# Two bimetallic-doped (Fe/Co, Mn) polyoxometalate-based hybrid compounds for visible-light-driven $CO_2$ reduction

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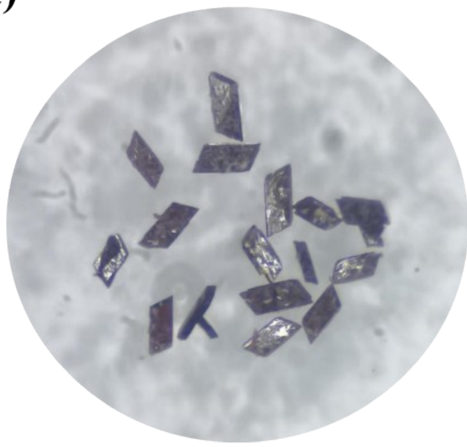
**Contents**

## Section 1. Materials and Physical Property Studies

The $K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]\cdot 24H_2O$ $\{P_2W_{12}\}$ and organic ligand DAPSC were prepared by following the basis of previous literature methods,[1,2] and other directly used reagents and solvents were purchased from commercial markets without any further purification. The powder X-ray diffraction (PXRD) analysis was performed via a Bruker D8X diffractometer within the limits of 5-50°, which with monochromatized Cu-$K_\alpha$ radiation ($\lambda$ = 0.15418 nm). Within the scope of 4000-400 $cm^{-1}$ of IR spectra were obtained on a Nicolet Impact 410 FT-IR spectrometer with pressing KBr pellets. Besides, thermogravimetric analysis (TGA) was executed on a Diamond thermogravimetric analyzer, increasing the heating rate from 25 to 1000°C at 10°C·$min^{-1}$ under an encircling $N_2$ surrounding. With a Hitachi TM 3000 scanning electron microscope at an accelerating voltage of 20 kV, the SEM and EDS-mapping images were collected. Elemental analyses of C, H, and N were carried out using a Perkin-Elmer 2400 CHN elemental analyzer. And in the range of 200-800 nm of the UV-vis diffuse reflection spectra of the target compounds were measured by a Shimadzu UV-2600 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was identified on a Thermo Escalab 250. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on an OPTMA 20000 V spectrometer to determine the contents of relevant elements (Fe, Co and Mn) in compounds.

## Section 2. Crystal Structures

(a)



(b)

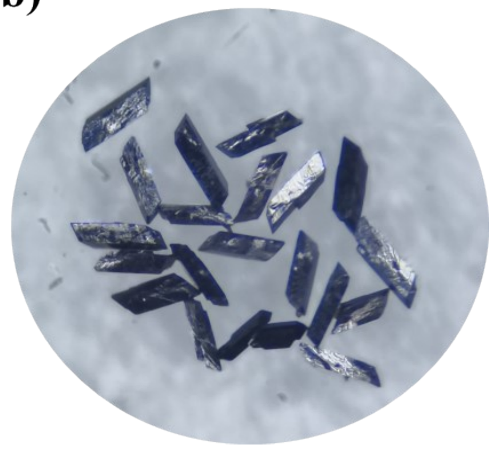


**Figure S1** The crystal images of compounds **1-2** under an optical microscope.

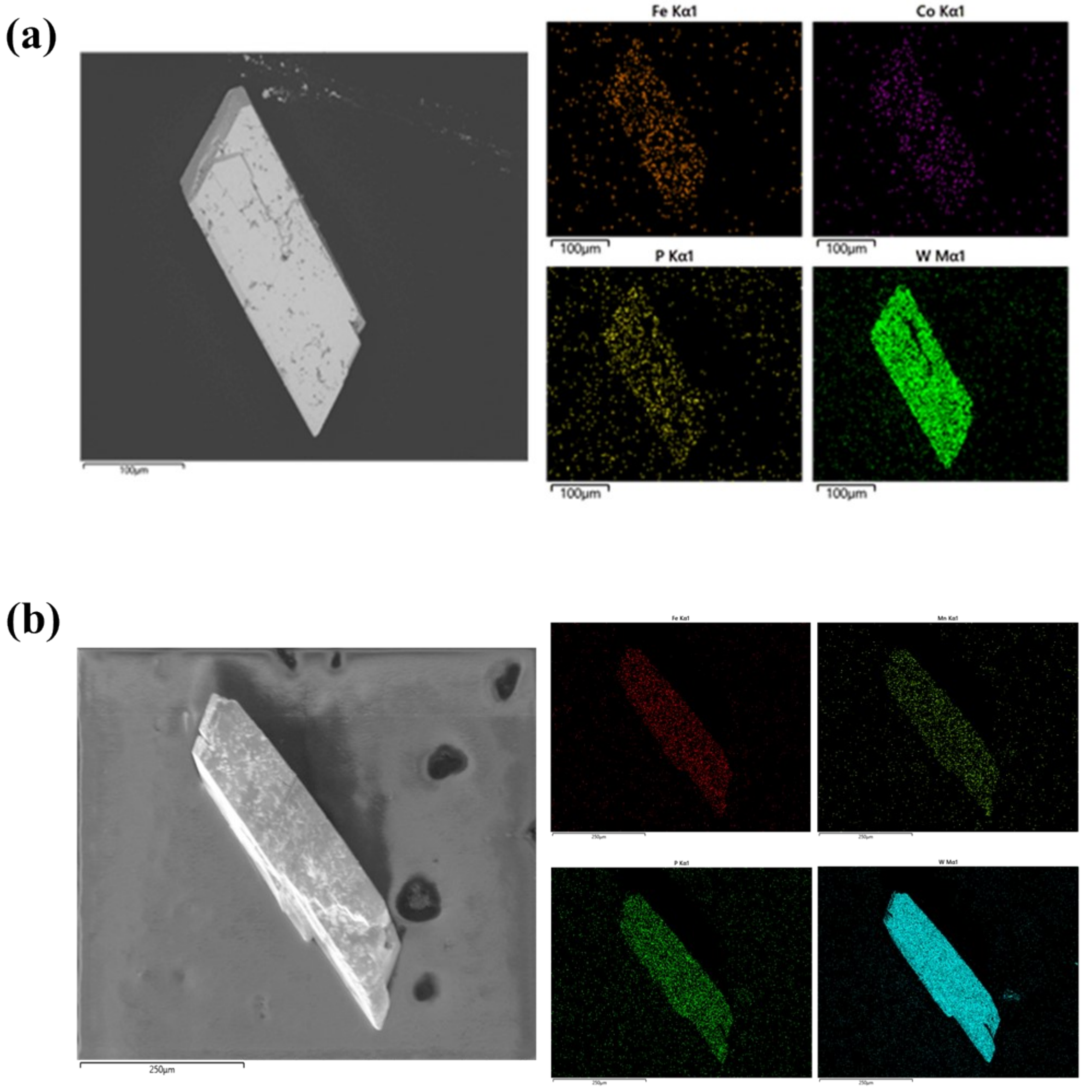



**Figure S2** The SEM image and EDS mapping of compounds **1-2**.

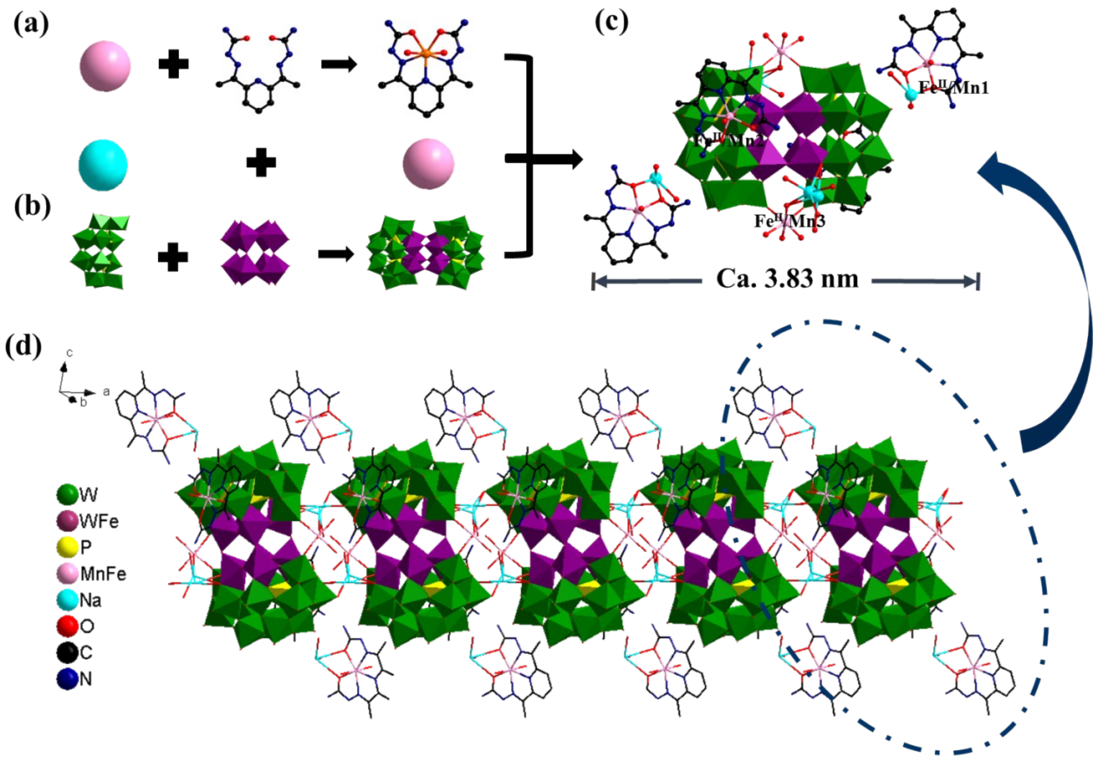



**Figure S3** (a) Schematic representation of Synthesis of metal-organic complexes in compound **2** and (b) the **2a** unit; (c) Polyhedral/ball-and-stick representation of compound **2**; (d) Stick and polyhedral diagram of the two-dimensional supramolecular layer of compound **2**. Color codes: $PO_4$ (yellow tetrahedra); $WO_6$ (green octahedra); Fe/$WO_6$ (purple octahedra); Fe/Mn (pink); Fe/W (purple); W (green); P (yellow); Na (wathet); O (red); C (black) and N (blue).

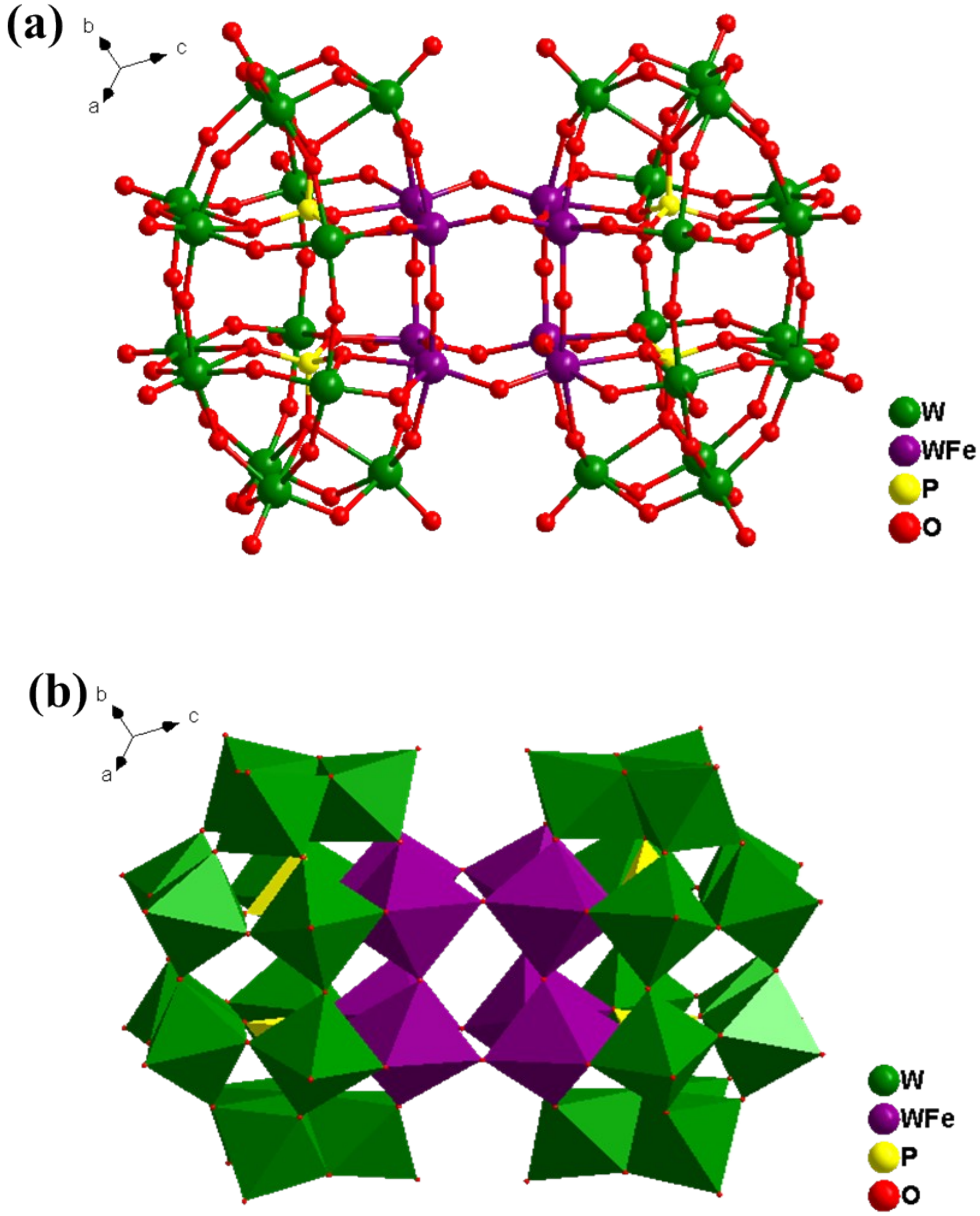



**Figure S4** (a) Ball-and-stick and (b) polyhedral representation of the formula unit of **1a-2a**. Color codes: W (green); Fe/W (purple); P (yellow); O (red) (all the H atoms and free $H_2O$ have been omitted for clarity).

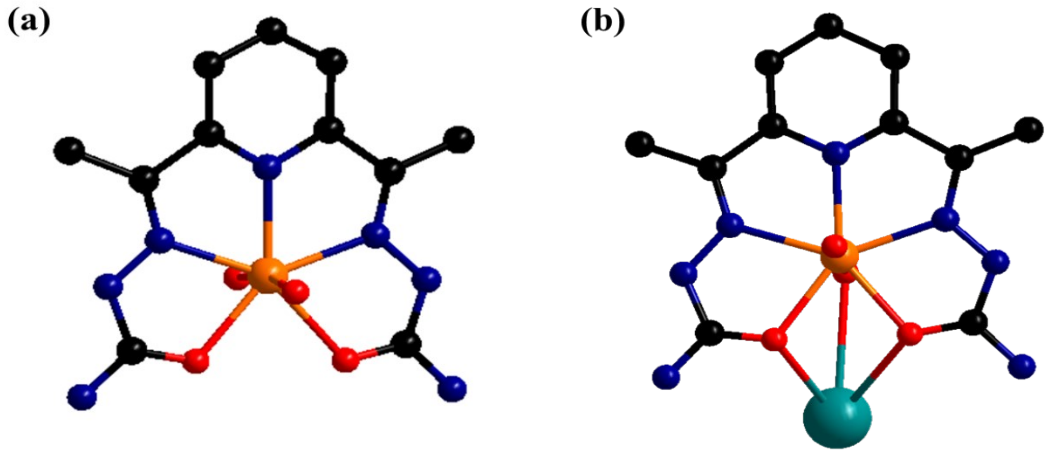



**Figure S5** Two types of the $Fe^{II}$/Co metal-organic complexes (a) $Fe^{II}$/Co2; (b) $Fe^{II}$/Co1 in compound **1**.

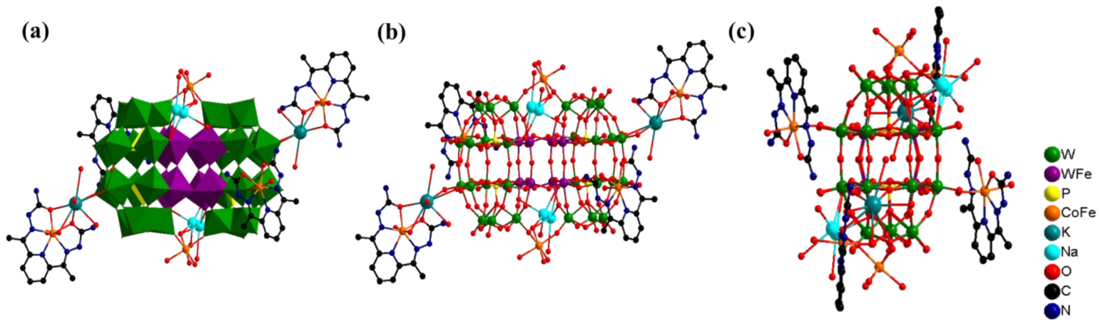



**Figure S6** (a) Polyhedral/ball-and-stick presentation and (b) ball-and-stick model of compound **1**; (c) top views of compound **1**.

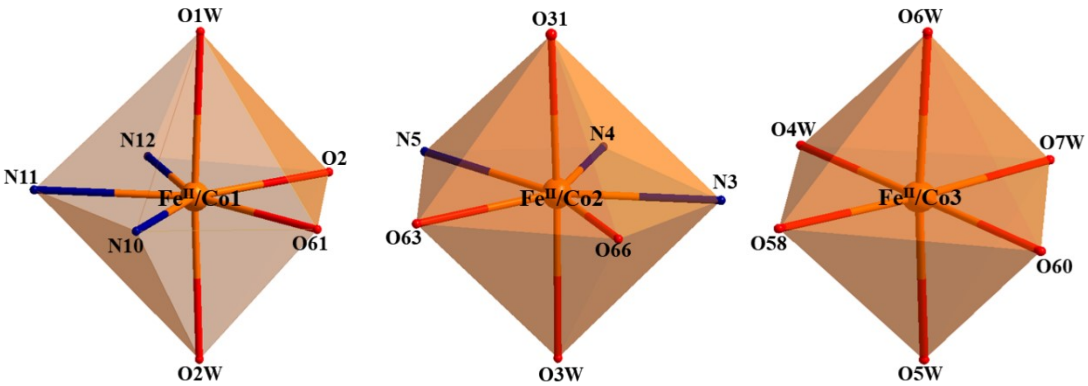



**Figure S7** Diverse coordination environment of $Fe^{II}$/Co in compound **1**.

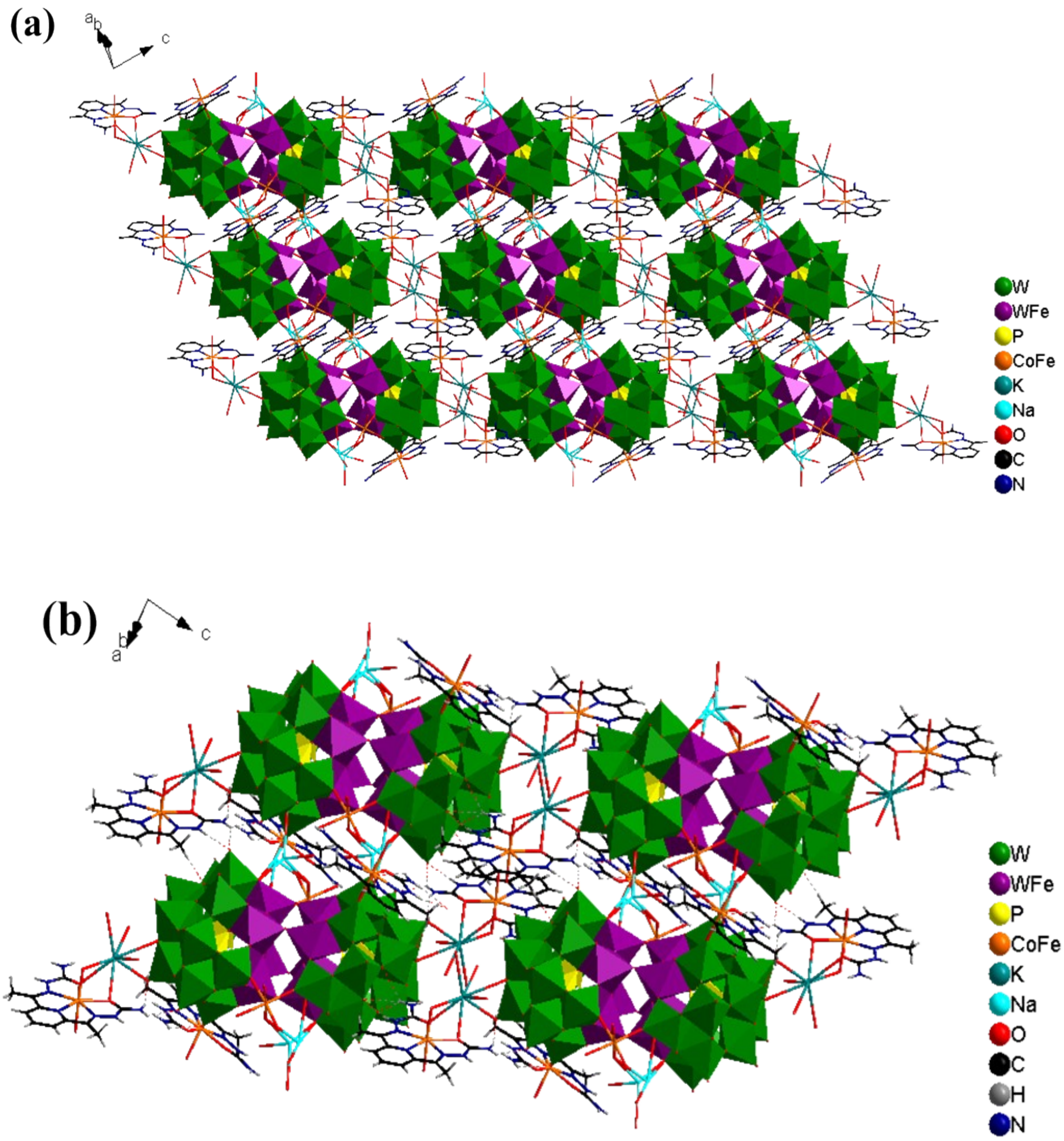



**Figure S8** (a) Polyhedral and stick representation of 3D supramolecular framework of compound **1**; (b) the hydrogen-bonding interactions in compound **1**.

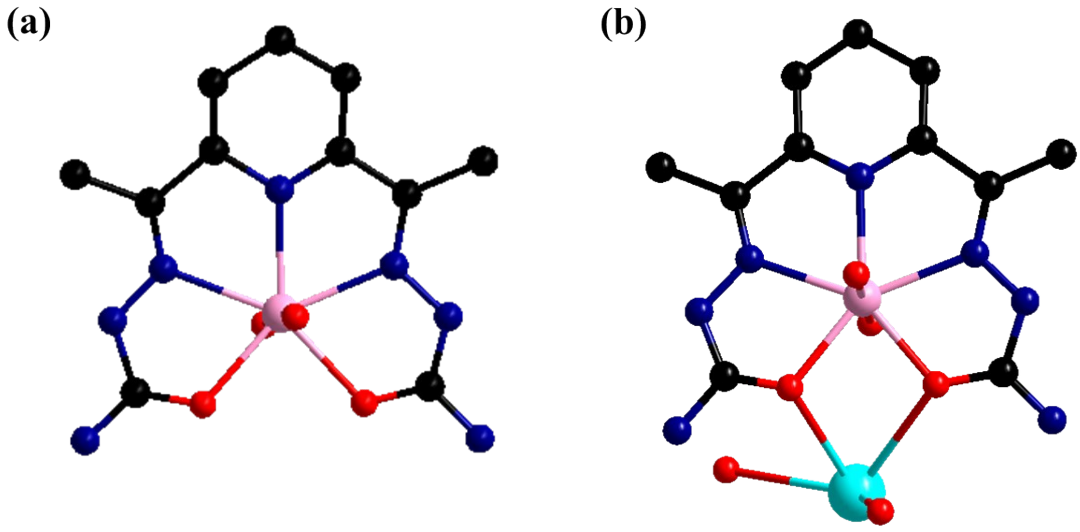



**Figure S9** Two types of the $Fe^{II}$/Mn metal-organic complexes (a) $Fe^{II}$/Mn2; (b) $Fe^{II}$/Mn1 in compound **2**.

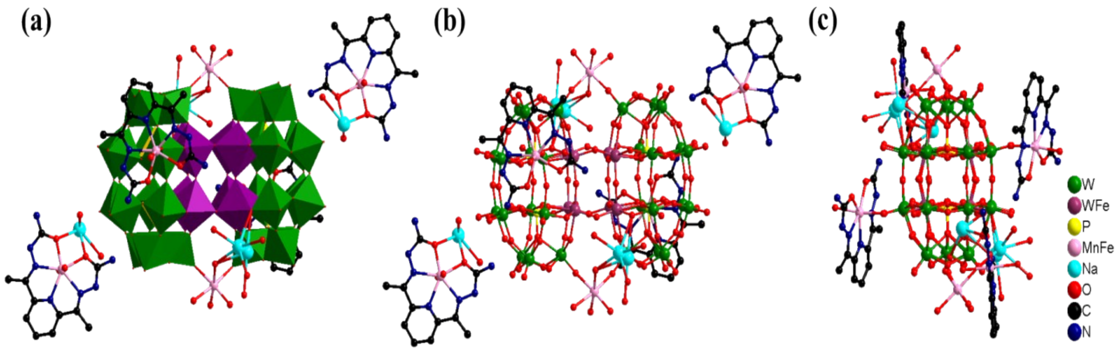



**Figure S10** (a) Polyhedral/ball-and-stick presentation and (b) ball-and-stick model of compound **3**; (c) top views of compound **2**.

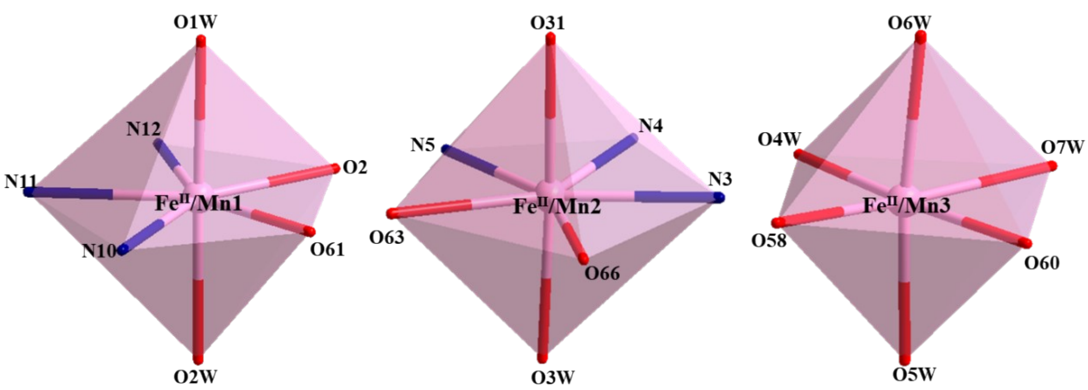
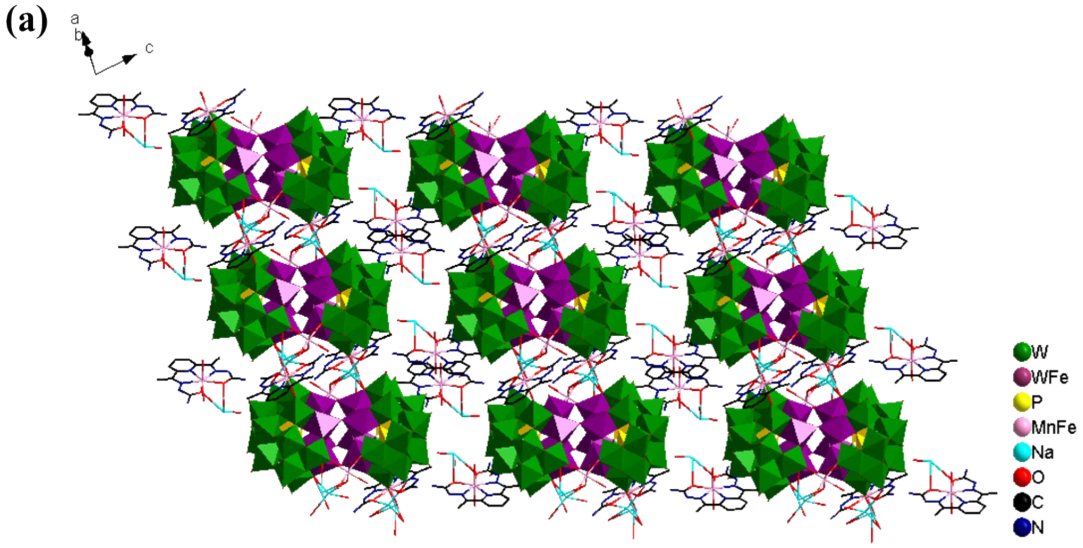



**Figure S11** Diverse coordination environment of $Fe^{II}$/Mn in compound **2**.



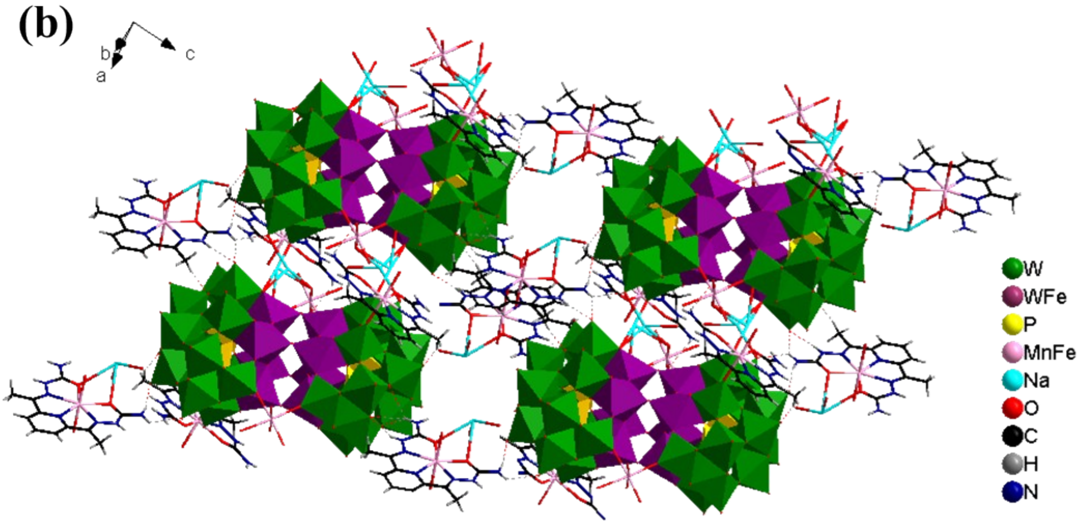




**Figure S12** (a) Polyhedral and stick representation of 3D supramolecular framework of compound **2**; (b) the hydrogen-bonding interactions in compound **2**.

## Section 3. Characterization

### XRD

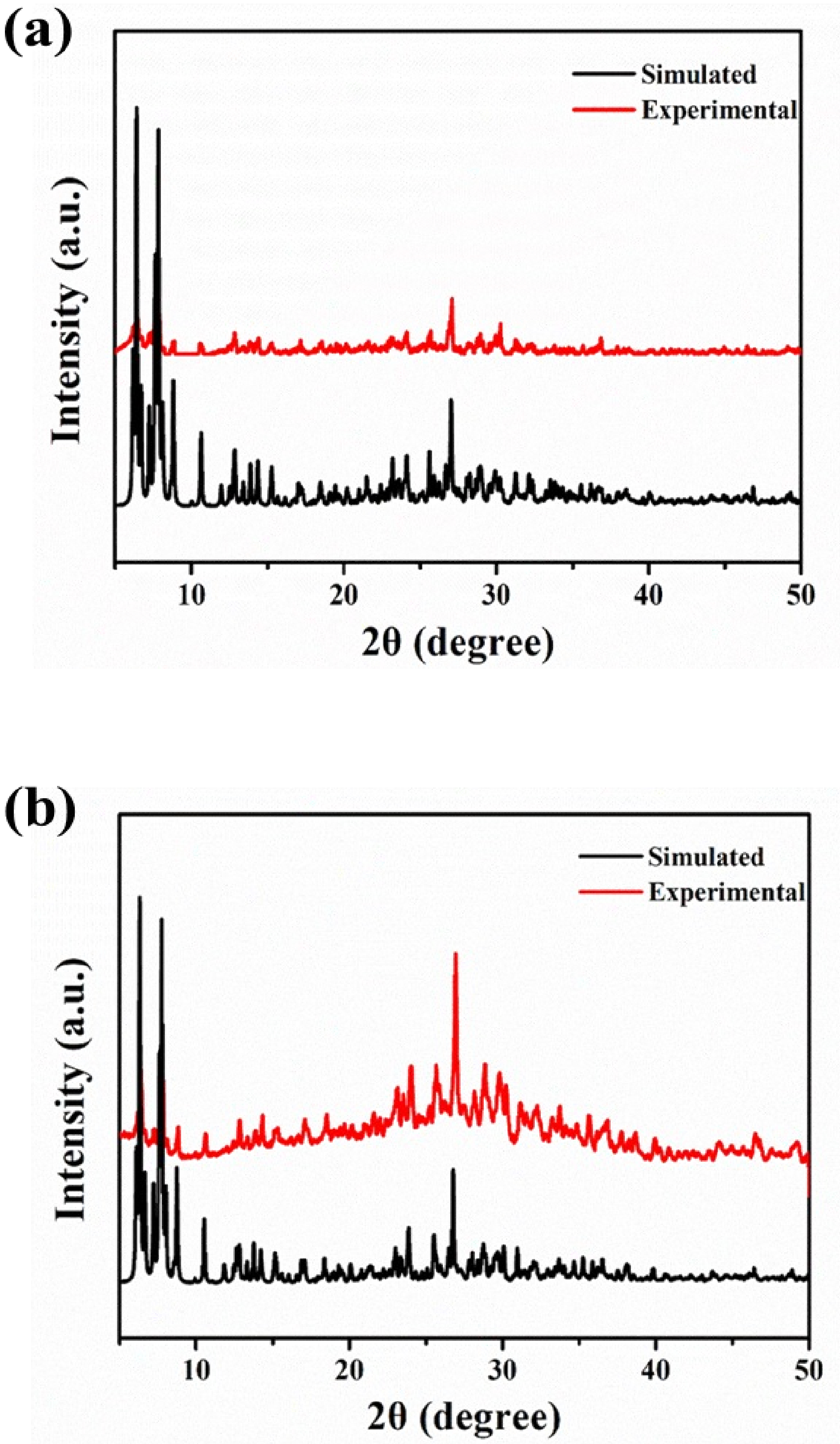



**Figure S13** The XRD patterns of compounds **1-2**.

**IR**

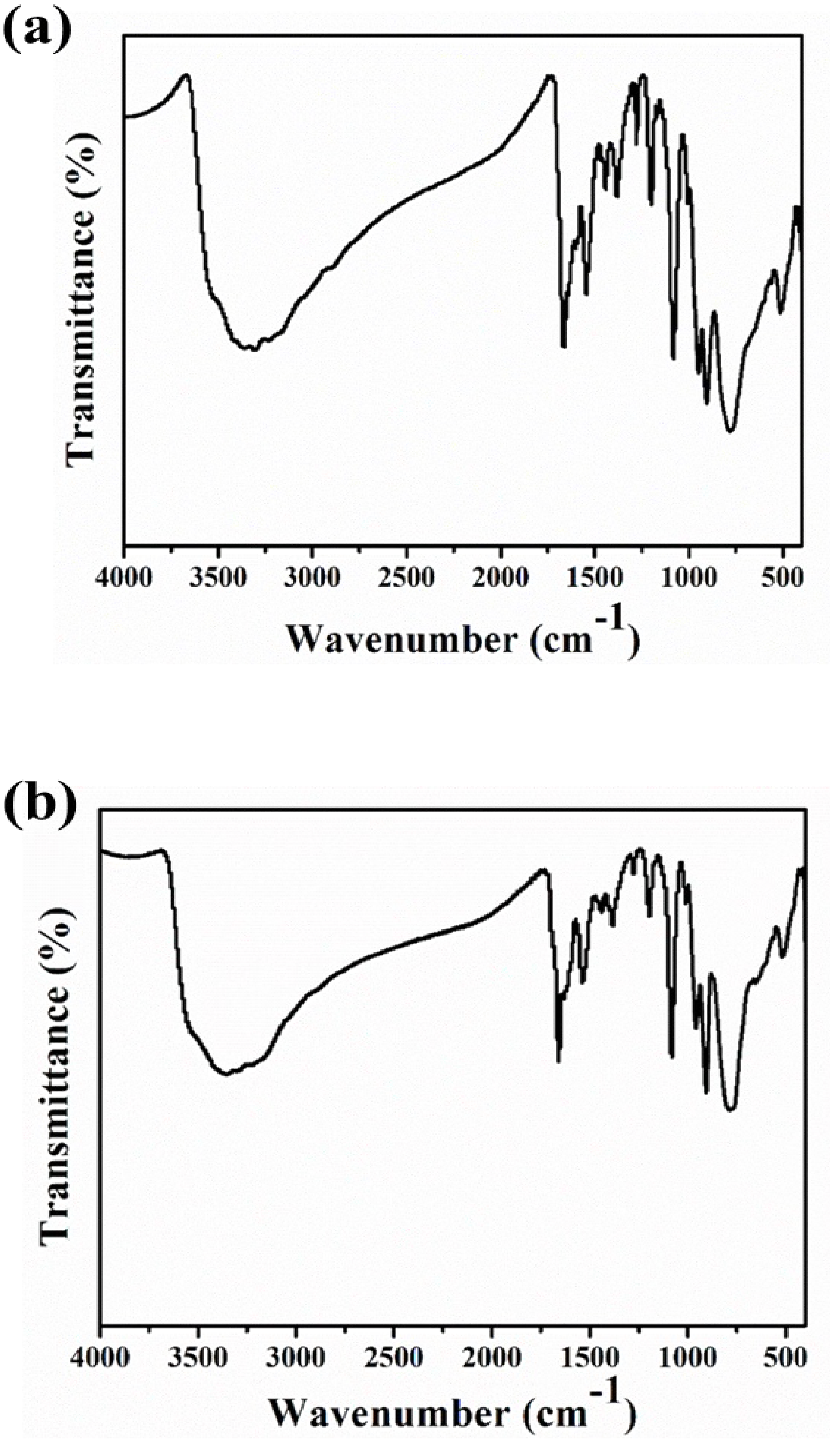



**Figure S14** The IR spectra of compounds **1-2**.

**TG**

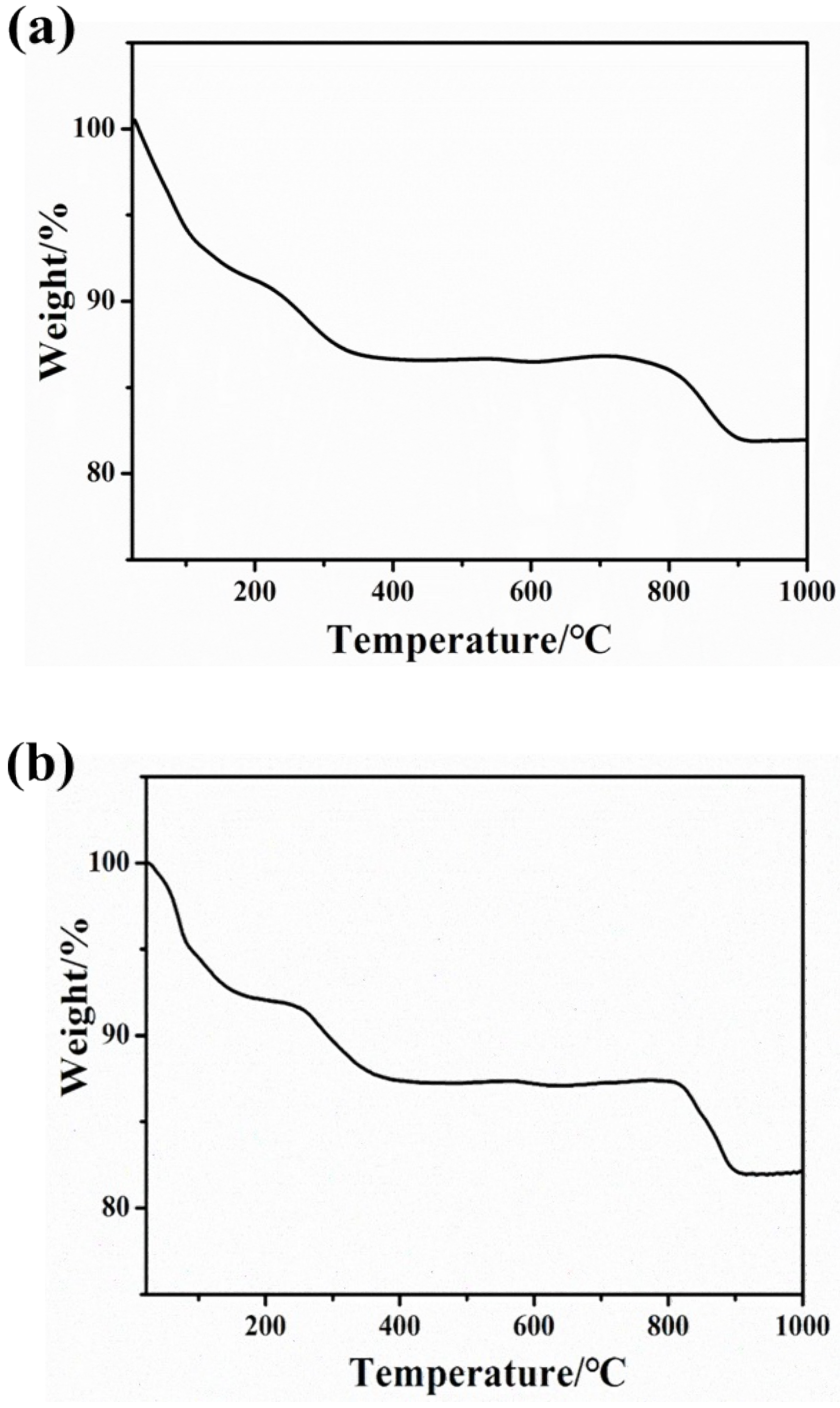
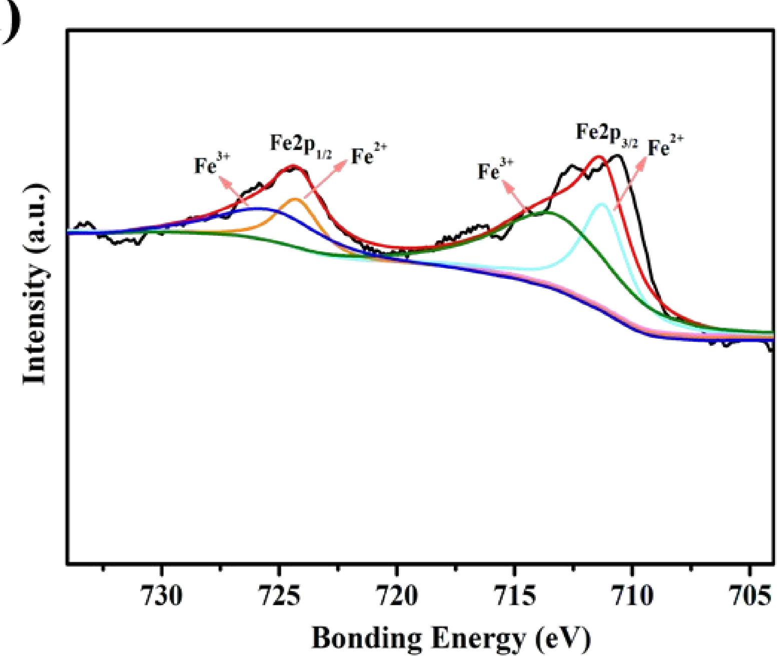



**Figure S15** The TG curves of compounds **1-2**.

The thermal behavior of **2** is analogous to that of **1**. For **2**, the weight loss is 7.62% (calcd 7.56%), which is below 200℃, is regarded as the loss of all water molecules in the first part. In the second part, the miss of 10.71% (calcd 10.58%) is strongly attributed to the removal of DAPSC ligands at temperatures ranging from 183 to 842°C. After that, a partial skeleton collapsed.

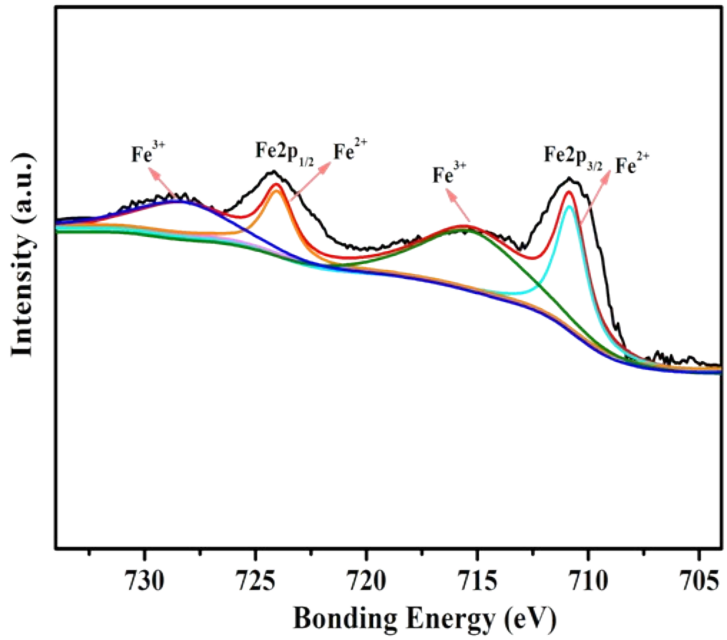
**XPS**

(a)



Fe3+
Fe2p1/2
Fe2+
Fe3+
Fe2p3/2
Fe2+
Intensity (a.u.)
730
725
720
715
710
705
Bonding Energy (eV)


(b)



Fe3+
Fe2p1/2
Fe2+
Fe3+
Fe2p3/2
Fe2+
Intensity (a.u.)
730
725
720
715
710
705
Bonding Energy (eV)

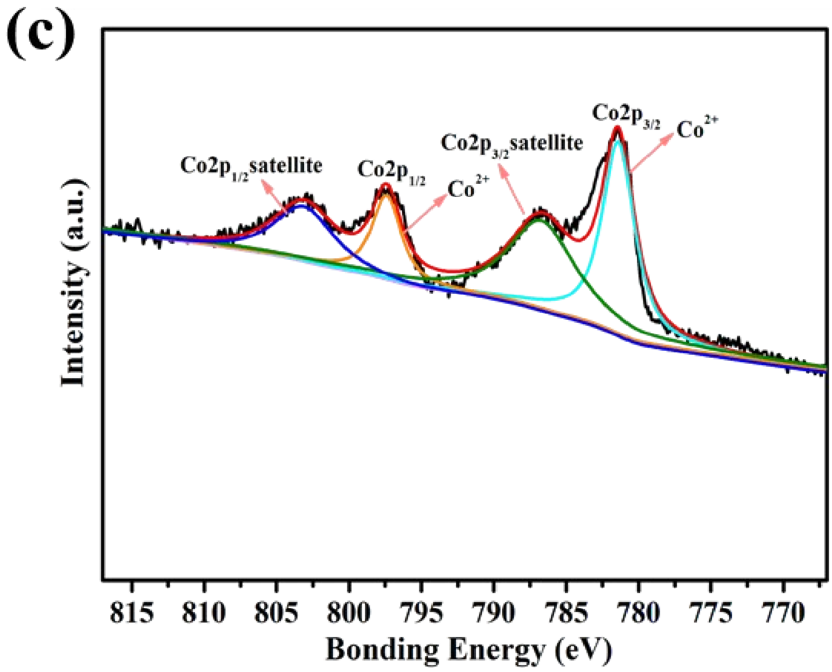



**Figure S16** XPS spectra showing the binding energies of (a-b) Fe 2p in compounds **1-2** and (c) Co 2p in compound **1**.

The XPS of **2** is analogous to that of **1**. Take **1**, for example, the Fe 2p energy spectrum exhibited four classical peaks at 727.9, 724.7, 714.3, and 711.2 eV, of which the peaks at 727.9 and 714.3 eV could suggest the presence of $Fe^{3+}$ and the other peaks located at 711.2 and 724.7 eV were assignable to $Fe^{2+}$.[3] Besides, the Co $2p_{3/2}$ and $2p_{1/2}$ peaks at 781.3 eV and 796.8 eV of the Co 2p spectrum, indicating cobalts in compound **1** is bivalent.[4-5]

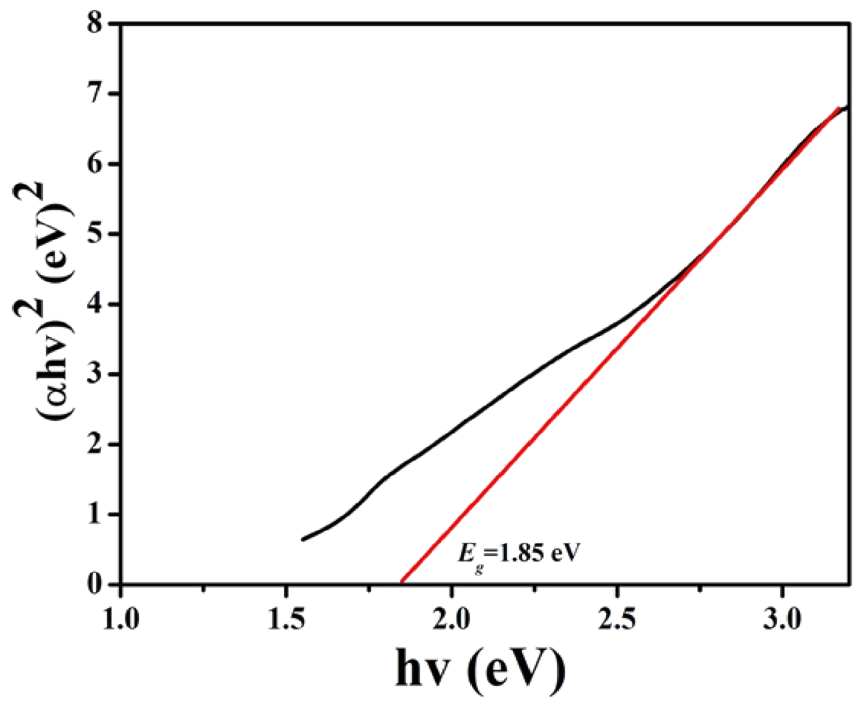



**Figure S17** $(ahv)^2$ vs. *hv* curves of compound **2**.

**MS**

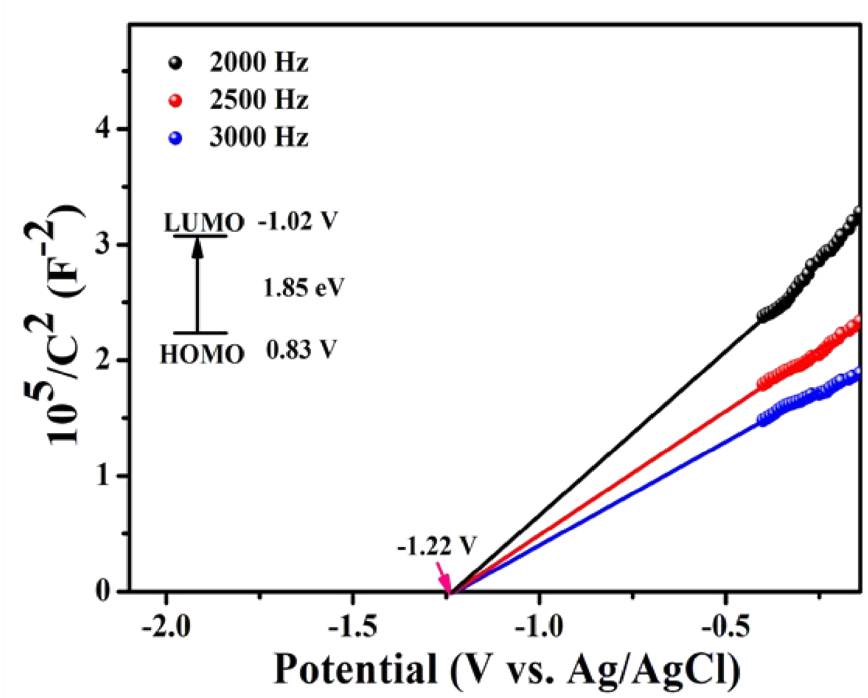



**Figure S18** The Mott–Schottky plots for compound **2**.

## Section 4. The Procedure of the $CO_2$ Photoreduction

**Electrochemical measurements.**

In a standard three-electrode system, the Mott–Schottky spots were performed with the electrochemical workstation (CHI 760e) in ambient surroundings. More precisely, the carbon cloth (CC, 1 cm×1 cm) embellished via catalyst samples, carbon rods and Ag/AgCl played the roles of the working, counter and reference electrodes respectively. Notably, the above-mentioned three electrodes were dipped in the 0.2 M $Na_2SO_4$ aqueous solution during the whole experimental period. And details were as follows: firstly, milling the catalyst (5 mg) into powder and dissolving in the 0.5% Nafion liquid (1 mL) to come into being a homogeneous ink through ultrasonication. Later, the carbon cloth, which was deposited 200 μL of the ink, dried at 25°C for Mott-Schottky spots measurements. Ultimately, within a diverse current (AC) frequency of 2000 Hz, 2500 Hz and 3000 Hz, the Mott-Schottky plots were carried out.

**Photocatalytic $CO_2$ reduction experiments.**

The photocatalytic performance of the compound was investigated by utilizing it for the photocatalytic reduction of $CO_2$ (CEL-SPH2N-S9, AULTT, China). The experiment was executed in a 100 mL Pyrex flask under the irradiation of visible light, where the source was a 300 W xenon arc lamp (CEL-PAEM-D8, AULTT, China) (photocurrent: 14.5 A) with a UV-cutoff filter (420-800 nm). In this system, the synthesized substance was served as a photocatalyst (10 mg), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (11.3 mg) as a photosensitiser, putting them into a mixed dissolvant of TEOA (as a sacrificial agent) and $CH_3CN$ (1:4 v/v, 50 mL). In addition, the system was degassed with $CO_2$ (99.999%) for half an hour prior to irradiation to remove the air and to keep the whole system carried out in a $CO_2$ atmosphere. And the reaction mixtures were stirred with a magnetic stirrer at a constant rate to guarantee that the photocatalyst particles were adequately mixed in the suspension. Afterwards, using nitrogen (99.999%) as the carrier gas, the products were detected through gas chromatography (GC7920-TF2Z, AULTT, China). A flame ionisation detector (FID) was used to measure the levels of CO and $CH_4$ and a thermal conductivity detector (TCD) was afterwards the amount of $H_2$.

$$CO_{selectivity} = \frac{n(CO)}{n(CO) + n(CH_4) + n(H_2)} \times 100\%$$

**Photographs of the $CO_2$ reduction devices.**

**Figure S19** The photograph of the $CO_2$ photoreduction devices.

## Section 5. Other Tables

**Table S1** Selected bond lengths (Å) and bond angles (˚) for compound **1**.

| | | | |
|---|---|---|---|
| Fe(4)-O(15) | 1.832(8) | Fe(1)-N(12) | 2.197(11) |
| Fe(4)-O(37) | 1.837(9) | Fe(1)-O(2W) | 2.214(11) |
| Fe(4)-O(5)#1 | 1.868(9) | Fe(1)-K(1) | 3.837(5) |
| Fe(4)-O(6) | 2.001(9) | Fe(2)-O(31) | 2.122(10) |
| Fe(4)-O(33) | 2.110(9) | Fe(2)-O(3W) | 2.148(13) |
| Fe(4)-O(43) | 2.260(8) | Fe(2)-O(66) | 2.170(10) |
| Fe(5)-O(5) | 1.840(9) | Fe(2)-N(4) | 2.181(13) |
| Fe(5)-O(4) | 1.847(9) | Fe(2)-N(5) | 2.200(12) |
| Fe(5)-O(9) | 1.854(9) | Fe(2)-N(3) | 2.202(12) |
| Fe(5)-O(39) | 2.014(9) | Fe(2)-O(63) | 2.252(11) |
| Fe(5)-O(41) | 2.096(9) | Fe(3)-O(4W) | 2.024(12) |
| Fe(5)-O(36) | 2.317(9) | Fe(3)-O(60) | 2.044(9) |
| Fe(6)-O(4) | 1.823(9) | Fe(3)-O(58)#1 | 2.071(9) |
| Fe(6)-O(15) | 1.834(8) | Fe(3)-O(7W) | 2.148(12) |
| Fe(6)-O(3) | 1.841(9) | Fe(3)-O(5W) | 2.177(12) |
| Fe(6)-O(20) | 2.017(9) | Fe(3)-O(6W) | 2.231(11) |
| Fe(6)-O(21) | 2.079(9) | O(3)-Fe(7)#1 | 1.856(8) |
| Fe(6)-O(46) | 2.293(9) | O(5)-Fe(4)#1 | 1.868(9) |
| Fe(7)-O(9) | 1.813(9) | O(58)-Fe(3)#1 | 2.071(9) |
| Fe(7)-O(37) | 1.838(9) | O(15)-Fe(4)-O(37) | 96.2(4) |
| Fe(7)-O(3)#1 | 1.856(8) | O(15)-Fe(4)-O(5)#1 | 104.4(4) |
| Fe(7)-O(17) | 2.014(9) | O(37)-Fe(4)-O(5)#1 | 99.9(4) |
| Fe(7)-O(38) | 2.098(9) | O(15)-Fe(4)-O(6) | 158.9(4) |
| Fe(7)-O(64) | 2.288(9) | O(37)-Fe(4)-O(6) | 89.3(4) |
| Fe(1)-O(61) | 2.147(10) | O(5)#1-Fe(4)-O(6) | 94.7(4) |
| Fe(1)-N(10) | 2.172(13) | O(15)-Fe(4)-O(33) | 85.6(4) |
| Fe(1)-N(11) | 2.184(11) | O(37)-Fe(4)-O(33) | 170.3(4) |
| Fe(1)-O(2) | 2.184(10) | O(5)#1-Fe(4)-O(33) | 88.8(4) |
| Fe(1)-O(1W) | 2.186(12) | O(6)-Fe(4)-O(33) | 85.8(4) |
| O(15)-Fe(4)-O(43) | 85.5(3) | O(3)-Fe(6)-O(46) | 169.0(3) |
| O(37)-Fe(4)-O(43) | 88.3(3) | O(20)-Fe(6)-O(46) | 74.4(3) |

| | | | |
|---|---|---|---|
| O(5)#1-Fe(4)-O(43) | 166.3(4) | O(21)-Fe(6)-O(46) | 80.6(3) |
| O(6)-Fe(4)-O(43) | 74.3(3) | O(9)-Fe(7)-O(37) | 95.6(4) |
| O(33)-Fe(4)-O(43) | 82.3(3) | O(9)-Fe(7)-O(3)#1 | 103.3(4) |
| O(5)-Fe(5)-O(4) | 98.7(4) | O(37)-Fe(7)-O(3)#1 | 97.4(4) |
| O(5)-Fe(5)-O(9) | 100.3(4) | O(9)-Fe(7)-O(17) | 157.3(4) |
| O(4)-Fe(5)-O(9) | 96.5(4) | O(37)-Fe(7)-O(17) | 90.8(4) |
| O(5)-Fe(5)-O(39) | 100.0(4) | O(3)#1-Fe(7)-O(17) | 97.4(4) |
| O(4)-Fe(5)-O(39) | 90.5(4) | O(9)-Fe(7)-O(38) | 86.6(4) |
| O(9)-Fe(5)-O(39) | 157.2(4) | O(37)-Fe(7)-O(38) | 170.4(4) |
| O(5)-Fe(5)-O(41) | 90.9(4) | O(3)#1-Fe(7)-O(38) | 91.1(4) |
| O(4)-Fe(5)-O(41) | 169.4(4) | O(17)-Fe(7)-O(38) | 83.7(4) |
| O(9)-Fe(5)-O(41) | 86.2(4) | O(9)-Fe(7)-O(64) | 85.8(3) |
| O(39)-Fe(5)-O(41) | 83.3(3) | O(37)-Fe(7)-O(64) | 88.7(4) |
| O(5)-Fe(5)-O(36) | 171.0(4) | O(3)#1-Fe(7)-O(64) | 168.4(3) |
| O(4)-Fe(5)-O(36) | 88.5(3) | O(17)-Fe(7)-O(64) | 72.6(3) |
| O(9)-Fe(5)-O(36) | 84.1(3) | O(38)-Fe(7)-O(64) | 82.2(3) |
| O(39)-Fe(5)-O(36) | 74.4(3) | O(61)-Fe(1)-N(10) | 71.9(4) |
| O(41)-Fe(5)-O(36) | 81.6(3) | O(61)-Fe(1)-N(11) | 143.0(4) |
| O(4)-Fe(6)-O(15) | 97.2(4) | N(10)-Fe(1)-N(11) | 71.1(5) |
| O(4)-Fe(6)-O(3) | 100.9(4) | O(61)-Fe(1)-O(2) | 73.8(4) |
| O(15)-Fe(6)-O(3) | 99.8(4) | N(10)-Fe(1)-O(2) | 145.5(5) |
| O(4)-Fe(6)-O(20) | 91.0(4) | N(11)-Fe(1)-O(2) | 143.3(4) |
| O(15)-Fe(6)-O(20) | 156.5(4) | O(61)-Fe(1)-O(1W) | 85.2(4) |
| O(3)-Fe(6)-O(20) | 100.2(4) | N(10)-Fe(1)-O(1W) | 90.6(5) |
| O(4)-Fe(6)-O(21) | 168.6(4) | N(11)-Fe(1)-O(1W) | 93.7(4) |
| O(15)-Fe(6)-O(21) | 86.2(4) | O(2)-Fe(1)-O(1W) | 89.5(4) |
| O(3)-Fe(6)-O(21) | 89.2(4) | O(61)-Fe(1)-N(12) | 146.3(4) |
| O(20)-Fe(6)-O(21) | 81.9(4) | N(10)-Fe(1)-N(12) | 141.7(5) |
| O(4)-Fe(6)-O(46) | 88.9(4) | N(11)-Fe(1)-N(12) | 70.7(4) |
| O(15)-Fe(6)-O(46) | 83.7(3) | O(2)-Fe(1)-N(12) | 72.7(4) |
| O(1W)-Fe(1)-N(12) | 91.7(4) | N(4)-Fe(2)-O(63) | 140.2(4) |
| O(61)-Fe(1)-O(2W) | 91.4(4) | N(5)-Fe(2)-O(63) | 70.3(4) |
| N(10)-Fe(1)-O(2W) | 90.2(4) | N(3)-Fe(2)-O(63) | 149.7(4) |
| N(11)-Fe(1)-O(2W) | 90.3(4) | O(4W)-Fe(3)-O(60) | 174.6(4) |
| O(2)-Fe(1)-O(2W) | 87.6(4) | O(4W)-Fe(3)-O(58)#1 | 93.7(4) |

| | | | |
|---|---|---|---|
| O(1W)-Fe(1)-O(2W) | 176.0(4) | O(60)-Fe(3)-O(58)#1 | 91.7(4) |
| N(12)-Fe(1)-O(2W) | 90.1(4) | O(4W)-Fe(3)-O(7W) | 89.5(5) |
| O(61)-Fe(1)-K(1) | 48.9(3) | O(60)-Fe(3)-O(7W) | 85.1(4) |
| N(10)-Fe(1)-K(1) | 109.4(4) | O(58)#1-Fe(3)-O(7W) | 175.9(4) |
| N(11)-Fe(1)-K(1) | 148.3(3) | O(4W)-Fe(3)-O(5W) | 92.1(4) |
| O(2)-Fe(1)-K(1) | 45.7(3) | O(60)-Fe(3)-O(5W) | 87.8(4) |
| O(1W)-Fe(1)-K(1) | 54.9(3) | O(58)#1-Fe(3)-O(5W) | 93.7(4) |
| N(12)-Fe(1)-K(1) | 103.0(3) | O(7W)-Fe(3)-O(5W) | 88.6(4) |
| O(2W)-Fe(1)-K(1) | 121.2(3) | O(4W)-Fe(3)-O(6W) | 94.3(4) |
| O(31)-Fe(2)-O(3W) | 170.1(4) | O(60)-Fe(3)-O(6W) | 85.7(4) |
| O(31)-Fe(2)-O(66) | 84.7(4) | O(58)#1-Fe(3)-O(6W) | 87.6(4) |
| O(3W)-Fe(2)-O(66) | 86.7(4) | O(7W)-Fe(3)-O(6W) | 89.7(4) |
| O(31)-Fe(2)-N(4) | 94.7(4) | O(5W)-Fe(3)-O(6W) | 173.4(4) |
| O(3W)-Fe(2)-N(4) | 95.1(5) | O(2)-K(1)-Fe(1) | 34.1(2) |
| O(66)-Fe(2)-N(4) | 140.9(4) | O(21W)-K(1)-Fe(1) | 92.4(3) |
| O(31)-Fe(2)-N(5) | 97.4(4) | O(61)-K(1)-Fe(1) | 33.7(2) |
| O(3W)-Fe(2)-N(5) | 87.3(5) | O(48)-K(1)-Fe(1) | 106.3(2) |
| O(66)-Fe(2)-N(5) | 148.8(4) | O(22W)-K(1)-Fe(1) | 116.2(8) |
| N(4)-Fe(2)-N(5) | 70.1(5) | O(29)-K(1)-Fe(1) | 148.7(2) |
| O(31)-Fe(2)-N(3) | 86.5(4) | O(1W)-K(1)-Fe(1) | 34.7(2) |
| O(3W)-Fe(2)-N(3) | 95.5(5) | O(14W)-K(1)-Fe(1) | 148.5(5) |
| O(66)-Fe(2)-N(3) | 71.2(4) | Fe(1)-K(1)-W(4) | 126.33(13) |
| N(4)-Fe(2)-N(3) | 69.8(5) | C(20)-O(2)-Fe(1) | 118.0(9) |
| N(5)-Fe(2)-N(3) | 139.9(5) | Fe(1)-O(2)-K(1) | 100.2(4) |
| O(31)-Fe(2)-O(63) | 86.7(4) | Fe(6)-O(3)-Fe(7)#1 | 132.2(5) |
| O(3W)-Fe(2)-O(63) | 86.8(4) | Fe(6)-O(4)-Fe(5) | 151.3(5) |
| O(66)-Fe(2)-O(63) | 78.8(4) | Fe(5)-O(5)-Fe(4)#1 | 131.0(5) |
| W(11)-O(6)-Fe(4) | 119.0(5) | W(14)-O(58)-Fe(3)#1 | 154.9(5) |
| Fe(7)-O(9)-Fe(5) | 156.7(5) | Co(3)#1-O(58)-Fe(3)#1 | 0.0 |
| Fe(4)-O(15)-Fe(6) | 157.7(5) | W(13)-O(60)-Fe(3) | 148.8(5) |
| W(5)-O(17)-Fe(7) | 120.5(4) | C(12)-O(61)-Fe(1) | 117.6(10) |
| W(8)-O(20)-Fe(6) | 119.3(5) | Fe(1)-O(61)-K(1) | 97.4(4) |
| W(13)-O(21)-Fe(6) | 143.2(5) | C(9)-O(63)-Fe(2) | 115.7(10) |
| W(5)-O(31)-Fe(2) | 161.1(5) | P(1)-O(64)-Fe(7) | 127.5(5) |
| W(13)-O(33)-Fe(4) | 141.5(5) | Fe(7)-O(64)-W(5) | 92.0(3) |

| | | | |
|---|---|---|---|
| P(1)-O(36)-Fe(5) | 128.2(5) | C(1)-O(66)-Fe(2) | 117.7(11) |
| Fe(5)-O(36)-W(7) | 90.0(3) | C(2)-N(3)-Fe(2) | 123.1(10) |
| Fe(4)-O(37)-Fe(7) | 152.5(5) | N(2)-N(3)-Fe(2) | 116.6(10) |
| W(14)-O(38)-Fe(7) | 142.7(5) | C(3)-N(4)-Fe(2) | 122.4(10) |
| W(7)-O(39)-Fe(5) | 118.3(5) | C(7)-N(4)-Fe(2) | 121.0(10) |
| Fe(5)-O(39)-Na(2) | 103.7(4) | C(8)-N(5)-Fe(2) | 122.7(11) |
| W(14)-O(41)-Fe(5) | 143.9(5) | N(6)-N(5)-Fe(2) | 116.6(9) |
| Fe(5)-O(41)-Na(2) | 99.5(4) | N(9)-N(10)-Fe(1) | 115.6(10) |
| P(2)-O(43)-Fe(4) | 128.5(5) | C(13)-N(10)-Fe(1) | 122.3(11) |
| Fe(4)-O(43)-W(11) | 91.7(3) | C(14)-N(11)-Fe(1) | 119.1(10) |
| P(2)-O(46)-Fe(6) | 129.6(5) | C(18)-N(11)-Fe(1) | 118.3(9) |
| Fe(6)-O(46)-W(8) | 90.8(3) | C(19)-N(12)-Fe(1) | 123.2(9) |
| N(13)-N(12)-Fe(1) | 113.0(8) | Fe(3)-O(6W)-Na(1)#2 | 137.0(8) |
| C(20)-N(13)-N(12) | 117.8(12) | Fe(3)-O(6W)-Na(2)#1 | 122.8(6) |
| Fe(1)-O(1W)-K(1) | 90.4(4) | | |

**Table S2** Selected bond lengths (Å) and bond angles (˚) for compound **2**.

| | | | |
|---|---|---|---|
| Fe(4)-O(15) | 1.843(12) | Fe(7)-O(38) | 2.036(13) |
| Fe(4)-O(5)#1 | 1.868(11) | Fe(7)-O(64) | 2.278(11) |
| Fe(4)-O(37) | 1.872(12) | Fe(1)-O(61) | 2.139(15) |
| Fe(4)-O(6) | 2.027(12) | Fe(1)-O(2) | 2.164(14) |
| Fe(4)-O(33) | 2.073(12) | Fe(1)-O(1W) | 2.218(18) |
| Fe(4)-O(43) | 2.275(11) | Fe(1)-N(12) | 2.233(17) |
| Fe(5)-O(4) | 1.847(12) | Fe(1)-N(10) | 2.249(16) |
| Fe(5)-O(9) | 1.857(12) | Fe(1)-O(2W) | 2.283(14) |
| Fe(5)-O(5) | 1.875(12) | Fe(1)-N(11) | 2.283(17) |
| Fe(5)-O(39) | 2.016(12) | Fe(2)-O(3W) | 2.150(16) |
| Fe(5)-O(41) | 2.092(12) | Fe(2)-O(31) | 2.190(14) |
| Fe(5)-O(36) | 2.303(12) | Fe(2)-O(66) | 2.229(15) |
| Fe(6)-O(15) | 1.871(11) | Fe(2)-O(63) | 2.263(14) |
| Fe(6)-O(3) | 1.881(12) | Fe(2)-N(5) | 2.272(16) |
| Fe(6)-O(4) | 1.899(13) | Fe(2)-N(4) | 2.28(2) |
| Fe(6)-O(20) | 2.022(11) | Fe(2)-N(3) | 2.331(18) |
| Fe(6)-O(21) | 2.068(12) | Fe(3)-O(4W) | 2.047(17) |

| | | | |
|---|---|---|---|
| Fe(6)-O(46) | 2.297(13) | Fe(3)-O(60) | 2.113(14) |
| Fe(7)-O(9) | 1.836(12) | Fe(3)-O(58)#1 | 2.126(14) |
| Fe(7)-O(37) | 1.864(13) | Fe(3)-O(5W) | 2.190(14) |
| Fe(7)-O(3)#1 | 1.870(11) | Fe(3)-O(7W) | 2.261(16) |
| Fe(7)-O(17) | 2.011(13) | Fe(3)-O(6W) | 2.294(17) |
| O(3)-Fe(7)#1 | 1.870(11) | O(5)-Fe(5)-O(41) | 91.9(5) |
| O(5)-Fe(4)#1 | 1.868(11) | O(39)-Fe(5)-O(41) | 85.7(5) |
| O(3)-Fe(7)#1 | 1.870(11) | O(4)-Fe(5)-O(36) | 89.9(5) |
| O(15)-Fe(4)-O(5)#1 | 104.3(5) | O(9)-Fe(5)-O(36) | 85.0(5) |
| O(15)-Fe(4)-O(37) | 94.7(5) | O(5)-Fe(5)-O(36) | 172.6(5) |
| O(5)#1-Fe(4)-O(37) | 97.0(5) | O(39)-Fe(5)-O(36) | 73.9(5) |
| O(15)-Fe(4)-O(6) | 160.8(5) | O(41)-Fe(5)-O(36) | 82.2(5) |
| O(5)#1-Fe(4)-O(6) | 94.0(5) | O(15)-Fe(6)-O(3) | 99.6(5) |
| O(37)-Fe(4)-O(6) | 88.7(5) | O(15)-Fe(6)-O(4) | 95.4(5) |
| O(15)-Fe(4)-O(33) | 88.1(5) | O(3)-Fe(6)-O(4) | 98.5(5) |
| O(5)#1-Fe(4)-O(33) | 90.6(5) | O(15)-Fe(6)-O(20) | 158.7(5) |
| O(37)-Fe(4)-O(33) | 170.9(5) | O(3)-Fe(6)-O(20) | 99.9(5) |
| O(6)-Fe(4)-O(33) | 85.9(5) | O(4)-Fe(6)-O(20) | 90.3(5) |
| O(15)-Fe(4)-O(43) | 85.4(5) | O(15)-Fe(6)-O(21) | 88.3(5) |
| O(5)#1-Fe(4)-O(43) | 168.5(5) | O(3)-Fe(6)-O(21) | 90.3(5) |
| O(37)-Fe(4)-O(43) | 88.3(5) | O(4)-Fe(6)-O(21) | 169.7(5) |
| O(6)-Fe(4)-O(43) | 75.8(4) | O(20)-Fe(6)-O(21) | 82.9(5) |
| O(33)-Fe(4)-O(43) | 83.4(4) | O(15)-Fe(6)-O(46) | 85.0(5) |
| O(4)-Fe(5)-O(9) | 97.0(5) | O(3)-Fe(6)-O(46) | 170.6(5) |
| O(4)-Fe(5)-O(5) | 95.6(5) | O(4)-Fe(6)-O(46) | 89.2(5) |
| O(9)-Fe(5)-O(5) | 99.2(5) | O(20)-Fe(6)-O(46) | 74.5(4) |
| O(4)-Fe(5)-O(39) | 87.3(5) | O(21)-Fe(6)-O(46) | 81.6(5) |
| O(9)-Fe(5)-O(39) | 158.5(5) | O(9)-Fe(7)-O(37) | 96.0(5) |
| O(5)-Fe(5)-O(39) | 101.3(5) | O(9)-Fe(7)-O(3)#1 | 103.9(5) |
| O(4)-Fe(5)-O(41) | 170.7(5) | O(37)-Fe(7)-O(3)#1 | 95.4(5) |
| O(9)-Fe(5)-O(41) | 87.2(5) | O(9)-Fe(7)-O(17) | 158.6(5) |
| O(37)-Fe(7)-O(17) | 89.4(5) | O(3W)-Fe(2)-O(31) | 172.5(5) |
| O(3)#1-Fe(7)-O(17) | 96.1(5) | O(3W)-Fe(2)-O(66) | 88.2(6) |
| O(9)-Fe(7)-O(38) | 87.2(5) | O(31)-Fe(2)-O(66) | 85.6(5) |
| O(37)-Fe(7)-O(38) | 171.7(5) | O(3W)-Fe(2)-O(63) | 87.5(5) |

| | | | |
|---|---|---|---|
| O(3)#1-Fe(7)-O(38) | 91.3(5) | O(31)-Fe(2)-O(63) | 87.8(5) |
| O(17)-Fe(7)-O(38) | 84.9(5) | O(66)-Fe(2)-O(63) | 84.1(5) |
| O(9)-Fe(7)-O(64) | 85.9(5) | O(3W)-Fe(2)-N(5) | 87.8(6) |
| O(37)-Fe(7)-O(64) | 89.4(5) | O(31)-Fe(2)-N(5) | 96.0(6) |
| O(3)#1-Fe(7)-O(64) | 168.5(4) | O(66)-Fe(2)-N(5) | 153.5(6) |
| O(17)-Fe(7)-O(64) | 73.4(4) | O(63)-Fe(2)-N(5) | 69.6(5) |
| O(38)-Fe(7)-O(64) | 83.1(5) | O(3W)-Fe(2)-N(4) | 92.7(7) |
| O(61)-Fe(1)-O(2) | 78.5(5) | O(31)-Fe(2)-N(4) | 94.6(6) |
| O(61)-Fe(1)-O(1W) | 87.1(6) | O(66)-Fe(2)-N(4) | 138.5(6) |
| O(2)-Fe(1)-O(1W) | 90.0(6) | O(63)-Fe(2)-N(4) | 137.4(6) |
| O(61)-Fe(1)-N(12) | 149.5(6) | N(5)-Fe(2)-N(4) | 67.8(6) |
| O(2)-Fe(1)-N(12) | 71.1(6) | O(3W)-Fe(2)-N(3) | 94.8(6) |
| O(1W)-Fe(1)-N(12) | 91.5(6) | O(31)-Fe(2)-N(3) | 86.9(6) |
| O(61)-Fe(1)-N(10) | 71.5(7) | O(66)-Fe(2)-N(3) | 69.9(7) |
| O(2)-Fe(1)-N(10) | 149.8(7) | O(63)-Fe(2)-N(3) | 153.7(7) |
| O(1W)-Fe(1)-N(10) | 90.6(6) | N(5)-Fe(2)-N(3) | 136.6(7) |
| N(12)-Fe(1)-N(10) | 139.0(7) | N(4)-Fe(2)-N(3) | 68.7(8) |
| O(61)-Fe(1)-O(2W) | 91.3(5) | O(4W)-Fe(3)-O(60) | 174.0(6) |
| O(2)-Fe(1)-O(2W) | 89.7(5) | O(4W)-Fe(3)-O(58)#1 | 94.9(6) |
| O(1W)-Fe(1)-O(2W) | 178.4(6) | O(60)-Fe(3)-O(58)#1 | 91.1(5) |
| N(12)-Fe(1)-O(2W) | 89.9(6) | O(4W)-Fe(3)-O(5W) | 90.7(6) |
| N(10)-Fe(1)-O(2W) | 88.8(6) | O(60)-Fe(3)-O(5W) | 89.5(5) |
| O(61)-Fe(1)-N(11) | 141.4(6) | O(58)#1-Fe(3)-O(5W) | 96.6(5) |
| O(2)-Fe(1)-N(11) | 140.1(5) | O(4W)-Fe(3)-O(7W) | 89.8(6) |
| O(1W)-Fe(1)-N(11) | 92.0(6) | O(60)-Fe(3)-O(7W) | 84.1(6) |
| N(12)-Fe(1)-N(11) | 69.0(6) | O(58)#1-Fe(3)-O(7W) | 173.0(5) |
| N(10)-Fe(1)-N(11) | 70.0(7) | O(5W)-Fe(3)-O(7W) | 88.5(5) |
| O(2W)-Fe(1)-N(11) | 89.3(5) | O(4W)-Fe(3)-O(6W) | 93.2(6) |
| O(60)-Fe(3)-O(6W) | 86.2(6) | W(14)-O(38)-Fe(7) | 143.1(6) |
| O(58)#1-Fe(3)-O(6W) | 86.6(6) | W(7)-O(39)-Fe(5) | 119.6(7) |
| O(5W)-Fe(3)-O(6W) | 174.7(6) | Fe(5)-O(39)-Na(2A)#2 | 101.9(5) |
| O(7W)-Fe(3)-O(6W) | 88.0(6) | W(14)-O(41)-Fe(5) | 142.7(7) |
| C(20)-O(2)-Fe(1) | 118.8(14) | Fe(5)-O(41)-Na(2A)#2 | 101.4(6) |
| Fe(1)-O(2)-Na(1) | 100.8(5) | P(2)-O(43)-Fe(4) | 127.6(6) |
| Fe(7)#1-O(3)-Fe(6) | 132.0(6) | Fe(4)-O(43)-W(11) | 90.8(4) |

| | | | |
|---|---|---|---|
| Fe(5)-O(4)-Fe(6) | 148.6(7) | P(2)-O(46)-Fe(6) | 127.8(7) |
| Fe(4)#1-O(5)-Fe(5) | 132.5(7) | Fe(6)-O(46)-W(8) | 90.9(4) |
| W(11)-O(6)-Fe(4) | 116.9(6) | W(14)-O(58)-Fe(3)#1 | 155.9(7) |
| Fe(7)-O(9)-Fe(5) | 154.8(7) | Mn(3)#1-O(58)-Fe(3)#1 | 0.0 |
| Fe(4)-O(15)-Fe(6) | 153.2(7) | W(13)-O(60)-Fe(3) | 148.3(8) |
| W(5)-O(17)-Fe(7) | 119.5(6) | C(12)-O(61)-Fe(1) | 119.9(14) |
| W(8)-O(20)-Fe(6) | 118.6(6) | C(9)-O(63)-Fe(2) | 118.5(13) |
| W(13)-O(21)-Fe(6) | 143.8(6) | P(1)-O(64)-Fe(7) | 127.8(7) |
| W(5)-O(31)-Fe(2) | 160.7(8) | Fe(7)-O(64)-W(5) | 92.1(4) |
| W(13)-O(33)-Fe(4) | 142.1(7) | C(1)-O(66)-Fe(2) | 120.4(15) |
| P(1)-O(36)-Fe(5) | 128.7(6) | C(2)-N(3)-Fe(2) | 122.1(17) |
| Fe(5)-O(36)-W(7) | 90.1(4) | N(2)-N(3)-Fe(2) | 114.0(15) |
| Fe(7)-O(37)-Fe(4) | 149.9(7) | C(18)-N(11)-Fe(1) | 118.1(14) |
| C(7)-N(4)-Fe(2) | 121.3(15) | C(14)-N(11)-Fe(1) | 119.2(13) |
| C(3)-N(4)-Fe(2) | 122.1(15) | C(19)-N(12)-Fe(1) | 122.4(14) |
| C(8)-N(5)-Fe(2) | 122.9(14) | N(13)-N(12)-Fe(1) | 113.5(13) |
| N(6)-N(5)-Fe(2) | 113.8(12) | Fe(3)-O(6W)-Na(2)#6 | 137.1(12) |
| C(13)-N(10)-Fe(1) | 122.9(15) | Fe(3)-O(6W)-Na(2A)#6 | 120.4(8) |
| N(9)-N(10)-Fe(1) | 114.3(15) | | |

**Table S3** Hydrogen bonds for compound **1** [Å and °].

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N1—H1A···O40 | 0.86 | 2.49 | 3.105(17) | 129 |
| N1—H1B···O17W | 0.86 | 2.42 | 3.19(2) | 148 |
| N2—H2A···O17W | 0.86 | 2.15 | 2.96(2) | 156 |
| N6—H6A···O17 | 0.86 | 2.02 | 2.777(16) | 147 |
| N7—H7A···O7W | 0.86 | 2.45 | 3.30(2) | 170 |
| N8—H8A···O13W | 0.86 | 2.17 | 3.02(3) | 174 |
| N8—H8B···O12 | 0.86 | 2.54 | 3.230(17) | 138 |
| N8—H8B···O22 | 0.86 | 2.34 | 3.035(17) | 138 |
| N8—H8B···O23 | 0.86 | 2.57 | 3.285(17) | 141 |
| N9—H9A···O23 | 0.86 | 2.06 | 2.876(15) | 158 |
| N13—H13A···O13 | 0.86 | 1.97 | 2.771(15) | 154 |
| N14—H14A···O48 | 0.86 | 2.27 | 3.066(18) | 155 |
| N14—H14B···O13 | 0.86 | 2.39 | 3.109(16) | 141 |
| N14—H14B···O35 | 0.86 | 2.32 | 3.022(15) | 139 |
| C10—H10C···O45 | 0.96 | 2.18 | 3.10(2) | 161 |
| C11—H11C···O37 | 0.96 | 2.37 | 3.23(2) | 149 |

| | | | | |
|---|---|---|---|---|
| C16—H16A···O44 | 0.93 | 2.42 | 3.06(2) | 126 |
| C22—H22B···O59 | 0.96 | 2.52 | 3.446(19) | 162 |

**Table S4** Hydrogen bonds for compound **2** [Å and °].

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| N6—H6A···O17 | 0.86 | 1.99 | 2.76(2) | 150 |
| N7—H7A···O5W | 0.86 | 2.53 | 3.13(3) | 127 |
| N8—H8A···O13W | 0.86 | 2.19 | 3.04(4) | 170 |
| N8—H8B···O12 | 0.86 | 2.49 | 3.17(2) | 136 |
| N8—H8B···O22 | 0.86 | 2.34 | 3.01(2) | 135 |
| N8—H8B···O23 | 0.86 | 2.48 | 3.22(2) | 145 |
| N9—H9A···O23 | 0.86 | 2.12 | 2.92(2) | 154 |
| N14—H14A···O48 | 0.86 | 2.30 | 3.14(2) | 165 |
| N14—H14B···O35 | 0.86 | 2.38 | 3.05(2) | 135 |
| C10—H10B···O45 | 0.96 | 2.24 | 3.16(3) | 159 |
| C11—H11B···O37 | 0.96 | 2.33 | 3.20(3) | 150 |

**Table S5** The ICP results of compounds **1-2**.

| Sample | Fe (mg/L) | Co (mg/L) | W (mg/L) | Na (mg/L) | n(Co):n(Fe) | n(W):n(Fe) | n(W):n(Na) |
|---|---|---|---|---|---|---|---|
| **1** | 0.454 | 0.307 | 7.739 | 0.0616 | 0.64 | 5.18 | 15.71 |
| Sample | Fe (mg/L) | Mn (mg/L) | W (mg/L) | Na (mg/L) | n(Mn):n(Fe) | n(W):n(Fe) | n(W):n(Na) |
| **2** | 0.427 | 0.315 | 7.365 | 0.113 | 0.63 | 5.24 | 8.15 |

The ICP results manifest that the experimental values are consistent well with the theoretical values from the single crystal X-ray diffraction.

**Table S6** BVS analysis of compound **1-2** for iron atoms.

| **Compound 1** | Fe1 | Fe2 | Fe3 | Fe4 | Fe5 | Fe6 | Fe7 |
|---|---|---|---|---|---|---|---|
| **value** | 2.27 | 2.04 | 2.18 | 3.24 | 3.19 | 3.31 | 3.28 |
| **Compound 2** | Fe1 | Fe2 | Fe3 | Fe4 | Fe5 | Fe6 | Fe7 |
| **value** | 2.04 | 1.78 | 1.89 | 3.14 | 3.12 | 3.30 | 3.23 |

**Table S7** $CO_2$ photoreduction of the reported POM-based materials.

| **Photocatalyst** | **Photosensitizer Sacrificial agent** | **Main product** | **Rate$_{CO}$ (μmol g$^{-1}$ h$^{-1}$)** | **Sectivity$_{CO}$ (%)** | **Ref.** |
|---|---|---|---|---|---|
| **{$Fe_8Co_2P_4W_{32}$}** | **[Ru(bpy)$_3$]Cl$_2$·6H$_2$O triethanolamine** | **CO** | **6885.1** | **90.8** | **this work** |

| | | | | | |
|---|---|---|---|---|---|
| $H_{26.5}K_{2.5}Na(H_2O_{16}[Ni_6(OH)(BO_3)_2(dien)_2(B\text{-}\alpha\text{-}SiW_{10}O_{37})_2]_2\cdot 24H_2O$ | $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ triethanolamine | CO | 6988 | 84.2 | [6] |
| $\{Co_4Mo_{24}\}$ | $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ triethanolamine | CO | 1848.3 | 97.0 | [7] |
| $K_4Na_{28}[\{Co_4(O\text{-}H)_3(VO_4)\}_4(SiW_9O_{34})_4]\cdot 66H_2O$ | $[Ru(phen)_3](PF_6)_2$ triethanolamine | CO | 839.2 | 99.6 | [8] |
| $Na_6[Co(H_2O)_2(H_2tib)]_2\{Co[Mo_6O_{15}(HPO_4)_4]_2\}\cdot 5H_2O$ | $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ triethanolamine | CO | 1.09 | 84.2 | [9] |
| $H\{[Na_6CoMn_3(PO_4)(H_2O)_4]_3\{[Mo_6O_{12}(OH)_3(HPO_4)_3(PO_4)]_4[Co_{1.5}Mn_{4.5}]\}\cdot 21H_2O$ | $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ triethanolamine | $CH_4$ | 40.2 | 85.5 | [10] |

**Table S8** The research of reaction conditions for compound **1**.

| **Entry** | **CO (μmol)** | **$H_2$ (μmol)** | **$CH_4$ (μmol)** | **CO selectivity (%)** |
|---|---|---|---|---|
| 1[a] | 165.24 | 13.46 | 3.24 | 90.8 |
| 2[b] | n.d.[c] | n.d. | n.d. | - |
| 3[d] | 1.35 | 0.76 | 0.12 | 60.5 |
| 4[e] | n.d. | n.d. | n.d. | - |
| 5[f] | n.d. | n.d. | n.d. | - |
| 6[g] | n.d. | n.d. | n.d. | - |

[a]Reaction conditions: photocatalyst (10 mg), $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ (11.3 mg), a mixed solvent (TEOA/MeCN, 1/4 v/v, 50 mL), $CO_2$ (1 atm), $\lambda \geq 420$ nm, 298 K, 7 h reaction time; CO selectivity = (n(CO))/(n(CO+$CH_4$)) × 100%. [b]In the dark. [c]Not detectable. [d]No photocatalyst. [e]No $[Ru(bpy)_3]Cl_2\cdot 6H_2O$. [f]No TEOA. [g]Ar replaced $CO_2$.

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