

# Encapsulating a Co(II) Molecular Photocatalyst in Metal–Organic Framework for Visible-Light-Driven H<sub>2</sub> Production: Boosting Catalytic Efficiency via Spatial Charge Separation

Zhe Li, Juan-Ding Xiao, and Hai-Long Jiang\*

Hefei National Laboratory for Physical Sciences at the Microscale, CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China

**Supporting Information** 

**ABSTRACT:** The photodriven  $H_2$  generation from water splitting, providing a high-performance energy source, has been recognized to be a promising pathway for solar energy conversion. However, the efficient charge separation for photocatalysts remains a critical issue. In this work, we have rationally encapsulated a Co(II) molecular photcatalyst,  $[Co^{II}(TPA)CI][CI]$  (TPA = tris(2-pyridylmethyl)-amine), inside the cages of a metal—organic framework (MOF) photosensitizer, MIL-125-NH<sub>2</sub>, for visible-light-driven H<sub>2</sub> production. This noble-metal-free composite photocatalyst facilitates the photo-induced charge transfer from MIL-125-NH<sub>2</sub> to the Co(II) complex and greatly improves the spatial charge separation, thus significantly boosting the photocatalytic efficiency of H<sub>2</sub> production. In addition, MIL-125-NH<sub>2</sub> behaves as a host matrix to achieve hetrogenization of the Co(II) complex, and thus, the composite can be well-recycled.



**KEYWORDS:** metal-organic framework, microporous materials, Co(II) complex, photocatalytic H<sub>2</sub> production, charge separation

#### **1. INTRODUCTION**

The shortage of fossil fuels and environmental pollution are emerging as challenging issues we face nowadays. It is imperative to develop high-performance clean energy technologies as alternatives. One promising solution is to immobilize solar energy in chemical bonds of energy-dense molecules, among which  $H_2$  is an ideal candidate as it is a kind of high energy and clean fuel.<sup>1</sup> To actualize  $H_2$  evolution from water splitting, it is necessary to develop a cost-effective catalyst system which not only integrates visible-light harvesting, charge transfer, and catalysis together but also demonstrates effectiveness and durability under the photocatalytic conditions.<sup>2</sup>

Traditional photocatalytic water splitting catalysts such as molecular catalysts (e.g., metal complexes) and inorganic semiconductors have their respective advantages but suffer from some severe drawbacks. Although some kinds of metal complex molecular catalysts (e.g., cobalt and iron complexes) exhibit good photocatalytic performances, expensive photosensitizers are required in addition to their homogeneous nature, and thus, they cannot be recycled.<sup>3</sup> The inorganic semiconductors have limited tailorability and quite long transport distance (through bulk semiconductor to surface) of the photogenerated charge carriers, which causes the inevitable electron—hole volume recombination, thus reducing  $H_2$  generation efficiency.

To achieve efficient charge separation, metal-organic frameworks (MOFs), emerging as a class of crystalline porous materials with great structural diversity and tailorability and also potential applications in many fields,<sup>4,5</sup> have primarily shown their advantages in photocatalyisis.<sup>6</sup> The high porosity of MOFs would greatly suppress the classical volume recombination of electron-hole, thanks to the short transport distance of charge carriers to the pore surface throughout the structure for reactions; the crystalline nature also avoids the defects that might produce recombination centers.<sup>6,7</sup> Despite this, the photogenerated electrons and holes are prone to recombine in a single MOF. Therefore, the classical electron acceptors, noble metals such as Pt, have been introduced to MOFs for boosting charge separation and photocatalytic activity.<sup>8</sup> Due to the high cost and limited reserves of Pt, cost-effective cocatalysts would be preferred. In this context, the encapsulation of base metal complexes as catalytically active sites inside MOFs with matched size and energy levels for electron transfer would be an ideal choice. However, to the best our knowledge, the related report remains very limited.<sup>2b,9</sup>

In this work, a Co(II) complex,  $[Co^{II}(TPA)CI][CI]$  (TPA = tris(2-pyridylmethyl)amine), has been encapsulated into the

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cages of a visible-light photoactive MOF, MIL-125-NH<sub>2</sub>  $(Ti_8O_8(OH)_4(BDC-NH_2)_6$ , BDC-NH<sub>2</sub>= 2-aminobenzene-1,4-dicarboxylate),<sup>6g,10</sup> via a "ship-in-a-bottle" synthetic strategy to afford a composite catalyst,  $[Co^{II}(TPA)CI][CI]@MIL-125-NH_2$ , simply denoted as  $Co(II)@MIL-125-NH_2$  (Scheme 1). In

Scheme 1. Schematic Illustration of the "Ship-in-a-Bottle" Synthesis of Co(II)@MIL-125-NH<sub>2</sub>



the composite, the MOF with visible-light responsive linker facililates prompt light harvesting, as well as size and energy level-matching Co(II) complex as guests encapsulated in the MOF cages accumulate electrons, which are accessible to protons and electron donors. In this way, the spatial separation of electrons and holes has been effectively realized for highly efficient proton reduction. Moreover, the Co(II) complex is heterogenized by the MOF cage encapsulation. As a result, this composite catalyst exhibits several orders of magnitude higher activity than both single components and their physical mixture, and the catalyst also possesses excellent recyclability in the visible-light driven H<sub>2</sub> production from water splitting.

The band gap of MIL-125-NH<sub>2</sub> was reported to be 2.6 eV. The redox levels are 2.0 V and -0.6 V vs. NHE for HOMO and LUMO, respectively.<sup>11</sup> It is almost accepted that the HOMO is mainly localized at the organic linker while LUMO resides primarily at the metal-oxo cluster in MOFs.<sup>8d,11</sup> Meanwhile, the HOMO and LUMO levels of BDC-NH<sub>2</sub> are 0.7 V and -1.9 V vs NHE, respectively.<sup>6d</sup> To fabricate a composite system, in which MIL-125-NH<sub>2</sub> or BDC-NH<sub>2</sub> acts as a photosensitizer while the metal complex accepts electrons for feasible H<sub>2</sub> production, the LUMO of active metal complex should be located between the LUMO of MIL-125-NH<sub>2</sub> (or BDC-NH<sub>2</sub>) and  $H^+/H_2$  potentials (Scheme 2a). With this in mind, a Co(II) complex, [Co<sup>II</sup>(TPA)Cl][Cl], has been synthesized,<sup>12</sup> and its cyclic voltammogram curve shows its first reduction peak of approximately -0.8 V vs.  $Fc^{+/0}$  that is assignable to the  $Co^{II/I}$ reduction peak (Figure S1), and thus, the potential of Co(II) complex is -0.4 V vs NHE, falling between the LUMO energy level of MIL-125-NH<sub>2</sub> (also BDC-NH<sub>2</sub>) and the  $H^+/H_2$ potential, which theoretically satisfies the above requirement. It is anticipated that there are two possible routes for electron transfer: (1) the photoelectrons from the ligand BDC-NH<sub>2</sub> to Ti-oxo cluster, followed by the Co(II) complex, prior to the proton reduction (Scheme 2b); (2) the photoelectrons from the ligand BDC-NH<sub>2</sub> directly to the Co(II) complex for reducing protons to H<sub>2</sub> (Scheme 2c). Based on the above considerations, this composite catalyst with matching energy levels of its components is feasible for photocatalytic H<sub>2</sub> production from water.

The Co(II) complex, possessing larger sizes than the pore opening of MIL-125-NH<sub>2</sub>, was assembled inside the MOF cages (Scheme 1). Typically, the flexible TPA ligands were able to diffuse into the MOF cages, followed by the introduction of Co(II) cations, leading to the formation of the rigid Co(II) complex,<sup>12</sup> which was confirmed by <sup>1</sup>H NMR and mass spectra (Figure S2, S3). Due to its rigidity and relatively large size (10 Å), falling between the pore window (6 Å) and cage diameter (12 Å), the complex should be well-entrapped inside the MOF

Scheme 2. (a) Schematic Diagram of Redox Potentials of MIL-125-NH<sub>2</sub>, BDC-NH<sub>2</sub>, the Co(II) Complex and  $H^+/H_2$ . Proposed Electron Transfer Route (b) between MIL-125-NH<sub>2</sub> and the Co(II) Complex; and (c) between BDC-NH<sub>2</sub> and the Co(II) Complex



cages, resulting in the successful synthesis of  $Co(II)@MIL-125-NH_2$  (Scheme 1).

By introducing different amounts of TPA and  $CoCl_2 \cdot 6H_2O$  precursors, the contents of the Co(II) complex in the composite can be facilely tuned to afford Co1@MIL-125-NH<sub>2</sub>, Co2@MIL-125-NH<sub>2</sub>, and Co3@MIL-125-NH<sub>2</sub>, respectively, containing 1.70%, 1.93%, and 0.97% Co contents, based on ICP results (Table S1). Unexpectedly, a limited amount of Co(II) complex can be included in the MOF. Too many precursors introduced into the synthetic systems simutaneously might cause the congestion around the pore windows of the MOF, leading to even a lower loading amount of Co(II) complex (Table S1).

### 2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation. All chemicals were purchased from commercial sources and used without further purification otherwise mentioned. Deionized water with the specific resistance of 18.2 M $\Omega$  cm was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Cyclic voltammetry was performed using a CHI 760E electrochemical analyzer (CH Instruments, Inc., Shanghai). <sup>1</sup>H NMR was recorded on a Bruker AC-400 FT (400 MHz) using TMS as internal reference. Mass spectrum was performed on Bruker Daltonics Autoflex mass spectrometry using DCTB as matrix dissolved by CH<sub>2</sub>Cl<sub>2</sub>. The contents of Co in the composites were determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Powder X-ray diffraction (XRD) studies were carried out on a Japan Rigaku SmartLab rotation anode X-ray diffractometer or Holland X'Pert PRO fixed anode X-ray diffractometer equipped with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda$  = 1.54 Å). The N<sub>2</sub> sorption isotherms were measured by using an automatic volumetric adsorption equipment (Micrometritics ASAP 2020). Prior to N<sub>2</sub> adsorption/desorption measurement, the samples were degassed overnight at 423 K under vacuum. UV-vis diffuse reflectance data were recorded in a Shimadzu Solid Spec-3700 spectrophotometer, and a white standard of BaSO<sub>4</sub> was used as a reference. Steady-state photoluminescence (PL) emission spectra were obtained over an LS-55 fluorescence spectrometer made by PerkinElmer (The experiments were performed by using the suspensions of 1 mg of a solid in 10 mL of CH<sub>3</sub>CN). Scanning electron microscopy (SEM) images were taken with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). The HAADF-STEM observation and elemental mapping analysis were conducted by using a JEM-ARM 200F scanning transmission electron microscope, with a Gatan Quantum 965 spectrometer for electron energy loss spectroscopy (EELS) analysis. The catalytic reaction products were analyzed and identified by gas chromatography (Shimadzu GC-2014).

**2.2. Preparation of Samples.** *2.2.1. Preparation of MIL-125-NH*<sub>2</sub>. The synthesis of MIL-125-NH<sub>2</sub> was performed by dissolving 2.86 g (15.8 mmol) of 2-aminoterephthalic acid in a mixture of 40 mL of dry *N*,*N'*-dimethylformamide (DMF) and 10 mL of dry methanol at room temperature. Then 2.86 mL (9.7 mmol) of titanium isopropoxide was introduced and the mixture was placed into a Teflon-lined stainless steel autoclave, which was heated at 110 °C for 72 h. After the mixture was cooled to room temperature, the product was filtered and washed with DMF to give yellow solid. The obtained solid was dispersed in DMF and kept under stirring overnight (50 mL of DMF per 1 g of product) to remove residual organic ligand. Then, the same procedure was repeated twice using methanol instead of DMF to exchange the DMF within the pores. The solid was finally dried under air at 100  $^{\circ}$ C.

2.2.2. Preparation of [Co<sup>II</sup>(TPA)CI][CI]. The Co(II) complex was prepared by stirring methanolic solution containing TPA (0.48 mmol) with CoCl<sub>2</sub>·6H<sub>2</sub>O (0.48 mmol) for 1 h.<sup>12</sup> The successful synthesis of the Co(II) complex was confirmed by <sup>1</sup>H NMR and mass spectra (Figure S2, S3).

2.2.3. Preparation of Co(II)@MIL-125-NH<sub>2</sub>. For the synthesis of Co1@ MIL-125-NH2, typically, 290.4 mg of MIL-125- $NH_2$  (174.2  $\mu$ mol) was suspended in 50 mL of methanol in a conical flask. Then 69.7 mg of TPA (0.24 mmol) was added under continuous stirring. The mixture was stirred overnight for the encapsulation of TPA, subsequently the suspension was filtered, washed with methanol for three times to remove the TPA ligand adsorbed on the outer surface of the MOF. Upon further suspending the obtained wet solid in 50 mL of methanol, 57.1 mg of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.24 mmol) was introduced under continuous stirring. After 3 h of stirring for the incorporation of Co(II) and the coordination between Co(II) and TPA ligand, the wet solid was filtered again and washed with methanol for three times to remove the Co complex possibly formed on the outer surface. The assynthesized Co1@MIL-125-NH2 composite photocatalyst was dried under vacuum at 50 °C. The Co2@ MIL-125-NH2 and Co3@MIL-125-NH<sub>2</sub> were prepared following the same procedure except changing the amounts of both TPA ligand and CoCl<sub>2</sub>·6H<sub>2</sub>O as listed in Table S1.

**2.3. Cyclic Voltammetry Measurement for the Co(II) Complex.** Cyclic voltammetry was performed on a conventional three electrode system. Glassy carbon electrode (GCE, 5 mm in diameter), an Ag/AgCl with saturated KCl, and a Pt wire were used as the working electrode, reference and counter electrode, respectively. The electrolyte solution was made up of CH<sub>3</sub>CN (working as solvent) and 0.1 M  $[(n-Bu)_4N][PF_6]$  (working as the supporting electrolyte). The solution was saturated with N<sub>2</sub> by purging with N<sub>2</sub> for 15 min prior to experiment.

2.4. Photocatalytic H<sub>2</sub> Production. In a typical experiment, Co(II) complex@ MIL-125-NH<sub>2</sub> (6.0 mg) was suspended in a mixture of acetonitrile (CH<sub>3</sub>CN, 27.6 mL), triethanolamine (TEOA, 1.4 mL), and deionized water (1 mL) and then underwent ultrasonication for 5 min to obtain a homogeneous suspension. Afterward the yellow suspension was transferred to a photoreactor (total volume approximately 100 mL) degassed by bubbling  $N_2$  for approximately 30 min during stirring. The sample was irradiated by visible light with a 300 W xenon lamp using a 380 nm UV cutoff filter. The evolved H<sub>2</sub> was determined using a gas injector by gas chromatography (Shimadzu GC-2014, molecular sieve column, N<sub>2</sub> carrier, TCD detector) and was quantified by a calibration plot to the internal hydrogen standard. The time-course of photocatalytic H<sub>2</sub> production under visible-light irradiation over Co2@MIL-125-NH<sub>2</sub> for 7.5 h was conducted with intermittent  $N_2$ evacuation every 2.5 h.

**2.5. Electron Spin Resonance (ESR) Measurements.** Samples were prepared by suspending the pristine MIL-125-NH<sub>2</sub>, Co2@MIL-125-NH<sub>2</sub> or Co(II) complex in a solution of TEOA/CH<sub>3</sub>CN/H<sub>2</sub>O. The volume for the suspension placed into the ESR resonator was 50–60  $\mu$ L. Each sample was degassed by several freeze–pump–thaw procedures and then



**Figure 1.** (a) UV–vis spectra of MIL-125-NH<sub>2</sub>, the Co(II) complex, Co1@MIL-125-NH<sub>2</sub>, Co2@MIL-125-NH<sub>2</sub>, and Co3@MIL-125-NH<sub>2</sub>. (b) Photoluminescence emission spectra ( $\lambda_{ex}$  = 380 nm, refer to its UV–vis spectrum) for MIL-125-NH<sub>2</sub>, the Co(II) complex, the physical mixture, Co1@MIL-125-NH<sub>2</sub>, Co2@MIL-125-NH<sub>2</sub>, and Co3@MIL-125-NH<sub>2</sub>. (c) HAADF-STEM image of Co2@MIL-125-NH<sub>2</sub>, and the (d) Co, (e) N, (f) Ti, (g) O elemental mapping for the selected area in (c).



Figure 2. (a) Photocatalytic H<sub>2</sub> production from water splitting over different catalysts. (b) Recycling tests for Co2@MIL-125-NH<sub>2</sub>. Reaction conditions: 6 mg of catalyst, 27 mL of CH<sub>3</sub>CN, 0.4 M TEOA, 1 mL of H<sub>2</sub>O, 500 W xenon lamp using  $\lambda > 380$  nm cutoff filter.

sealed. The samples were exposed to visible light irradiation if necessary. The spectra were measured using a JEOL JES-FA200 ESR spectrometer at 110 K.

#### 3. RESULTS AND DISCUSSION

The powder X-ray diffraction (XRD) patterns of the three catalysts are the same as the pristine MIL-125-NH<sub>2</sub>, clearly demonstrating its well-retained structure in the composites (Figure S4). The similar N<sub>2</sub> isotherms at 77 K for all the composites show their similar porous character (Figure S5). The decreased N<sub>2</sub> sorption and pore volume of the composites in reference to the pristine MIL-125-NH<sub>2</sub> may be ascribed to the blocking of the pores by the Co(II) complex and/or its

mass contribution (Table S2). Among them, the Co2@MIL-125-NH<sub>2</sub> exhibits the lowest BET surface area and pore volume, revealing the highest loading of Co(II) complex, which is in good agreement with the ICP analysis indicated above (Table S1). The UV–vis diffuse spectrum of the Co(II) complex shows main peaks at  $\lambda = 273$  nm ( $\pi \rightarrow \pi^*$  of TPA ligand), 486 nm (d–d transition), and 634 nm (d–d transition) (Figure 1a).<sup>12</sup> In addition to the characteristic peak at approximately 380 nm originated from MIL-125-NH<sub>2</sub> (Figure 1a), the very broad shoulder peak ranging from 500 to 900 nm in all three composites should be due to the low contents of the Co(II) complex incorporated (Figure 1a). The highest loading of Co species leads to the strongest UV–vis shoulder peak in



Figure 3. ESR spectra for (a) pristine MIL-125-NH<sub>2</sub> and (b) Co2@ MIL-125-NH<sub>2</sub> in the dark or under light irradiation.

Co2@MIL-125-NH<sub>2</sub>, in accordance with its light green color changed from the yellow (Figure S6). Likewise, the photoluminescence emission spectroscopy of Co2@MIL-125-NH<sub>2</sub> is much weaker than others (Figure 1b), suggesting that the radiative recombination of electrons and holes is more effectively inhibited, which would be of great importance in photcatalysis and thus Co2@MIL-125-NH2 is expected to possess superior photocatalytic activity to other catalysts. The scanning electron microscope (SEM) observation for Co2@ MIL-125-NH<sub>2</sub> and MIL-125-NH<sub>2</sub> shows that the loading of the Co(II) complex does not affect the MOF morphology and the MOF crystals remain intact in the composite (Figure S7). No identifiable nanoparticles can be found, and the same contrast is shown in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image, implying that the incorporated Co(II) complexes are well-distributed throughout the MOF (Figure 1c), which is further evidenced by the elemental mapping results, uniform dispersion of Co, N, Ti, and O elements in the Co2@MIL-125-NH<sub>2</sub> composite (Figure 1d-g).

Encouraged by the above characterization results, we set out to investigate the photocatalytic efficiency of the Co(II)@MIL-125-NH<sub>2</sub> composites with different Co contents. Typically, the catalyst was suspended in a mixture of CH<sub>3</sub>CN (27 mL), TEOA (0.4 M), and deionized water (1000  $\mu$ L), which was deoxygenated by N<sub>2</sub> and exposed to visible-light illumination (Figure 2a and Figure S11). Apparently, the Co(II) complex alone cannot produce H<sub>2</sub> in the absence of additional photosensitizer.<sup>12</sup> The MIL-125-NH<sub>2</sub> was able to generate a minimal amount of H<sub>2</sub> (17  $\mu$ mol/g·h), based on the visible light absorption by BDC-NH<sub>2</sub>, the electron transfer from BDC-NH<sub>2</sub> to Ti-oxo clusters, where the phtoreduction occurs.<sup>6g</sup> In sharp contrast, the Co(II)@MIL-125-NH<sub>2</sub> composites exhibited significantly enhanced photocatalytic actvities, among which Co2@MIL-125-NH<sub>2</sub> possessed the highest H<sub>2</sub> production rate (553  $\mu$ mol/g·h), related to its highest loading of Co species (Figure 2a and Figure S11). For comparison, the physical mixture of MIL-125-NH<sub>2</sub> and the Co(II) complex with the same Co loading as that in Co2@MIL-125-NH<sub>2</sub> only gave a very low H<sub>2</sub> rate (37  $\mu$ mol/g·h) under identical conditions, revealing that the encapsulation of the Co(II) complex inside the pores of MIL-125-NH<sub>2</sub> was crucial for efficient electron transfer and photocatalysis. To rule out the leaching effect of the Co(II) complex from the cages of MIL-125-NH<sub>2</sub> in the composite, the photocatalytic H<sub>2</sub> generation over the supernatant solution was investigated and showed negligible activity (Figure 2a and Figure S11). Moreover, the colorless supernatant solution separated from the photocatalytic reaction system, which is significantly different from the Co complex solution in green (Figure S8), revealing the absence of leaching effect in the composite photocatalyst. In addition, the Co2@ MIL-125-NH<sub>2</sub> displayed almost unchanged activity during the recycling experiments up to three runs (Figure 2b), and powder XRD profile (Figure S9) and SEM observation (Figure S10) after catalytic recycles support its well-retained structural integrity, suggesting its high stability under photocatalytic conditions. All Co(II)@MIL-125-NH2 catalysts possess a relatively high TOF and also H<sub>2</sub> production rate compared to any component or their physical mixture in composite catalyst as listed in Table S3. Moreover, the H<sub>2</sub> production rate of Co2@MIL-125-NH<sub>2</sub> with earth-abundant inexpensive elements is higher than most of base metal photocatalysts and even many noble metal-involved MOF photocatalysts (Table S4).

To elucidate the possible mechanism in the photocatalytic process, ESR experiments on pristine MIL-125-NH<sub>2</sub>, Co2@ MIL-125-NH<sub>2</sub>, and the Co(II) complex were conducted at 110 K in the presence of an electron-donor upon visible light irradiation. The MIL-125-NH<sub>2</sub> did not give any signal in the interested field range in the dark. Upon 30 s of visible light irradiation, an intense ESR signal centered at 1.945 should be attributed to paramagnetic Ti<sup>3+</sup> generated by ligand-to-metal charge transfer (LMCT),<sup>6g,8d</sup> while the small downfield feature at 2.002 was associated with the TEOA free radicals, supported by the presence of such signal in both MIL-125-NH<sub>2</sub> and the Co(II) complex. The ESR spectrum of Co2@MIL-125-NH<sub>2</sub> in the dark showed a broad signal at 2.153 assignable to paramagnetic Co<sup>2+</sup> (Figure 3b), as the same signal was found in the Co(II) complex. The broad signal at 2.153 decreased upon light irradiation, inferring the change of Co<sup>2+</sup> to diamagnetic Co<sup>+</sup>. Compared with the pristine MOF, a stronger signal at 2.002 for Co2@MIL-125-NH<sub>2</sub> implied the generation of more free radicals, reflecting the efficient charge transfer from the ligand of MIL-125-NH<sub>2</sub> to the Co(II) complex in the composite. Unexpectedly, unlike that in the pristine MOF, exposing to light irradiation, no obvious Ti<sup>3+</sup> signal at 1.945 can be detected in Co2@MIL-125-NH2. Therefore, it is assumed that the photoelectrons excited by BDC-NH<sub>2</sub> directly transfer to the Co(II) complex, reducing Co<sup>2+</sup> to Co<sup>+</sup>, although the electrons might not or seldom pass through the Ti-oxo clusters. This assumption suggests that only the second route for electron transfer occurs or at least it dominates in Co2@MIL-125-NH<sub>2</sub> in the above proposed two routes, supported by the energy level of Co<sup>2+</sup>/Co<sup>+</sup> reduction potential falling between the LUMO energy level of BDC-NH<sub>2</sub> and the  $H^+/H_2$  potential

(Scheme 2a). In addition, the almost retained paramagnetic  $Co^{2+}$  signal for the Co(II) complex alone exposure to light irradiation further supports the efficient charge transfer between the MIL-125-NH<sub>2</sub> and the Co(II) complex in Co2@ MIL-125-NH<sub>2</sub> (Figure S12).

## 4. CONCLUSION

In conclusion, we have rationally synthesized MOF-based composites via a "ship-in-a-bottle" synthetic strategy based on the prerequisite of size and energy level-matching. The successful encapsulation of the photocatalytically active Co(II) complex into MIL-125-NH<sub>2</sub> results in the exponential increase in the H<sub>2</sub> production rate from visible-light photocatalytic water splitting, in reference to the pristine MOF, the Co(II) complex as well as their physical mixture. In the Co(II)@MIL-125-NH<sub>2</sub> composite, the MOF behaves as a visible-light photosensitizer and the Co(II) complex acts as the cocatalyst and active center; the two components synergistically boost the photocatalytic H<sub>2</sub> production. Based on the ESR analysis, upon visible light irradiation, the photoelectrons produced by BDC-NH<sub>2</sub> directly transfer to the Co(II) complex for reducing protons to  $H_2$ . The efficient charge transfer between the host MOF and guest Co(II) complex in Co(II)@MIL-125-NH<sub>2</sub> greatly facilitates the spatial charge separation, which should be responsible for its excellent activity. Moreover, the MIL-125-NH<sub>2</sub> provides an ideal platform for the hetergenization of the homogeneous Co(II) complex and makes the composite readily recyclable. The rational design and synthesis of the composite featuring synergistically improved catalytic performance in this work opens up an avenue to the MOF-based materials toward efficient photocatalysis.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b01293.

Cyclic voltammograms, <sup>1</sup>H NMR spectrum and mass spectrometry of the Co(II) complex; XRD patterns,  $N_2$  adsorption and desorption isotherms, the photographs of catalysts, SEM images, the photographs of reaction systems, the plots of  $H_2$  production vs time, ESR spectra of the Co(II) complex; Tables S1–S4 (PDF)

## AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: jianglab@ustc.edu.cn.

#### Notes

The authors declare no competing financial interest.

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