**

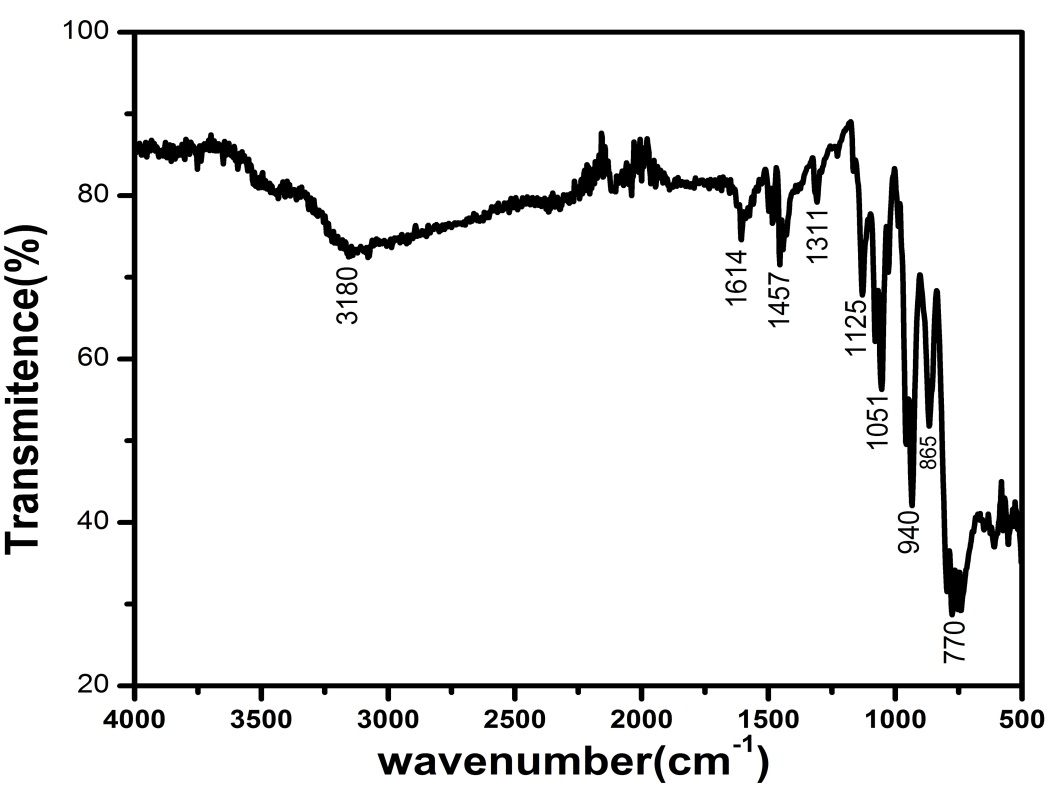
In the IR spectrum of compound **1** (Figure S7), four characteristic peaks of [PW12O40]4− are observed in the range of 1000-700 cm−1. The characteristic band at 1013 cm−1 is attributed to ν(P–O); band at 967 cm−1 is attributed to ν(W–Od); band at 913cm−1 is attributed to ν(W–Ob–W); band at 746 cm−1 is attributed to ν(W–Oc–W) respectively. In the IR spectrum of compound **2** (Figure S8), four characteristic peaks of [SiW12O40]3− are observed in the range of 1000-700 cm−1. The peaks assigned at 1018 cm−1, 967 cm−1, 911cm−1 and 742 cm−1 are attributed to the vibrations of *v*(W=Od), ν(Si–O), *v*(W–Ob/c–W), respectively. In the IR spectrum of compound **3** (Figure S9), four characteristic peaks of [PMo12O40]4− are observed in the range of 1000-700 cm−1. The peaks at 1013, 967, 913, and 746 cm−1 are attributed to the vibrations of *v*(P-O), *v*(Mo=Od) and *v*(Mo–Ob/c–Mo), respectively. In addition for all three compounds, the weaker peaks at ca. 2980-3118 cm−1are endorsed to the vibrations of the v(C-H) in phenyl rings of PBI ligand. Moreover, the Peaks in the regions of 1615-1300 cm−1 may belongs to the vibrations of the *v*(C=C), *v*(C=N) and *v*(C=N) in phenyl and pyradyl rings of PBI ligand in Compounds **1-3**. The peaks at ca. 3415 cm−1 are attributed to the vibrations of *v*(H2O).



**Figure S7.** IR spectrum of compound **1**.



**Figure S8.** IR spectrum of compound **2**.



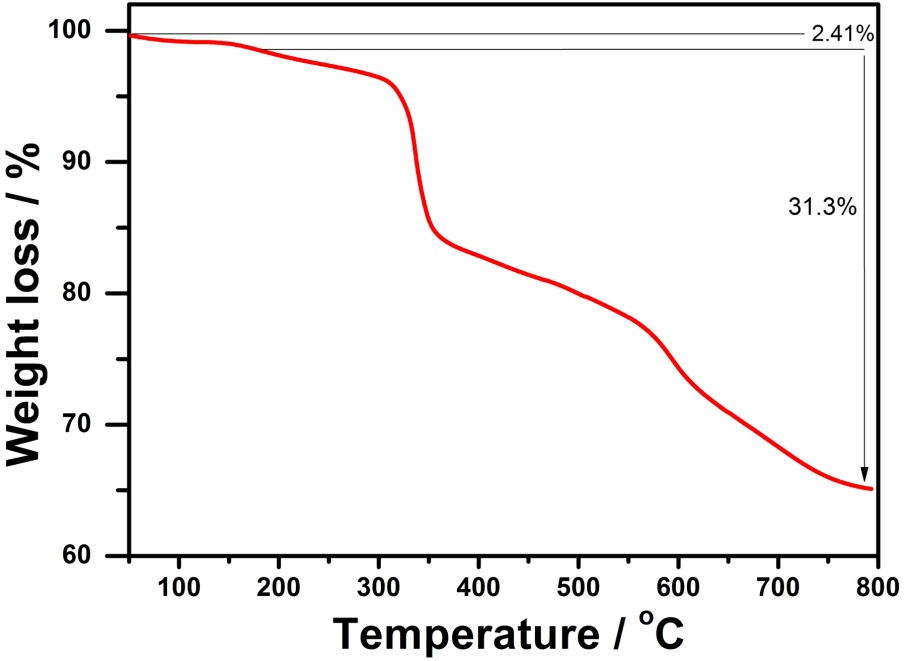
**Figure S9.** IR spectrum of compound **3**.

**3.2. TG curve obtained from compounds 1-3**

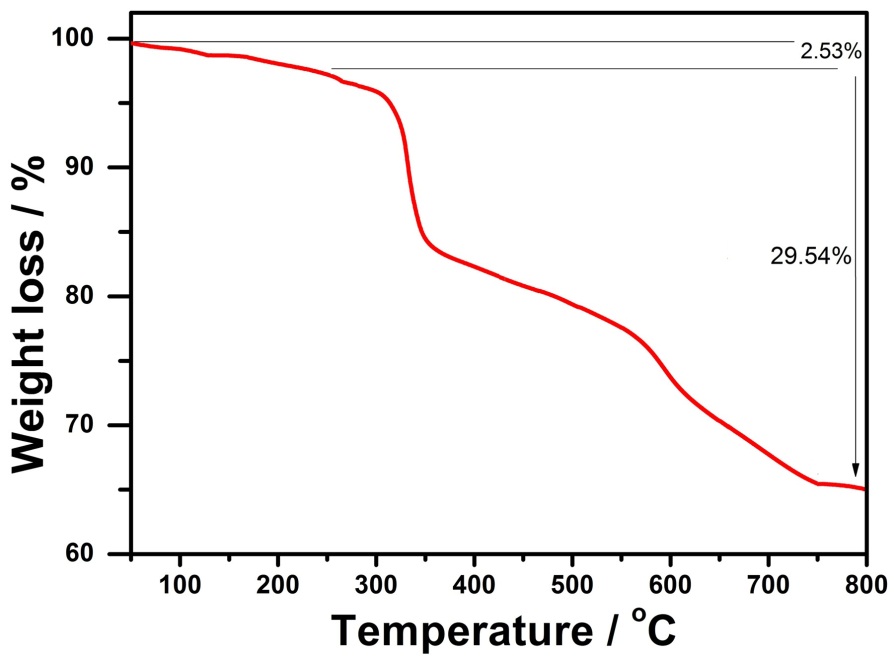
The TG curves of compounds **1-3** roughly show over all two-step weight loss. The TG curve of compound **1** shows two step weight loss (Fig. S10). The first step weight loss of 2.40% (calcd.2.36%) in the temperature range of 50 ~ 180 °C corresponds to the loss of five lattice water molecules and coordinated water molecules. The second weight loss from 350 ~ 800 °C is ascribed to the loss of C, N atoms (decomposition of organic ligand and the loss of composition water) and the formation of CuO and WO3. The whole weight loss of 31.3% is in agreement with the calculated value 31%.

Compound **2** display similar two step weight loss (Fig. S11). The first step weight loss of 3.53% (calcd.3.50%) in the temperature range of 50 ~ 230 °C corresponds to the loss of four lattice water molecules and coordinated water molecules. The second weight loss from 300 ~ 800 °C is ascribed to the loss of C, N atoms and the formation of CuO and WO3. The whole weight loss of 29.54% is in agreement with the calculated value 28.1%.

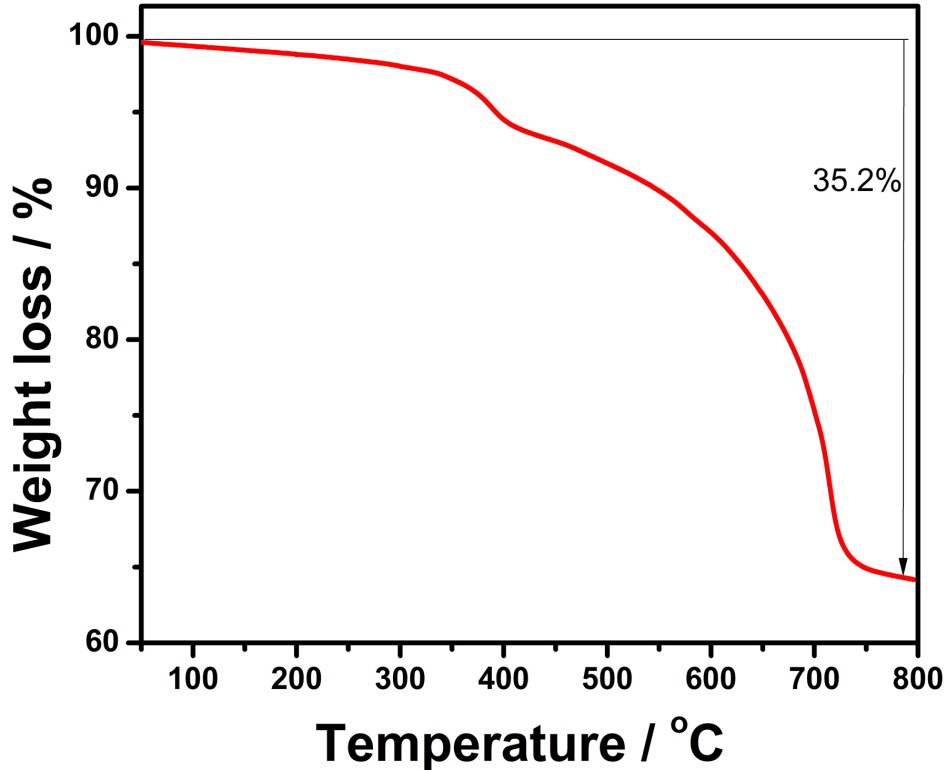
The TG curve of compound **3** show two step weight loss (Fig.S12). The first step weight loss up to 350 °C assigned to the loss of lattice and composed water molecules. The second sharp weight loss 400 ~ 800 °C is ascribed to the loss of C, N atoms and the formation of CuO and MoO3. The whole weight loss of 35.2% is in agreement with the calculated value 34.8%.



**Figure S10.** TG curve of compound **1**.



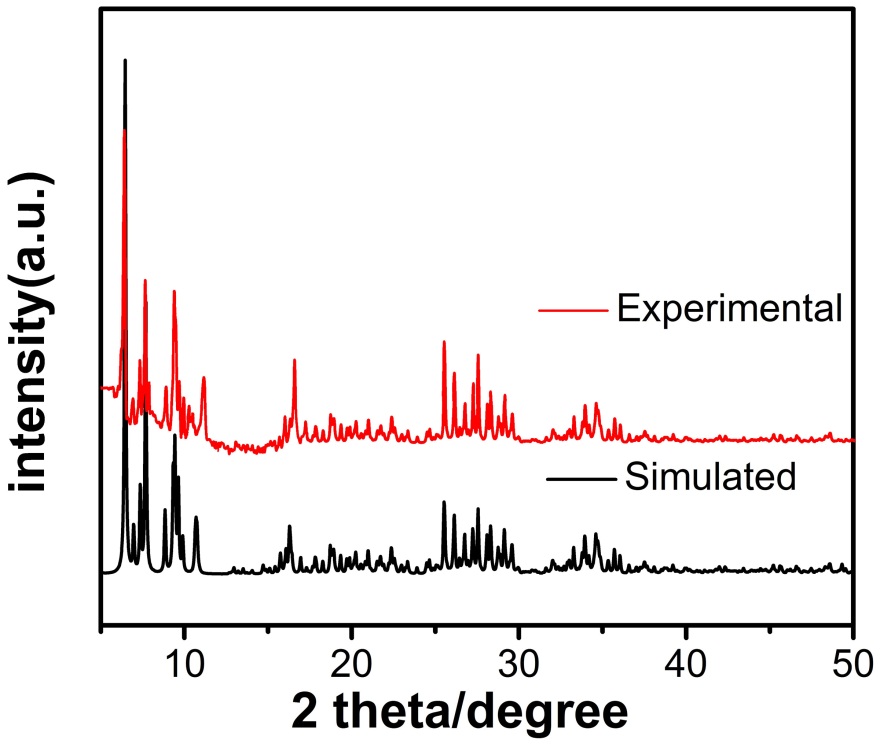
**Figure S11.** TG curve of compound **2**.

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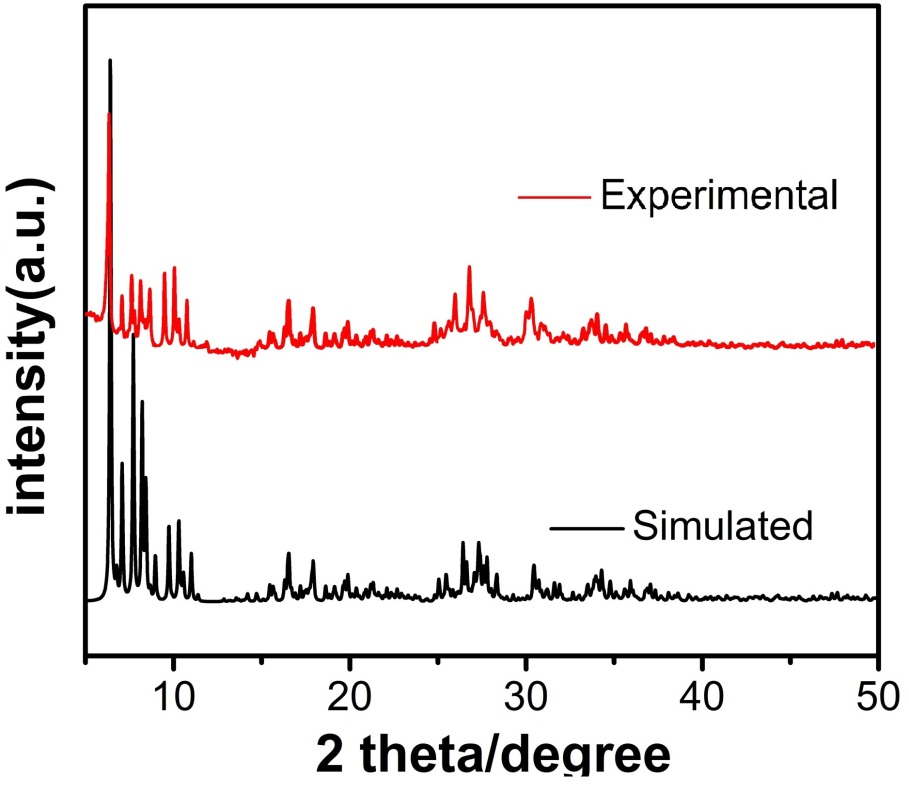
**Figure S12.** TG curve of compound **3**.

**3.3. Powder X-ray diffractions**

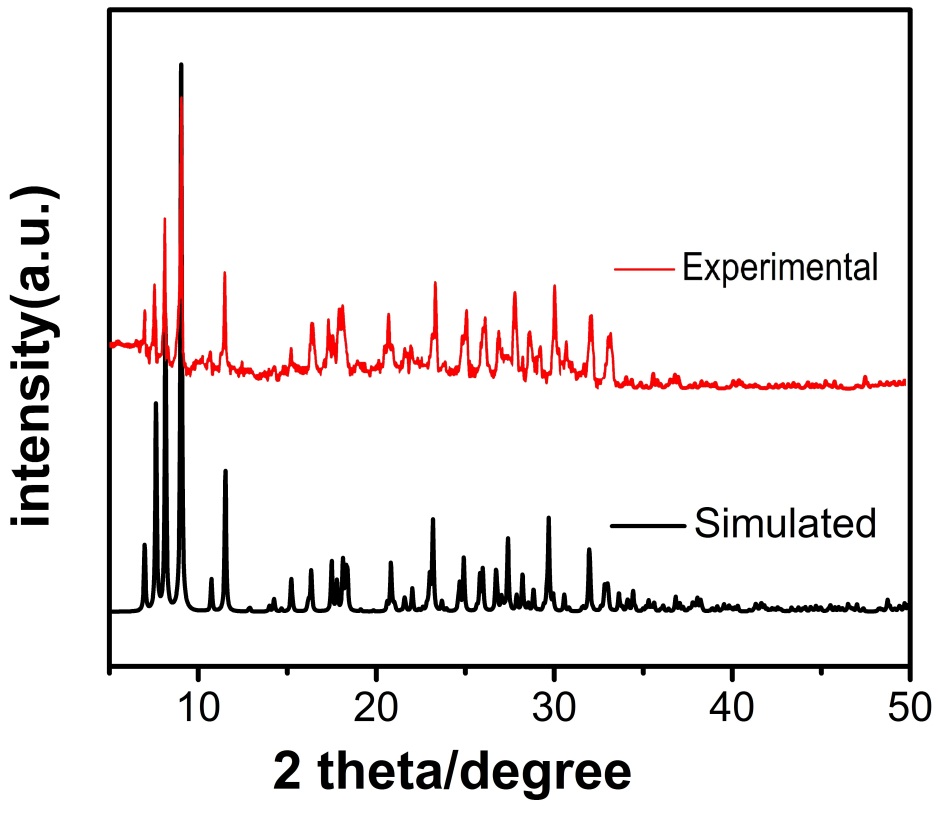
Phase purities of compounds **1–3** were checked by PXRD comparisons of the samples with simulated single-crystal XRD data at room temperature. As shown in Fig13-15, the simulated and experimental XRD peak patterns of compounds **1-3** are all in good agreement, perhaps a slightly differences in reflection intensities are probably due to preferential orientations in the powder samples of compounds **1-3**.



**Figure S13.** Simulated (black) and experimental (red) XRD patterns of compound **1**.

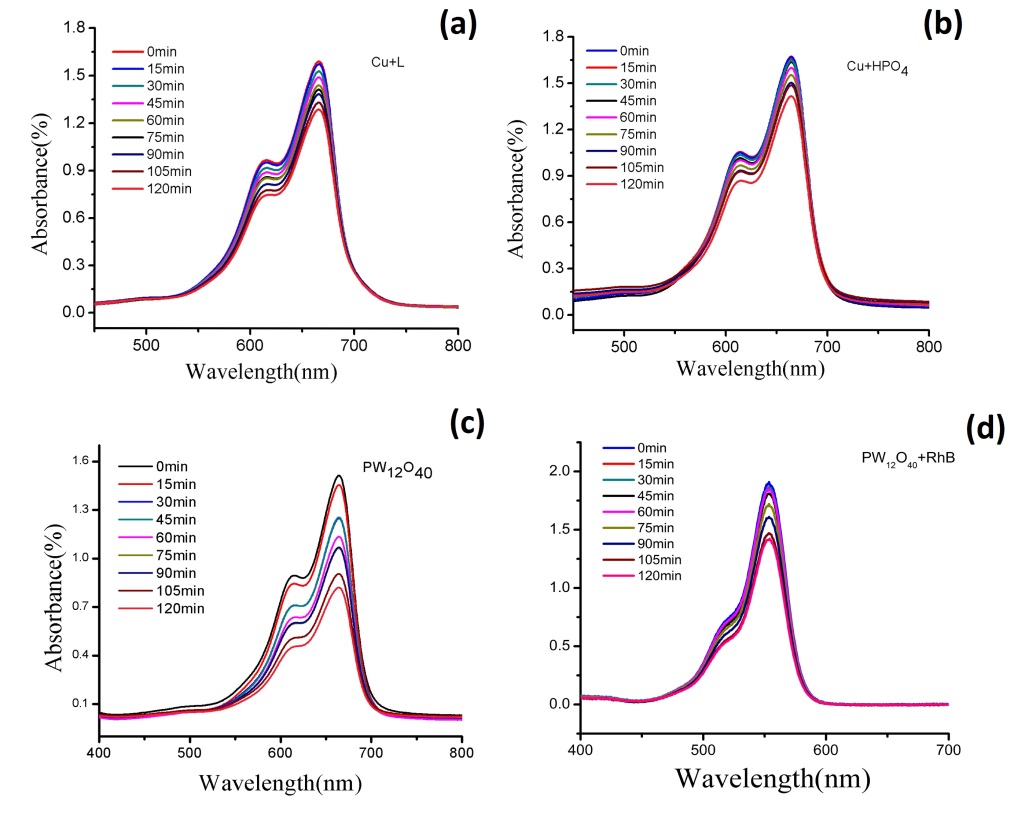


**Figure S14.** Simulated (black) and experimental (red) XRD patterns of compound **2**.



**Figure S15.** Simulated (black) and experimental (red) XRD patterns of compound **3**.

**3.4. The catalytic results of comparative experiments of starting materials and naked POM**



**Figure S16.** Photocatalytic degradation experiment of the precursors **(a)** MB+Cu+PBI, **(b)**MB+Cu+Na2HPO4, **(c)** MB+H3PW12O40, **(d)** RhB+ H3PW12O40.

**3.5. Preparations of n-CPE (n=1–4)**

The n-CPE (n =1–3) was prepared as follows: 10 mg of compound and 90 mg of graphite powder were mixed, and ground together to homogeneous, into which 0.2 mL of paraffinic oil was added with stirring. The such-obtained paste was packed into a glass tube with 2.0 mm inner diameter, and the surface was wiped with paper. The electrical contact was established with a copper rod through the back of the electrode.

**References**

[1] I.D. Brown, D. Altermatt. *Acta Crystallogr.*, **B41**, 244 (1985).

[2] W. Liu, H.H. Thorp. *Inorg. Chem.*, **32**, 4102 (1993).