

## Supporting Information

### **[W<sub>10</sub>O<sub>32</sub>]<sup>4-</sup>-based POMOFs with different nuclear cobalt clusters for photoreduction CO<sub>2</sub> to syngas production**

Si-Qi You,<sup>a,†</sup> Yu-Jiao Dong,<sup>a,†</sup> Bao-Shan Hou,<sup>a</sup> Man Dong,<sup>a</sup> Jia-Lin Tong,<sup>a</sup> Ling-Xin Wang,<sup>b</sup> Xin-Long Wang,<sup>\*a</sup> Chun-Yi Sun,<sup>\*a</sup> Wei Guan<sup>\*a</sup> and Zhong-Min Su<sup>ab</sup>

<sup>a</sup> Key Laboratory of Polyoxometalate Science of Ministry of Education, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China.

<sup>b</sup> Jilin Provincial Science and Technology Innovation Center of Optical Materials and Chemistry, School of Chemistry and Environmental Engineering, Changchun University of Science and Technology Changchun, Jilin, China.

#### 1. General Methods

##### **Experimental Section**

##### **Materials characterizations**

All the reagents and solvents were purchased from commercial sources and used without further purification.

Crystallographic data of Compound 1 and 2 was collected on a Bruker Apex-II CCD. Powder X-ray diffractions (PXRD) patterns were recorded on a Siemens D5005 diffractometer with Cu KR ( $\lambda = 1.5418 \text{ \AA}$ ) radiation in the range of 5-50°. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm<sup>-1</sup> on a Mattson Alpha-Centauri spectrometer. UV-Vis absorption spectra were obtained by using a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200-800 nm. All the DFT calculation were performed using the Gaussian 09 program. Photoluminescence (PL) spectra are scanned on a photoluminescence spectrometer (Hitachi F-4600) under an excitation wavelength of 520 nm. I-t curves and Mott-Schottky plots are tested at CHI660e (CH Instruments, Inc., USA) electrochemical workstation. In situ IR were carried out on a 6700 Flex FTIR spectrometer equipped with smart iTRTM attenuated total reflectance (ATR) sampling accessory. The gas product in photocatalytic reaction was measured by flame ionization detector (FID) in Shimadzu Gas Chromatography equipped with a packed molecular sieve column (TDX-01 mesh). The HP 6890GC-5973MSD gas chromatography-mass spectrometer (GCMS) was employed to analyze the <sup>13</sup>CO the <sup>13</sup>CO<sub>2</sub> (98% enriched) isotope experiments. All the measurements are performed at room temperature unless otherwise noted.

## Photocatalytic Test

The photocatalytic reaction was carried out in a 50 mL sealed quartz tube. Compound **1** or Compound **2** was dispersed in a mixed solution containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (7.5mg, 10umol), acetonitrile (4mL), triethanolamine (1mL), and water (1mL). High-purity CO<sub>2</sub> was bubbled in a quartz tube (10 min) until the CO<sub>2</sub> concentration was at 1 atm. The reaction system was irradiated using a 300W xenon lamp with an AM1.5 filter and the temperature was controlled at 20°C by circulating condensate. Time-course experiment was sampled the gas periodically. In the cycle experiment, fresh [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> was added to the system and CO<sub>2</sub> gas was bubbled after 1h reaction. At the end of the reaction the gaseous product was collected and quickly analyzed by gas chromatography (GC-9800). Isotopic experiments were carried out under the same conditions except for <sup>13</sup>CO<sub>2</sub> replacing CO<sub>2</sub>. The gas-phase products were analyzed by gas chromatography-mass spectrometry (GC-MS).

### Photocatalytic performance in diluted CO<sub>2</sub> conditions (0.03%, 5%, 15%, 30%)

The photocatalytic reaction was carried out in a 50 mL sealed quartz tube. Compound **1** (1 mg) was dispersed in a mixed solution containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (7.5 mg, 10 umol), acetonitrile (4 mL), triethanolamine (TEOA, 1 mL) and water (1 mL). High purity Ar (99.99%) gas bubbled in the mixed solution for around 20 min until the dissolved oxygen was removed completely. Then, the Air gas (contain 0.03% CO<sub>2</sub>) and diluted 5%/15%/30% CO<sub>2</sub>/Ar mixed gas was input into this system for about 15 seconds at a flow rate of 80 mL/min. The reaction system was irradiated using a 300 W xenon lamp with an AM1.5 filter and maintained at 20 °C by circulating condensate. At the end of the reaction the gaseous product was collected and quickly analyzed by gas chromatography (GC-9800).

### Photocatalytic performance in simulated flue gas (15% CO<sub>2</sub> + 0.2%H<sub>2</sub>S + 0.2% NO<sub>x</sub> + 0.2%SO<sub>x</sub>+N<sub>2</sub>).

H<sub>2</sub>S, NO<sub>x</sub> and SO<sub>x</sub> gases were prepared according to available literature.<sup>1</sup> The photocatalytic reaction was carried out in a 50 mL sealed quartz tube. Compound **1** (1 mg) was dispersed in a mixed solution containing [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (7.5 mg,10 umol), acetonitrile (4 mL), triethanolamine (1 mL) and water (1 mL). The quartz tube was bubbled with diluted CO<sub>2</sub>/N<sub>2</sub>. 0.1 mL of H<sub>2</sub>S, 0.1 mL of NO<sub>x</sub> and 0.1 mL of SO<sub>x</sub> were subsequently injected into the quartz tube using a syringe with a long needle. The reaction system was irradiated using a 300 W xenon lamp with an AM1.5 filter and maintained at 20 °C by circulating condensate. At the end of the reaction the gaseous product was collected and quickly analyzed by gas chromatography (GC-9800).

### **Photocurrent Measurements**

Photocurrent testing was performed on an electrochemical workstation (CHI660e, CH Instruments, Inc., USA) using a three-electrode architecture. The working electrode was prepared by isolating a 1 cm × 1 cm space on ITO glass using tape and loading the catalyst on it. The ground catalyst (5 mg) was dispersed in acetonitrile (1 mL) using an ultrasonicator to form a suspension. 100uL of the suspension was applied to the ITO glass and dried. The Ag/AgCl electrode and Pt sheet electrode were used as the reference electrode and auxiliary electrode, respectively. The light source was a 300W xenon lamp with an AM1.5 filter. Tetrabutylammonium hexafluorophosphate was dissolved in acetonitrile as the electrolyte solution (0.1 M).

### **Mott-Schottky analysis.**

Mott-Schottky tests were performed on an electrochemical workstation (CHI660e, CH Instruments, Inc., USA). The working electrode was prepared in the same way as the photocurrent test.

### **Density functional theory (DFT) calculations**

All the DFT calculation were performed using the Gaussian 09 program.<sup>2</sup> The geometry optimization calculation of monomer was carried out using the (U)B3LYP functional in the gas phase. A mixed basis sets were employed with LanL2DZ<sup>3</sup> for Co and W, and 6-31G(d)<sup>4</sup> for the other main-group elements, respectively. The LUMO maps were characterized by Multiwfn software.<sup>5</sup>

The unit cell of Compound 1 contains 1/2 [W<sub>10</sub>O<sub>32</sub>]<sup>4-</sup>. When the structural stability is considered, we extend the unit cell into one [W<sub>10</sub>O<sub>32</sub>]<sup>4-</sup>. Compounds 1 and 2 were end-sealed using ammonia and water molecules.

### **Cyclic Voltammetry Measurement for Compound 1 and 2.**

Cyclic voltammetry was was performed on an electrochemical workstation (CHI660e, CH Instruments, Inc., USA) using a three-electrode architecture. The working electrode was prepared Glassy carbon electrode and loading the catalyst on it. The ground catalyst (5 mg) was dispersed in acetonitrile (1 mL) using an ultrasonicator to form a suspension. 100uL of the suspension was applied to the Glassy carbon electrode and dried. The Ag/AgCl electrode and Pt sheet electrode were used as the reference electrode and auxiliary electrode, respectively. Tetrabutylammonium hexafluorophosphate was dissolved in

acetonitrile as the electrolyte solution (0.1 M). The solution was saturated with N<sub>2</sub> prior to experiment.

**Table 1** Crystal data and structure refinement for Compound **1**.

Identification code	Compound <b>1</b>
CCDC	2245817
Empirical formula	C <sub>44</sub> H <sub>42</sub> Co <sub>2</sub> N <sub>14</sub> O <sub>40</sub> W <sub>10</sub>
Formula weight	3363.27
Temperature/K	173.0
Crystal system	triclinic
Space group	P-1
a/Å	10.6145(7)
b/Å	12.4466(8)
c/Å	15.8221(11)
α/°	110.368(2)
β/°	101.525(2)
γ/°	103.223(2)
Volume/Å <sup>3</sup>	1816.1(2)
Z	1
ρ <sub>calc</sub> /cm <sup>3</sup>	3.075
μ/mm <sup>-1</sup>	16.306
F(000)	1518.0
Crystal size/mm <sup>3</sup>	0.24 × 0.22 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	5.262 to 50.222
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -18 ≤ l ≤ 18
Reflections collected	22521
Independent reflections	6460 [R <sub>int</sub> = 0.0785, R <sub>sigma</sub> = 0.0737]
Data/restraints/parameters	6460/1186/506
Goodness-of-fit on F <sup>2</sup>	1.017
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0360, wR <sub>2</sub> = 0.0652
Final R indexes [all data]	R <sub>1</sub> = 0.0667, wR <sub>2</sub> = 0.0735

Largest diff. peak/hole / e Å<sup>-3</sup> 2.38/-1.50

**Table 2** Crystal data and structure refinement for Compound **2**.

Identification code	Compound <b>2</b>
CCDC	2245818
Empirical formula	C <sub>76</sub> H <sub>36</sub> Co <sub>4</sub> N <sub>12</sub> O <sub>44</sub> W <sub>10</sub>
Formula weight	3895.4072
Temperature/K	297.16
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	14.2920(16)
b/Å	12.7209(15)
c/Å	24.794(3)
α/°	90
β/°	97.725(4)
γ/°	90
Volume/Å <sup>3</sup>	4466.8(9)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	2.896
μ/mm <sup>-1</sup>	13.620
F(000)	3140.0
Crystal size/mm <sup>3</sup>	0.24 × 0.22 × 0.2
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.472 to 50.34
Index ranges	-16 ≤ h ≤ 17, -15 ≤ k ≤ 15, -29 ≤ l ≤ 29
Reflections collected	67961
Independent reflections	7963 [R <sub>int</sub> = 0.1105, R <sub>sigma</sub> = 0.0612]
Data/restraints/parameters	7963/6/507
Goodness-of-fit on F <sup>2</sup>	1.022
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0388, wR <sub>2</sub> = 0.0799
Final R indexes [all data]	R <sub>1</sub> = 0.0671, wR <sub>2</sub> = 0.0911

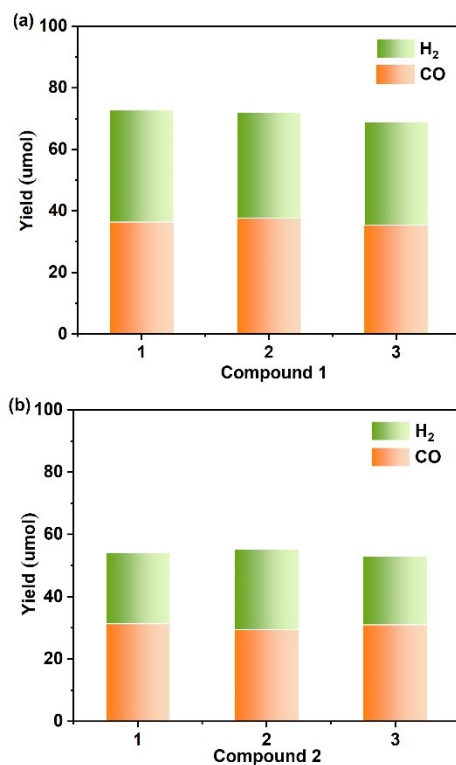


Figure S1 Cycling tests for (a) Compound 1; (b) Compound 2.

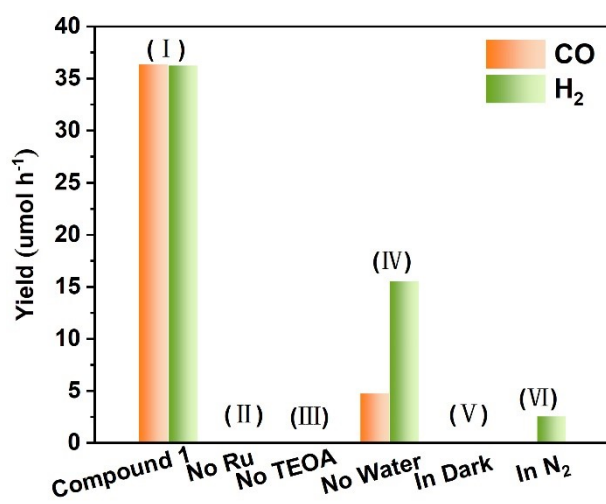
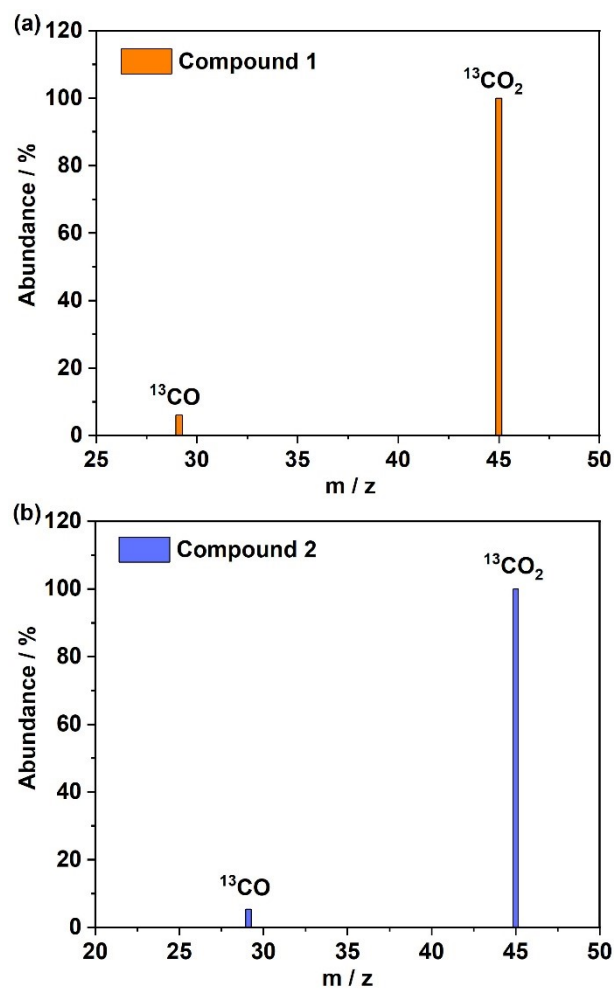
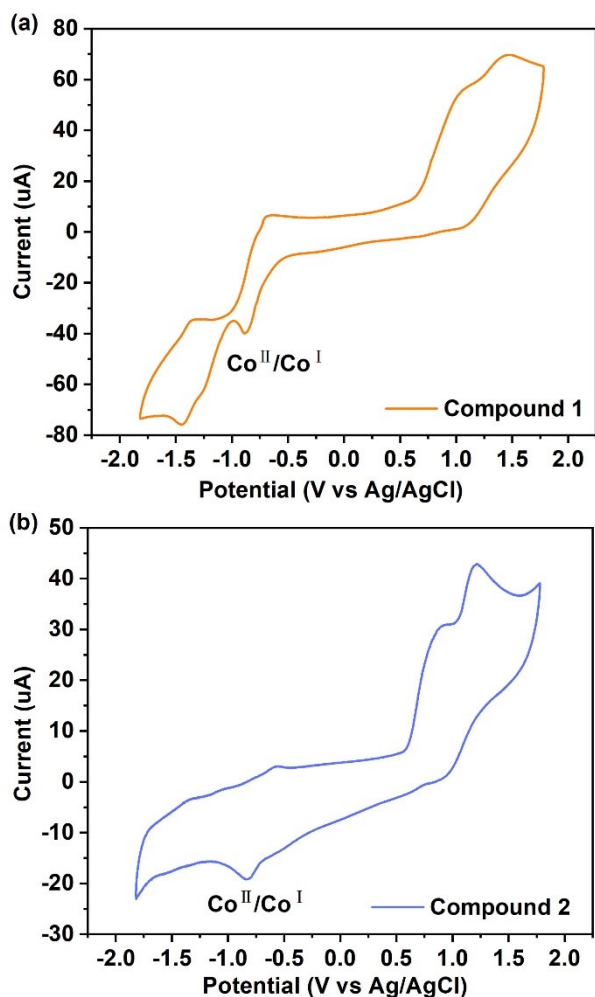


Figure S2 Catalytic test plots of Compound 1 (1mg) under different test conditions.



**Figure S3** (a) (b) Compound 1 (1mg) and 2 (1mg)  $^{13}\text{CO}_2$  isotope labeling experiment.



**Fig. S4** cyclic voltammetry of (a) Compound **1** and (b) Compound **2** in acetonitrile solution of 0.1M tetrabutylammonium hexafluorophosphate under N<sub>2</sub>. Reference electrode: Ag/AgCl; counter electrode: platinum (Pt) wire; scan rate: 100 mV/s.

Quantum efficiency (QE) measurements were performed by a blue-LED light source with a single wavelength (420 nm). The power density of irradiation was measured as 135 mW cm<sup>-2</sup> and the spot area is 0.785 cm<sup>2</sup>. The samples were irradiated for 60min. The amounts of CO produced by Compound **1** and compound **2** were 4.2 and 3.9 µmol, respectively.

The QE was calculated by the following equation:

$$N = \frac{E\lambda}{hc} = \frac{135 \times 10^{(-3)} \times 0.785 \times 420 \times 10^{(-9)} \times 60 \times 60}{6.626 \times 10^{(-34)} \times 3 \times 10^{(8)}} = 8 \times 10^{20}$$

$$QE = \frac{(2 \times \mu\text{mol of CO}) \times \text{Avogadro number}}{\text{the number of incident photons}} \times 100\%$$



$$QE_{\text{Compound 1 (co)}} = \frac{(2 \times 4.2 \times 10^{-6}) \times 6.02 \times 10^{23}}{8 \times 10^{20}} \times 100\% = 0.63\%$$

$$QE_{\text{Compound 2 (co)}} = \frac{(2 \times 3.9 \times 10^{-6}) \times 6.02 \times 10^{23}}{8 \times 10^{20}} \times 100\% = 0.59\%$$

,Table S3. Comparison of Quantum efficiency performance.

Catalyst	Wavelength	Photosensitizer	QE	Reference
MR-N <sub>0.2</sub> C <sub>0.8</sub> O	475 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	2.39%	S6
Co-ZIF-9@CdS	420 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	1.93%	S7
Co-ZIF-9	420 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	1.48%	S8
Co <sub>3</sub> O <sub>4</sub> -NS	420 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.71%	S9
Compound 1	420 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.63%	This work
Compound 2	420 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.59%	This work
Co-2,3-DHTA-COF	450 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.47%	S10
Co <sub>3</sub> O <sub>4</sub> HNSs	450 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.42%	S11
ZrOCoII/IrOx/ SBA-15 silica	355 nm	<sup>a</sup> MMCT chrom-ophore [Ir(acac) <sub>3</sub> ]	0.17%	S12
66-IS-Ni	400 nm.	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.14%	S13
BIF-29	440 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.078 %	S14
Co <sub>3</sub> O <sub>4</sub> platelets	450 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	0.069%	S15
<b>PMMCoCC-1200</b>	450 nm	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	<b>0.049%</b>	S16
[Co <sub>2</sub> (OH)L <sup>1</sup> ](ClO <sub>4</sub> ) <sub>3</sub>	450 nm	[Ru(phen) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	0.04%	S17
Nickel N-heterocyclic Carbene-isoquinoline complex	500 nm	Ir(ppy) <sub>3</sub>	0.01%	S18
Iron porphyrin	400 (420) nm	9-cyanoanthracene, Ir(ppy) <sub>3</sub>	0.0008%	S19

## Notes and references

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