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# Semiconductive Amine-Functionalized Co(II)-MOF for Visible-Light-Driven Hydrogen Evolution and CO<sub>2</sub> Reduction

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S Supporting Information

ABSTRACT: A Co-MOF, [Co<sub>3</sub>(HL)<sub>2</sub>·4DMF·4H<sub>2</sub>O] was simply synthesized through a one-pot solvothermal method. With the semiconductor nature, its band gap was determined to be 2.95 eV by the Kubelka-Munk method. It is the first trinuclear Co-MOF employed for photocatalytic hydrogen evolution and CO<sub>2</sub> reduction with cobalt-oxygen clusters as catalytic nodes. Hydrogen evolution experiments indicated the activity was related to the photosensitizer, TEOA, solvents, and size of catalyst. After optimization, the best activity of H<sub>2</sub> production was 1102  $\mu$ mol/ (g h) when catalyst was ground and then soaked in photosensitizer solution before photoreaction. To display the integrated design of Co-MOF, we used no additional photosensitizer and cocatalyst in the CO<sub>2</sub> reduction system. When -NH<sub>2</sub> was used for light



absorption and a Co-O cluster was used as catalyst, Co-MOF exhibited an activity of 456.0  $\mu$ mol/(g h). The photocatalytic mechanisms for hydrogen evolution and CO<sub>2</sub> reduction were also proposed.

# INTRODUCTION

The concerns on global warming and the energy crisis have prompted researchers to develop sustainable and clean energy sources. Visible-light-driven catalytic studies on hydrogen or oxygen evolution, CO<sub>2</sub> reduction, and organic synthesis have been explored in many kinds of materials, such as metal oxide and metal-organic frameworks (MOFs).<sup>2</sup> In general, MOFs often act as supporter, photosensitizer (PS) unit, catalyst unit, or both photosensitizer and catalysis units in photocatalytic reaction.<sup>3</sup> Among these, some cluster-based MOFs as node catalysts for hydrogen evolution have been explored for their efficient activity and stability in catalysis.<sup>4</sup> In 2009, Mori group<sup>5</sup> reported the first metal-oxygen cluster MOF,  $[Ru_2(p BDC)_2]_n$  (p-BDC = 1,4-benzenedicarboxylate), for photocatalytic water reduction to produce hydrogen molecules in the presence of  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy = 2,2'-bipyridine), MV<sup>2+</sup> (N,N'dimethyl-4,4'-bipyridinium), and EDTA-2Na. The above Ru(II)-MOF catalyst was based on noble metal, whereas several noble-metal-free cluster MOFs were also investigated. To mimic the [NiFe]-hydrogenase, the Du group synthesized a 2D [Ni<sub>2</sub>S]-based MOF,  $[Ni_2(PymS)_4]_n$  (PymSH = pyrimidine-2-thiol), exhibiting high stability in aqueous conditions.<sup>6</sup> They also prepared a 2D double-layered MOF, [Ni(Hmna)(mna)- $(H_2O)_{10}] \cdot (H_2O)_{11} (H_2mna = 2$ -mercaptonicotinic acid) for  $H_2$ production with a TON of 685.4 with fluorescein as photosensitizer after 48-h photoreduction. Recently, Du's group reported a Cu<sub>2</sub>I<sub>2</sub>-based cluster MOF, Cu-I-bpy (bpy= 4,4'-bipyridine), showing highly efficient activity (7.09 mmol/ (g h)) for hydrogen evolution without cocatalyst and photosensitizer.

The research on photocatalytic CO<sub>2</sub> reduction has been concerned because of its useful chemical conversion of CO<sub>2</sub> into chemicals and fuels, otherwise, slowing down the global warming effect. MOFs have been employed for photocatalytic CO<sub>2</sub> reduction for its accessible voids and stability, and the related reports were summarized.<sup>2a,8</sup> Among them, only several clusters-based MOF catalyst were explored.<sup>9</sup> Li group synthesized an amine-functionalized NH<sub>2</sub>-MIL-125(Ti) which could produce HCOO<sup>-</sup> from CO<sub>2</sub> photoreduction in MeCN/TEOA (5/1) solution under visible-light irradiation. Later, they also investigated the performance of NH2-Uio-66(Zr), NH<sub>2</sub>-MIL-101(Fe), NH<sub>2</sub>-MIL-53(Fe), and NH<sub>2</sub>-MIL-88B(Fe) catalysts for CO<sub>2</sub> reduction, in which Fe-based MOFs showed a dual catalytic pathways based on direct excitation of Fe-O clusters and exciting -NH<sub>2</sub> functionality, respectively.<sup>90</sup> These examples emphasize the potential for CO<sub>2</sub> photoreduction by MOFs including a -NH<sub>2</sub> functional PS unit and metal-cluster catalytic unit.

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Figure 1. Crystal structure of Co-MOF (LIFM-45): (a)  $\{Co_3O_{14}\}$  cluster center; (b) coordination environment of ligand; and (c) 3D packing mode along *a* axis. Color indication: Co, green; O, pink; N, blue; C, gray. All hydrogen atoms were omitted for clarity.

Noble-metal free Co(II) complexes were applied to photocatalytic hydrogen evolution and CO<sub>2</sub> reduction for their high photoactivity in homogeneous solution.<sup>10</sup> But few works concerning Co(II)-based MOF heterogeneous catalyst has been developed for CO2 reduction, and PS was included in these systems.<sup>11</sup> Herein, we reported the first trinuclear Co-MOF, formulated as  $[Co_3(HL)_2 \cdot 4DMF \cdot 4H_2O]$   $(H_4L = 2' - 2')$ amino-[1,1':4',1"-terphenyl]-3,3",5,5"- tetracarboxylic acid) for both photocatalytic hydrogen evolution and CO<sub>2</sub> reduction. Various experiment conditions were employed to achieve the optimized results, and it reaches  $1102 \ \mu mol/(g h)$ in DMF/H<sub>2</sub>O (4/2) solution with TEOA as sacrificial agent for H<sub>2</sub> production. In order to perform the integrated functionality of frameworks, CO<sub>2</sub> reduction experiments without additional PS and cocatalyst were performed and it obtained a considerable selectively catalytic activity of 456.0  $\mu$ mol/(g h) for HCOO<sup>-</sup>. The photocatalytic mechanisms based on the redox of trinuclear cobalt cluster were also explored.

#### EXPERIMENTAL SECTION

**Chemicals and Materials.** Ru(bpy)<sub>3</sub>Cl<sub>2</sub> was purchased from HWRK Chem. 3,5-bis(methoxycarbonyl) phenylboronic acid pinacol ester was purchased from Shanghai UCHEM Inc. Cesium carbonate, Tetrakis (triphenylphosphine) palladium and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were purchased from Alfa Aesar. Triethanolamine (TEOA) was purchased from Sigma-Aldrich. All chemicals and solvents purchased from the commercial sources were of AR grade and used without further purification.

**Characterization and Methods.** Fourier transform infrared (FT-IR) spectra were performed on a Nicolet/Nexus-670 spectrometer in the wavenumber range between 4000 and 400 cm<sup>-1</sup> using the KBr disk. Elemental analysis (EA) measurement was measured on a Vario EL CHNS elemental analyzer. The <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer, applying TMS as the internal standard and using MestReNova software to analyze the spectra. The UV–vis absorption spectra were measured on a SHIMADZU UV-3600. Photoluminescence spectra were measured on EDINBURGH FLS980 fluorescence spectrophotometer. TG curve was carried out on a STA 449 F3 Jupiter instrument under a nitrogen

flow with a heating rate of 5 °C/min. PXRD data were recorded on a Rigaku SmartLab X-ray diffractometer with Cu–K $\alpha$  radiation ( $\lambda$  = 1.54056 Å) at room temperature. N<sub>2</sub> adsorption isotherms (77 K) of Co-MOF were carried out on a Quantachrome Autosorb-iQ2-MP instrument. SC-XRD data were collected on a Rigaku Oxford SuperNova X-RAY diffractometer system equipped with a Cu sealed tube ( $\lambda$  = 1.54178 Å) at 50 kV and 0.80 mA at 293 K. With the twin nature of obtained crystal, TWIN and BASF command was used to refine the crystal data. As solvents (DMF and water) were highly disordered in the framework, SQUEEZE process was employed by PLATON.<sup>12</sup> The electron count of solvent was then determined to be 200 in each unit cell, which indicated of four DMF and four water molecules. Scanning electron microscope (SEM) measurements were performed on Hitachi SU8010 scanning electron microscope.

Synthesis of [Co<sub>3</sub>(HL)<sub>2</sub>·4DMF·4H<sub>2</sub>O] (Co-MOF, LIFM-45). The ligand 2'-amino-[1,1':4',1"-terphenyl]-3,3",5,5"- tetracarboxylic acid (H<sub>4</sub>L) was prepared according to the previous references<sup>13</sup> and characterized by <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , 25 °C,  $\delta$ ): 13.34 (s, 4H), 8.45 (d, 2H), 8.41 (s, 2H), 8.24 (s, 2H), 7.24 (s, 1H), 7.20 (d, 2H), 7.06 (d, 2H), 5.25 (s, 2H). Then, 0.0105 g (0.025 mmol) of H<sub>4</sub>L and 0.0146 g (0.05 mmol) of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added into a 20 mL glass bottle equipped with cap. A mixture solution of 3 mL of  $DMF/H_2O(v/v, 1/1)$  was then injected. The bottle was sealed and sonicated for 2 min followed by a 24 h heating at 358 K. After the solvothermal reaction, the bottle was cooled naturally. The bulk crystals were separated and washed with 10 mL of DMF/H2O (v/v, 1/1) solvents for three times and dried under vacuum at room temperature. (Yield: 52%, based on H<sub>4</sub>L) FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3392 (m), 3139 (m), 1708 (m), 1656 (s), 1621 (s), 1575 (s), 1450 (m), 1400 (s), 1374 (s), 1249 (w), 1103 (w), 779(m), 746(m), 725 (m) (Figure S1). Found: C, 48.51%; H, 4.18%; N, 5.87%. Calcd: C, 48.81%; H, 4.39%; N, 6.10% indicating formula for  $C_{44}H_{24}N_2O_{16}\cdot$ 4(C<sub>3</sub>H<sub>7</sub>NO)·4H<sub>2</sub>O. Crystal data of Co-MOF was collected and is shown in Table S1 (CCDC:1834360).

**Evaluation of Photocatalytic Hydrogen Evolution and CO<sub>2</sub> Reduction.** For H<sub>2</sub> evolution in a typical experiment, 4 mg of Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as photosensitizer (PS), 4 mg of Co-MOF as catalyst, 1 mL of TEOA as sacrificial agent, and mixed solvents were added into a 55 mL glass bottle. The bottle was then sealed and degassed with N<sub>2</sub> gas for 20 min. The visible-light-driven hydrogen evolution was performed on a white LED lamp ( $\lambda = 420-780$  nm, 100 mW/cm<sup>2</sup>). For CO<sub>2</sub> reduction, 4 mg of Co-MOF as photocatalyst, 5 mL of



**Figure 2.** Photoelectronic properties of Co-MOF: (a) UV–vis absorption spectra of  $H_4L$  and Co-MOF in solid state. (b) Cyclic voltammogram of Co-MOF. Measured conditions: Ag/AgCl was used as the reference electrode, glassy carbon was used as the working electrode, and a platinum plate was used as counter electrode. Solvent, DMF; electrolyte,  $Bu_4NPF_6$  (0.1 M); scan rate, 0.1 V/s. (c)  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  curve for Co-MOF. The band gap is calculated by the Kubelka–Munk method. (d) Mott–Schottky plots for Co-MOF. The frequency is in the range of 500–1500 Hz.

MeCN or N,N-dimethylacetamide (DMAc) as solvent, and sacrificial agent were added into a 55 mL glass bottle. The bottle was then sealed and bubbled with CO<sub>2</sub> for 20 min. The visible-light-driven CO<sub>2</sub> reduction experiment was performed under a white LED lamp ( $\lambda = 400-780$  nm, 100 mW/cm<sup>2</sup>) or 300 W Xe lamp ( $\lambda > 400$  nm). The photocatalytic gas products were detected on a gas chromatograph (GC9790, Fuli Analytical Instrument Co., Ltd.) equipped by TCD (H<sub>2</sub> gas) and FID (CO gas). The liquid product HCOO<sup>-</sup> was determined by using an ion chromatograph (882 Compact IC pro, Metrosep) equipped with Metrosep A supp 5 250/4.0 column according to reported works.<sup>9c,14</sup>

**Electrochemical Measurement.** Electrochemical measurement was finished on a CHI 660e electrochemical workstation. Cyclic voltammetry (CV) measurement for Co-MOF were performed with a three-electrode cell, in which glassy carbon as working electrode, Pt as auxiliary electrode, and Ag/AgCl as reference electrode; 0.1 M tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) was used as electrolyte in dry and degassed DMF solvent during the experiment. For ease of measurement, Co-MOF crystals were first ground for 2 min in a mortar. Co-MOF powder was achieved, and 3 mg was dispersed in 0.5 mL of DMF solvent and 10  $\mu$ L of Nafion. Ten of microliters dispersion was injected onto the glassy carbon electrode and dried under infrared lamp for 30 min. Mott-schottky plots for Co-MOF in different frequencies (500, 1000, and 1500 Hz, respectively) were measured by Impedance-Potential technique. The amplitude was set to be 10 mV.

# RESULTS AND DISCUSSION

**Crystal Structure and Characterization.** Co-MOF (LIFM-45), formulated as  $[Co_3(HL)_2\cdot 4DMF\cdot 4H_2O]$ , was synthesized by the reaction of cobalt nitrate hexahydrate and H<sub>4</sub>L (2'-amino-[1,1':4',1"-terphenyl]-3,3",5,5"- tetracarboxylic acid) ligand under solvothermal condition at 358 K for 24 h. Appropriate crystal was selected for single-crystal X-ray diffraction (SCXRD), and crystal structure was achieved from refinement (Table S1 and Figure 1). Co-MOF crystal crystallizes in monoclinic system, space group C2/c. The

asymmetric unit of Co-MOF consists of one and a half Co<sup>2+</sup> ions, one HL<sup>3-</sup> ligand, two uncoordinated DMF molecules and two water molecules. In the coordination environment of metal center, there are two kinds of Co<sup>2+</sup> ions (Figure 1a). Co1 is hexa-coordinated by oxygen atoms coming from six different HL<sup>3-</sup> ligands, showing octahedral geometry. While Co2 is penta-coordinated by five oxygen atoms, among which three are from monodentate coordination of carboxylate groups and the other two are from chelated coordination of carboxylate group, respectively. Each HL<sup>3-</sup> ligand acts as a  $\mu_6$ -bridge to link six  $Co^{2+}$  ions, in which two carboxylate groups adopt  $\mu_2$ - $\eta^1:\eta^1$ , the other one adopts  $\mu_1-\eta^2$  and the fourth one adopts  $\mu_1$ - $\eta^1$ -bridging mode, respectively (Figure 1b). In general, in the Co-MOF crystal structure, {Co<sub>3</sub>O<sub>14</sub>} coordinated clustercenters are formed. Through the linkage between Co<sup>2+</sup> ions and HL<sup>3-</sup> ligands based on these clusters, 3D-network porous structure is constructed (Figure 1c). Calculated by PLATON<sup>12</sup> program, the total void volume is determined to be 1803 Å, approximately 34% of the total crystal volume.

Elemental analysis (EA), thermogravimetric (TG) analysis, powder X-ray diffraction (PXRD) and Fourier transform infrared (FT-IR) spectrum were performed to characterize Co-MOF. Knowing from TG curve, it shows that the first 5.2% weight loss of Co-MOF happens before 100 °C, this should be ascribed to the loss of water molecules (Figure S2a). And the second weight loss (21.2%) starting from 150 °C should be attributed to loss of DMF molecules. The third weight loss happens above 430 °C resulted from the collapsion of framework and decomposition of organic ligand. This result is consistent with those of EA and crystal data. PXRD pattern showed that the diffraction peaks of as synthesized Co-MOF matches well with the simulated one in spite of difference in peak intensity (Figure S2b). Scanning electron microscope (SEM) measurement indicates the Co-MOF crystals are like

thick blades in morphology with several hundred micrometers in length (Figure S2c). To explore the porous property of Co-MOF, N<sub>2</sub> adsorption-desorption isotherms were measured at 77 K (Figure S3a). According to the data of adsorption isotherm of N2 for Co-MOF, it indicates of not simple microporous adsorption. Pore size distribution was calculated by DFT method (Figure S3c), which indicates that there are both micropores (around 0.9 nm) and mesopores (between 3 and 5 nm) in Co-MOF samples. It shows that the adsorption amount has not reached the platform in the N2 77 K adsorption experiment. We also simulate N2 sorption under 77 K by Materials Studio software<sup>15</sup> (Figure S4). The simulated isotherm shows the trend of multiple steps, which indicates the existence of different sizes of pores. In this N2 77 K sorption simulation, the adsorption amount reaches its maximum value at  $p/p_0 = 0.48$ , which is different from the experiment result. However, the maximum adsorption uptake amount is basically coincident between the calculated and experimental results. And in general, both the experiment and simulation indicate of microporous and mesoporous feature in Co-MOF, which suggests the potential photocatalysis in Co-MOF. Brunauer-Emmett–Teller (BET) area was determined to be 343  $m^2/g$ . After immersed in mixed DMF/H<sub>2</sub>O (4/2,v/v) solution for 12 h, the PXRD pattern is almost the same to that of as synthesized, which indicates the crystallinity of Co-MOF is remained (Figure S5). N<sub>2</sub> adsorption and desorption isotherms at 77 K were also measured. The highly similar adsorption behavior comparing to that of as-synthesized indicates the framework and porosity are remained (Figure S3b).

**Optical and Eletrochemical Properties.** The solid-state UV-vis absorption spectra of H<sub>4</sub>L ligand and Co-MOF were measured and compared (Figure 2). To H<sub>4</sub>L, the board absorption below 450 nm should be ascribed to the K and Bbands of aromatic groups. After coordination of cobalt and H<sub>4</sub>L ligand in Co-MOF, these bands exhibit a little red-shift. Meanwhile, significant d-d transition absorption of Co<sup>2+</sup> appears at around 560 nm. To investigate the potential semiconductive property of Co-MOF, band gap energy  $(E_{\sigma})$ was determined to be 2.95 eV by Tauc plot through Kubelka-Munk method (Figure 2c). This low  $E_{g}$  value is quite comparable to some other metal-oxygen cluster-based MOF materials.<sup>16</sup> Mott-schottky method was usually applied to estimate the flat band position.<sup>17</sup> Herein, the flat band position of Co-MOF could be determined to be -1.54 V vs. Ag/AgCl (-1.34 V vs. NHE, Figure 2d). As it suggested that the bottom of conduction band (CB) in n-type semiconductors was 0.10 V more negative than flat band position,<sup>18</sup> the CB of Co-MOF is estimated to be -1.44 V vs. NHE. Therefore, valence band (VB) is calculated to be +1.51 V.

**Visible-Light-Driven H**<sub>2</sub> **Production.** Visible-light-driven hydrogen evolution experiments were performed in mixed solvents at room temperature with Co-MOF as catalyst, Ru(bpy)<sub>3</sub>Cl<sub>2</sub> as PS, and TEOA as sacrificial agent. When 4 mg of PS, 4 mg of Co-MOF, and 1 mL of TEOA were added into 6 mL of MeCN/H<sub>2</sub>O (5/1, v/v) solvents, hydrogen product was detected under light irradiation and the activity was 190  $\mu$ mol/(g h) in the first 3 h (Table S2, entry S1). Without PS or light in the experiment, no any hydrogen product was observed, which emphasized the photocatalytic nature (Table S2, entries S2 and S3). And it should be noted that little hydrogen was found without catalyst, which was ascribed to PS (Table S2, entry S4). As solvents, PS, catalyst and sacrificial agent were all essential to the hydrogen evolution, a series of

experiments were performed to optimize the photocatalytic activity. And some results achieved in different solvents and ratios were shown and compared (Figure 3). No hydrogen was



**Figure 3.** Hydrogen evolution results for Co-MOF in different kinds and ratios of solvents after different times. The volume ratio of DMAc (N,N-dimethylacetamide), isopropanol or DMSO to  $H_2O$  was 5/1. The volume ratio of DMF or MeCN to  $H_2O$  was 4/2. The times below zero means the experiment was performed without light irradiation.

found when these experiments performed without light irradiation. The hydrogen amount produced from these experiments shows a similar changing trend which increases quickly in the first hours but gradually slows down and eventually reaches maximum. Totally in 12 h, the experiment performed in DMF/H<sub>2</sub>O (v/v, 4/2) produced the most amount of hydrogen (10.0  $\mu$ mol), while the one in DMSO/H<sub>2</sub>O (v/v, 5/1) produced the least amount (1.37  $\mu$ mol). The decreasing reaction ratio late period of experiment should be ascribed to the decomposition of PS because it could be activated by addition of supplementary PS (Figure S6). Therefore, the first period experiment in 3 h might be rational to compare the catalytic activity in different solvents (Table S2).

We found H<sub>2</sub>O content in solvents would affect the activity on producing hydrogen, for example in  $DMF/H_2O$ , when the ratio varied from 5.9/0.1 (mL/mL) to 4/2, the activity enhanced from 165 to 488  $\mu$ mol/(g h) gradually, then reduced to 127  $\mu$ mol/(g h) at ratio of 3/3 (Table S2, entries S7–S10). Similar phenomenon happened in MeCN/H2O and Isopropanol/H2O solvents, and they achieved the best activity (68 and 394  $\mu$ mol/(g h), respectively) at solvent ratio of 4/2 and 5/1, respectively (Table S2, entries S5 and S19). The amount of solution also affects the photocatalytic activity. When we doubled the reaction solution, activity was reduced to 45  $\mu$ mol/(g h), and enhanced activity (366  $\mu$ mol/(g h)) was found when we halved the solution (Table S2, entries S11 and S12). Furthermore, increasing the catalyst amount or decreasing the PS amount would lead to a reduced catalytic activity, while decreasing the catalyst could enhance the activity (Table S2, entries S13 to S15). The influence of all these factors on catalytic activity should be ascribed to the effect on light absorption and electron transition during the photocatalytic process.

To achieve better hydrogen amount, we also investigated the influence of catalyst pretreatment on catalytic activity. For example, if Co-MOF catalyst was ground for 3 min, the thick blade solid transformed to granular morphology and the size decreased from several hundred micrometers in length to several micrometers in diameter (Figure S2c, d). After grinding, PXRD pattern of the particles was consistent with the original Co-MOF, which indicated the grinding operation did not destroy the MOF structure (Figure S2b). The obtained powder was taken for photocatalysis and achieved activity of 595  $\mu$ mol/(g h) in 3 h with DMF/H<sub>2</sub>O (5/1, mL/mL) as solvents, and this value was much better than that without grinding before reaction (Table 1, entries 1 and 2). Nearly

Table 1. Hydrogen Evolution Results with Different Catalyst Pretreatment (ground for 3 min or soaked with the PS solution for 12 h) before Experiments<sup>a</sup>

entry	pretreatment	$DMF/H_2O~(mL/mL)$	activity ( $\mu$ mol/(g h)			
1		5/1	203			
2	grinding	5/1	595			
3	soaking	5/1	488			
4	grinding+soaking	5/1	951			
5	grinding+soaking	4/2	1102			
<sup>a</sup> Conditions: 4 mg of PS, 4 mg of Co-MOF, and 1 mL of TEOA.						

twice the advantage should be ascribed to the enhanced amount of accessible cobalt center on the solid surface. The exposed metal sites promote the direct contact of the catalytic components, resulting in more efficient electron transfer in the photocatalytic process and thus enhanced catalytic activity. With potential porous nature, soaking catalyst in PS and TEOA solution before light irradiation might be another method to provide a platform for efficient contact among catalytic components. We thus performed this soaking experiment and it exhibited large increment in catalytic activity (488  $\mu$ mol/(g h)) with comparison to that without soaking (Table 1, entry 3). Further, combined grinding and soaking strategy leads to a nearly superimposed influence on catalytic activity (951  $\mu$ mol/(g h)). Through adjusting the appropriate solvent ratio, Co-MOF achieved its highest catalytic activity of 1102  $\mu$ mol/(g h) DMF/H<sub>2</sub>O (4 mL/2 mL) solvents during 3 h photocatalytic hydrogen evolution experiment (Table 1, entry 5). SEM image of Co-MOF powder after photocatalytic reaction indicated of maintained granular particle morphology (Figure S2e). And the unchanged PXRD pattern after catalysis indicates of good crystallinity in comparison to original Co-MOF (Figure S2b). To evaluate the photostability of Co-MOF, we have performed cycle experiments. The second and third cycle performances of Co-MOF were 1213 and 1017  $\mu$ mol/(g h), respectively, which indicates good photostability of Co-MOF catalyst.

To manifest the design of photocatalyst including both PS and catalyst unit, we investigated the photocatalytic CO<sub>2</sub> reduction of Co-MOF without additional PS (Table 2). All of the experiment mixture was purged with CO<sub>2</sub> for 20 min before photoreaction to remove the air. The products were determined by GC chromatography (CO, H<sub>2</sub>) and ion chromatography (HCOO<sup>-</sup>). When 4 mg of Co-MOF photocatalyst, 5 mL of MeCN solvent, and 0.1 g of BNAH (1-benzyl-1,4-dihydronicotinamide) were taken for the experiment, it achieved 1.9  $\mu$ mol of HCOO<sup>-</sup> and 0.05  $\mu$ mol of CO in 6 h irradiation with a LED lamp, whereas no hydrogen gas was found. It exhibited selective catalysis nature, and the selectivity of HCOO<sup>-</sup>/CO was up to 38. Correspondingly, the catalytic activity of Co-MOF for producing CO and HCOO<sup>-</sup> was 1.9 and 78.2  $\mu$ mol/(g h), respectively (Table 2, entry 3). It

Table 2. Results of Visible-Light-Driven Photocatalytic  $CO_2$ Reduction for Co-MOF in 6 h<sup>a</sup>

			$\mu mol/(g h)$		
entry	sacrificial agent	solvent	СО	$H_2$	HCOO <sup>-</sup>
$1^{b}$	0.1 g of BIH	MeCN	0	0	0
2 <sup>b</sup>	1 mL of TEOA	MeCN	0	0	0
3 <sup>b</sup>	0.1 g of BNAH	MeCN	1.9	0	78.2
4 <sup><i>c</i></sup>	0.1 g of BNAH	MeCN	1.1	5.9	264.4
5 <sup>°</sup>	0.1 g of BNAH	DMAc	1.4	7.5	456.0
6 <sup>d</sup>	0.1 g of BNAH	DMAc	0	0	0

<sup>*a*</sup>Conditions: catalyst (Co-MOF, 4 mg), solvent (5 mL). <sup>*b*</sup>Irradiated by LED lamp. <sup>*c*</sup>Irradiated by 300 W Xe lamp. <sup>*d*</sup>Without light irradiation.

should be noted that the kind of sacrificial agent played an important role in catalytic system. When BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole) or TEOA was used as sacrificial agent, no gas or liquid product was observed. Further, when the light source changed to 300 W Xe lamp, the amount of HCOO<sup>-</sup> increased up to 264.4  $\mu$ mol/(g h), whereas CO production decreased to 1.1  $\mu$ mol/(g h) (Table 2, entry 4). Comparatively, some hydrogen gas was also found. The solvent affected the catalytic activity as well, because the products exhibited a large enhancement when DMAc was used as solvent (Table 2, entry 5). The catalytic activity for HCOO<sup>-</sup> was 456.0  $\mu$ mol/(g h) and the selectivity of HCOO<sup>-</sup>/CO and HCOO<sup>-</sup>/H<sub>2</sub> was high up to 326 and 61, respectively. The value of 456.0  $\mu$ mol/(g h) was comparable to some similar metal–oxygen cluster based MOF catalysts.<sup>9</sup>

In order to testify the origin of carbon source for HCOO<sup>-</sup> product, we carried out <sup>13</sup>C isotope labeling experiments. The experimental condition is similar to Entry 4 in Table 2, except that CH<sub>3</sub>CN is changed to CD<sub>3</sub>CN and <sup>12</sup>CO<sub>2</sub> to <sup>13</sup>CO<sub>2</sub>. After the photocatalytic reaction, we tested the <sup>13</sup>C NMR of the solution, and found that the signal of H<sup>13</sup>COO<sup>-</sup> was observed at 169.8 ppm, and the signals at 168.2 and 159.4 ppm should be attributed to <sup>13</sup>CO<sub>3</sub><sup>2-</sup> and H<sup>13</sup>CO<sub>3</sub><sup>-</sup> (Figure S7).

We further investigated the photocatalytic mechanism of Co-MOF for H<sub>2</sub> evolution and CO<sub>2</sub>, photophysical properties were measured. To the best of our knowledge, when  $[\text{Ru}(\text{bpy})_3]^{2+}$  was used as photosensitizer, its excited state,  $[\text{Ru}(\text{bpy})_3]^{2+*}$ , might be either reductively or oxidatively quenched by an electron donor or acceptor resulting in a decreasing intensity in fluorescence.<sup>19</sup> In our hydrogen evolution, TEOA used as electron donor agent, but it could not reductively quench  $[\text{Ru}(\text{bpy})_3]^{2+*}$  excited state, because no reduction in fluorescence was observed when TEOA was added into  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  solution (Figure S8). Therefore, the photocatalytic hydrogen evolution might be ascribed to oxidatively quenching mechanism.

To confirm this assumption, we investigated the thermodynamics feasibility of the photoinduced electron transition (PET) that happened from  $Ru(bpy)_3Cl_2$  to Co-MOF. First, a cyclic voltammetry experiment of Co-MOF was carried out in drying and degassed DMF solution including 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>. Co-MOF powder was dropped on surface of the working electrode and dried under infrared lamp before measurement. The result showed an irreversible and a reversible reduction peaks at -0.83 and -0.96 V vs Ag/AgCl, respectively (Figure 2b). These two peaks should be ascribed to the single electron transfer from  $[Co^{II}Co^{II}Co^{II}]$  to  $[Co^{IC}O^{II}Co^{II}]$  and from  $[Co^{IC}O^{II}Co^{II}]$  to  $[Co^{IC}O^{II}Co^{II}]$ .

energy change ( $\Delta G^0$ ) could be estimated by the Rehm–Weller equation<sup>21</sup>

$$\Delta G^{\circ} = E_{\rm ox} - E_{\rm red} - E_{\rm T} - e^2 / \varepsilon d \tag{1}$$

Herein,  $E_{\rm ox}$  should be the oxidation potential of Ru(by)<sub>3</sub><sup>2+</sup> (+1.53 V vs NHE),<sup>19</sup>  $E_{\rm red}$  was the reduction potential of Co-MOF (-0.63 V vs NHE), and  $E_{\rm T}$  was the <sup>3</sup>MLCT excited state estimated to be 2.20 V from tangent to the high-energy side of emission spectrum of Ru(by)<sub>3</sub><sup>2+</sup> (Figure S5). The term  $e^2/\epsilon d$ could be negligible, because the dielectric constant ( $\epsilon$ ) of the polar solvents (such as, DMF and H<sub>2</sub>O) was quite large. Therefore, the  $\Delta G^0$  value was calculated to be -0.04 V< 0, which indicated that PET progress from Ru(bpy)<sub>3</sub><sup>2+</sup> to Co-MOF was thermodynamically favorable. Then the photocatalytic mechanism for hydrogen evolution could be described as following (Figure 4a). [Ru(bpy)<sub>3</sub>]<sup>2+</sup> is excited under light



Figure 4. Proposed photocatalytic mechanisms of (a) hydrogen evolution and (b)  $CO_2$  reduction for Co-MOF under visible-light irradiation.

irradiation and reaches its excited state  $[(Ru(bpy)_3]^{2+\ast}$ . The excited state is then quenched by Co-MOF catalyst, in which  $[Ru(bpy)_3]^{2+\ast}$  is oxidized to  $[Ru(bpy)_3]^{3+}$  and the  $[Co^{II}Co^{II}Co^{II}]$  center is reduced to  $[Co^{IC}O^{II}Co^{II}]$ . Thereafter,  $[Ru(bpy)_3]^{3+}$  is reduced by TEOA to reproduce  $[Ru(bpy)_3]^{2+}$ , and the reductive state  $[Co^{II}Co^{II}Co^{II}]$  was for proton reduction.

When no additional PS is used in photocatalytic  $CO_2$  reduction process, the organic linker  $HL^{3-}$  ligand in Co-MOF acts an antenna for absorption of visible light (Figure 4b). Under irradiation,  $HL^{3-}$  ligand achieves its excited state and transfers electron to Co–O cluster.  $[Co^{II}Co^{II}]$  center obtains the electron and is reduced to  $[Co^{IC}O^{II}]$  for reducing  $CO_2$  to CO or  $HCOO^-$  in the presence of BNAH sacrificial agent. BNAH acts as electron donor to ensure the favorable electron transition during the photoreaction.

#### CONCLUSION

The first trinuclear Co-MOF is synthesized and performed for photocatalytic hydrogen evolution and  $CO_2$  reduction. This Co-MOF exhibits its semiconductive behavior and the band gap is determined to be 2.95 eV. Various experiment conditions were optimized and it achieved the best activity (1102  $\mu$ mol/(g h)) when catalyst was ground and then soaked

in PS solution before photoreaction. As integrated photocatalyst of Co-MOF, it includes PS and catalyst units and thus provides a moderate activity for  $CO_2$  reduction. Proposed mechanisms indicate the proton and  $CO_2$  reduction results from the redox cycle of trinuclear  $[Co^{II}Co^{II}]$  cluster. Though the activity is to be enhanced, we believe that the present study has addressed the importance of noble-metal-free cluster MOFs for further artificial photosynthesis.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01265.

IR, TG, PXRD, SEM, and other figures for testifying the photocatalytic process (PDF)

#### Accession Codes

CCDC 1834360 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) (a) Qi, J.; Zhao, K.; Li, G.; Gao, Y.; Zhao, H.; Yu, R.; Tang, Z. Multi-shelled CeO<sub>2</sub> hollow microspheres as superior photocatalysts for water oxidation. *Nanoscale* **2014**, *6*, 4072–4077. (b) Zhao, K.; Zhao, S.; Qi, J.; Yin, H.; Gao, C.; Khattak, A. M.; Wu, Y.; Iqbal, A.; Wu, L.; Gao, Y.; Yu, R.; Tang, Z. Cu<sub>2</sub>O clusters grown on TiO<sub>2</sub> nanoplates as efficient photocatalysts for hydrogen generation. *Inorg. Chem. Front.* **2016**, *3*, 488–493. (c) Gao, C.; Meng, Q.; Zhao, K.; Yin, H.; Wang, D.; Guo, J.; Zhao, S.; Chang, L.; He, M.; Li, Q.; Zhao, H.; Huang, X.; Gao, Y.; Tang, Z. Co<sub>3</sub>O<sub>4</sub> hexagonal platelets with controllable facets enabling highly efficient visible-light photocatalytic reduction of CO<sub>2</sub>. *Adv. Mater.* **2016**, *28*, 6485–6490.

(2) (a) Meyer, K.; Ranocchiari, M.; van Bokhoven, J. A. Metal organic frameworks for photo-catalytic water splitting. *Energy Environ. Sci.* **2015**, *8*, 1923–1937. (b) Wang, W.; Xu, X.; Zhou, W.; Shao, Z. Recent progress in metal-organic frameworks for applications in electrocatalytic and photocatalytic water splitting. *Adv. Sci.* **2017**, *4*, 1600371. (c) He, H.; Perman, J. A.; Zhu, G.; Ma, S. Metal-organic frameworks for CO<sub>2</sub> chemical transformations. *Small* **2016**, *12*, 6309–6324. (d) Chen, Y.; Wang, D.; Deng, X.; Li, Z. Metal-organic frameworks (MOFs) for photocatalytic CO<sub>2</sub> reduction. *Catal. Sci. Technol.* **2017**, *7*, 4893–4904. (e) Zhang, Y.; Guo, J.; Shi, Y.; Zhu, Y.; Hou, K.; Zheng, Y.; Tang, Z. Tunable chiral metal organic frameworks toward visible light-driven asymmetric catalysis. *Sci. Adv.* **2017**, *3*,

e1701162. (f) Liao, W.-M.; Zhang, J.-H.; Wang, Z.; Yin, S.-Y.; Pan, M.; Wang, H.-P.; Su, C.-Y. Post-synthetic exchange (PSE) of UiO-67 frameworks by Ru/Rh half-sandwich units for visible-light-driven  $H_2$  evolution and CO<sub>2</sub> reduction. *J. Mater. Chem. A* **2018**, *6*, 11337–11345.

(3) (a) Wang, C.; deKrafft, K. E.; Lin, W. Pt nanoparticles@ photoactive metal-organic frameworks: efficient hydrogen evolution via synergistic photoexcitation and electron injection. J. Am. Chem. Soc. 2012, 134, 7211–7214. (b) Wen, M.; Mori, K.; Kamegawa, T.; Yamashita, H. Amine-functionalized MIL-101(Cr) with imbedded platinum nanoparticles as a durable photocatalyst for hydrogen production from water. Chem. Commun. 2014, 50, 11645–11648. (c) Pullen, S.; Ott, S. Photochemical hydrogen production with metal-organic frameworks. Top. Catal. 2016, 59, 1712–1721. (d) Hou, C.-C.; Li, T.-T.; Cao, S.; Chen, Y.; Fu, W.-F. Incorporation of a [Ru(dcbpy)(bpy)<sub>2</sub>]<sup>2+</sup> photosensitizer and a Pt(dcbpy)Cl<sub>2</sub> catalyst into metal-organic frameworks for photocatalytic hydrogen evolution from aqueous solution. J. Mater. Chem. A 2015, 3, 10386–10394.

(4) (a) Rimoldi, M.; Howarth, A. J.; DeStefano, M. R.; Lin, L.; Goswami, S.; Li, P.; Hupp, J. T.; Farha, O. K. Catalytic zirconium/ hafnium-based metal-organic frameworks. *ACS Catal.* **2017**, *7*, 997–1014. (b) Chinapang, P.; Okamura, M.; Itoh, T.; Kondo, M.; Masaoka, S. Development of a framework catalyst for photocatalytic hydrogen evolution. *Chem. Commun.* **2018**, *54*, 1174–1177.

(5) Kataoka, Y.; Sato, K.; Miyazaki, Y.; Masuda, K.; Tanaka, H.; Naito, S.; Mori, W. Photocatalytic hydrogen production from water using porous material  $[Ru_2(p-BDC)_2]_n$ . *Energy Environ. Sci.* **2009**, *2*, 397.

(6) Feng, Y.; Chen, C.; Liu, Z.; Fei, B.; Lin, P.; Li, Q.; Sun, S.; Du, S. Application of a Ni mercaptopyrimidine MOF as highly efficient catalyst for sunlight-driven hydrogen generation. *J. Mater. Chem. A* **2015**, *3*, 7163–7169.

(7) Shi, D.; Zheng, R.; Sun, M. J.; Cao, X.; Sun, C. X.; Cui, C. J.; Liu, C. S.; Zhao, J.; Du, M. Semiconductive copper(I)-organic frameworks for efficient light-driven hydrogen generation without additional photosensitizers and cocatalysts. *Angew. Chem., Int. Ed.* **2017**, *56*, 14637–14641.

(8) (a) Zhang, T.; Lin, W. Metal-organic frameworks for artificial photosynthesis and photocatalysis. *Chem. Soc. Rev.* 2014, 43, 5982–5993. (b) Shen, L.; Liang, R.; Wu, L. Strategies for engineering metal-organic frameworks as efficient photocatalysts. *Chin. J. Catal.* 2015, 36, 2071–2088. (c) Wang, S.; Wang, X. *Small* 2015, 11, 3097–3112. (d) Liao, W.-M.; Zhang, J.-H.; Hou, Y.-J.; Wang, H.-P.; Pan, M. Visible-light-driven CO<sub>2</sub> photo-catalytic reduction of Ru(II) and Ir(III) coordination complexes. *Inorg. Chem. Commun.* 2016, 73, 80–89.

(9) (a) Fu, Y.; Sun, D.; Chen, Y.; Huang, R.; Ding, Z.; Fu, X.; Li, Z. An amine-functionalized titanium metal-organic framework photocatalyst with visible-light-induced activity for  $CO_2$  reduction. *Angew. Chem., Int. Ed.* **2012**, *51*, 3364–3367. (b) Sun, D.; Fu, Y.; Liu, W.; Ye, L.; Wang, D.; Yang, L.; Fu, X.; Li, Z. Studies on photocatalytic  $CO_2$ reduction over NH<sub>2</sub>-Uio-66(Zr) and its derivatives: towards a better understanding of photocatalysis on metal-organic frameworks. *Chem.* -*Eur. J.* **2013**, *19*, 14279–14285. (c) Wang, D.; Huang, R.; Liu, W.; Sun, D.; Li, Z. Fe-based MOFs for photocatalytic  $CO_2$  reduction: role of coordination unsaturated sites and dual excitation pathways. *ACS Catal.* **2014**, *4*, 4254–4260.

(10) (a) Guo, Z.; Cheng, S.; Cometto, C.; Anxolabehere-Mallart, E.; Ng, S. M.; Ko, C. C.; Liu, G.; Chen, L.; Robert, M.; Lau, T. C. Highly efficient and selective photocatalytic CO<sub>2</sub> Reduction by iron and cobalt quaterpyridine complexes. *J. Am. Chem. Soc.* **2016**, *138*, 9413– 9416. (b) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. Splitting water with cobalt. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238–7266. (c) Di Giovanni, C.; Gimbert-Surinach, C.; Nippe, M.; Benet-Buchholz, J.; Long, J. R.; Sala, X.; Llobet, A. Dinuclear cobalt complexes with a decadentate ligand scaffold: hydrogen evolution and oxygen reduction catalysis. *Chem. - Eur. J.* **2016**, *22*, 361–369. (d) Ouyang, T.; Huang, H. H.; Wang, J. W.; Zhong, D. C.; Lu, T. B. A dinuclear cobalt cryptate as a homogeneous photocatalyst for highly selective and efficient visible-light driven  $CO_2$  reduction to CO in  $CH_3CN/H_2O$  solution. Angew. Chem., Int. Ed. **2017**, 56, 738–743.

(11) (a) Wang, S.; Yao, W.; Lin, J.; Ding, Z.; Wang, X. Cobalt imidazolate metal-organic frameworks photosplit  $CO_2$  under mild reaction conditions. *Angew. Chem., Int. Ed.* **2014**, *53*, 1034–1038. (b) Wang, Y.; Huang, N.-Y.; Shen, J.-Q.; Liao, P.-Q.; Chen, X.-M.; Zhang, J.-P. Hydroxide ligands cooperate with catalytic centers in metal-organic frameworks for efficient photocatalytic  $CO_2$  reduction. *J. Am. Chem. Soc.* **2018**, *140*, 38–41.

(12) Spek, A. L. Single-crystal structure validation with the program. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

(13) (a) Cai, J.; Wang, H.; Wang, H.; Duan, X.; Wang, Z.; Cui, Y.; Yang, Y.; Chen, B.; Qian, G. An amino-decorated NbO-type metalorganic framework for high  $C_2H_2$  storage and selective  $CO_2$  capture. *RSC Adv.* **2015**, *5*, 77417–77422. (b) Liao, W.-M.; Zhang, J.-H.; Yin, S.-Y.; Lin, H.; Zhang, X.; Wang, J.; Wang, H.-P.; Wu, K.; Wang, Z.; Fan, Y.-N.; Pan, M.; Su, C.-Y. Tailoring exciton and excimer emission in an exfoliated ultrathin 2D metal-organic framework. *Nat. Commun.* **2018**, *9*, 2401.

(14) Zhang, S.; Li, L.; Zhao, S.; Sun, Z.; Luo, J. Construction of interpenetrated ruthenium metal-organic frameworks as stable photocatalysts for  $CO_2$  reduction. *Inorg. Chem.* **2015**, *54*, 8375–8379. (15) *Materials Studio Release Notes*, Release 6.1.0; Accelrys Software,

Inc.: San Diego, 2012.
(16) (a) Silva, C. G.; Corma, A.; García, H. Metal-organic frameworks as semiconductors. J. Mater. Chem. 2010, 20, 3141.
(b) Hendon, C. H.; Tiana, D.; Fontecave, M.; Sanchez, C.; D'Arras, L.; Sassoye, C.; Rozes, L.; Mellot-Draznieks, C.; Walsh, A.

Engineering the optical response of the titanium-MIL-125 metalorganic framework through ligand functionalization. *J. Am. Chem. Soc.* **2013**, 135, 10942–10945.

(17) Ramírez-Ortega, D.; Meléndez, A. M.; Acevedo-Pena, P.; González, I.; Arroyo, R. Semiconducting properties of  $ZnO/TiO_2$  composites by electrochemical measurements and their relationship with photocatalytic activity. *Electrochim. Acta* **2014**, *140*, 541–549.

(18) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-based photocatalytic hydrogen generation. *Chem. Rev.* **2010**, *110*, 6503–6570.

(19) Narayanam, J. M.; Stephenson, C. R. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* 2011, 40, 102–113.

(20) Mandal, S.; Shikano, S.; Yamada, Y.; Lee, Y. M.; Nam, W.; Llobet, A.; Fukuzumi, S. Protonation equilibrium and Hydrogen Production by a dinuclear cobalt-hydride complex reduced by cobaltocene with trifluoroacetic acid. *J. Am. Chem. Soc.* **2013**, *135*, 15294–15297.

(21) Hirahara, M.; Masaoka, S.; Sakai, K. Syntheses, characterization, and photochemical properties of amidate-bridged Pt(bpy) dimers tethered to  $\text{Ru}(\text{bpy})_3^{2+}$  derivatives. *Dalton Trans.* **2011**, 40, 3967–3978.