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# Dual-Functionalized Mixed Keggin- and Lindqvist-Type Cu<sub>24</sub>-Based POM@MOF for Visible-Light-Driven H<sub>2</sub> and O<sub>2</sub> Evolution

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S Supporting Information

ABSTRACT: The development of logical visible-light-driven heterogeneous photosystems for water splitting is a subject of new research. As the first example of a noble-metal-free photocatalyst for both H<sub>2</sub> and O<sub>2</sub> production, a high-nuclear  $\{Cu_{24}^{I}(\mu_{3}-Cl)_{8}(\mu_{4}-Cl)_{6}\}$ -based polyoxometalate (POM)@metal-organic framework (MOF) (ZZULI-1) is rationally designed to serve as a robust dualfunctionalized photocatalyst. ZZULI-1 exhibits highly efficient photocatalytic H<sub>2</sub> evolution (6614  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>) and O<sub>2</sub> evolution (1032  $\mu$ mol g<sup>-1</sup> calculated for the first 6 min). The {Cu<sup>I</sup><sub>24</sub>( $\mu_3$ -Cl)<sub>8</sub>( $\mu_4$ -Cl)<sub>6</sub>} clusters and mixed POMs not only work as the active units for H<sub>2</sub> and O2 production, respectively, but also improve the effective electron transfer between the photosensitizer and ZZULI-1. The highly stable dual-functionalized ZZULI-1 affords new penetrations into the



development of cost-effective high-nuclear cluster-based POM@MOFs for efficient solar-to-fuel generation.

#### INTRODUCTION

Under the double pressure of the energy crisis and environmental pollution, sustainable clean energy is needed imminently to solve the fuel problem.<sup>1</sup> Photocatalytic water splitting has been widely researched because it affords an ecofriendly approach to the generation of H<sub>2</sub> and O<sub>2</sub>, which could be applied as renewable energy sources.<sup>2</sup> The decomposition of water contains two half-reactions, known as water oxidation (producing  $O_2$ ) and water reduction (generating  $H_2$ ), and it is inhibited by water oxidation because of its four-electron and four-proton-transfer processes.<sup>3</sup> As a rising kind of porous species, metal-organic frameworks (MOFs) afford a diversified platform for the development of water-splitting materials by advisable choices of bridging units and metal nodes.<sup>4</sup> In comparison with photocatalytic water reduction, less research of MOFs has been explored for water oxidation and very few studies have investigated potential heterogeneous photocatalysts for both H<sub>2</sub> and O<sub>2</sub> production.<sup>5</sup> Therefore, the development of dual-functionalized MOFderived photocatalysts for both H<sub>2</sub> and O<sub>2</sub> generation and the fact that the consequent composition has efficient fuelforming sustainability are the most demanding and challenging.

MOFs provide a promising configuration for the settling of functional units to enhance the photocatalytic properties because of their porous structures and wealthy chemical functionality.<sup>6</sup>  $Cu_m^T X_n$ -based (X = Cl, Br, or I) MOFs have been as one of the most significant families of hybrid materials because of their d<sup>10</sup> electronic configuration and relatively intense luminescent behavior as well as their considerable

application for light-induced processes recently.<sup>7</sup> In our previous work, we have demonstrated semiconductive  $Cu_{2}^{I}X_{2}$ -based MOFs (X = Cl, Br, or I) for efficient photocatalytic H<sub>2</sub> evolution without cocatalysts and photosensitizers. The {Cu12X2} units of Cu-X-bpy work as photoelectron producers to greatly improve the H<sub>2</sub> generation activity, offering suitable reaction locations for H<sub>2</sub> production.<sup>8</sup> If the incorporation of functional oxidative blocks into  $Cu_m^I X_n$ based MOF materials,  $\{Cu_m^I X_n\}$  clusters, and oxidative units of modified MOFs would work synergistically to provide dual functions, then they might be efficient photocatalysts for H<sub>2</sub> and O<sub>2</sub> evolution. As a huge class of nanosized inorganic units with oxygen-rich surfaces, polyoxometalates (POMs) can easily perform multielectron-transfer courses, therefore exhibiting remarkable candidates as water oxidation photocatalysts.<sup>9</sup> Imbedding inorganic POMs into the pores of Cu<sup>I</sup><sub>m</sub>X<sub>n</sub>-based MOFs is an excellent method to stabilize and heterogenize the reductive {Cu<sup>I</sup><sub>m</sub>X<sub>n</sub>} clusters and oxidative POMs for photocatalytic H<sub>2</sub> and O<sub>2</sub> production. It was not until 2018 that comparatively cost-effective P<sub>2</sub>W<sub>18</sub>Co<sub>4</sub>@MOF was reported for only O2 evolution<sup>10</sup> or Ni<sub>4</sub>P2@MOF and P2W18@UiO were reported for only H<sub>2</sub> evolution.<sup>11</sup> However, to our knowledge, no POM@MOF photosystems have been published in the literature that could photocatalyze water reduction and water oxidation, respectively (Table S2). Thus, the rational design of

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photocatalytic systems for both  $H_2$  and  $O_2$  generation by dualfunctionalized POM@MOFs is of great significance.

Bearing all of these in mind, by incorporating the oxidative  $[W_{12}O_{40}]^{8-}$  and  $[W_6O_{19}]^{2-}$  polyoxoanions within the pores of  $Cu^I_mX_n$ -based MOFs, in this work, we develop a new method to merge the photocatalytic water oxidation and water reduction within a novel dual-functionalized POM@MOF (Scheme 1). We envision that the mixed Keggin- and

Scheme 1. Dual-Functionalized Mixed Keggin- and Lindqvist-Type  $\{Cu_{24}^{I}(\mu_3\text{-}Cl)_8(\mu_4\text{-}Cl)_6\}$ -Based POM@ MOFs as Photocatalysts for Both H<sub>2</sub> and O<sub>2</sub> Evolution



Lindqvist-type POMs may work as oxidative photocatalysts to generate  $O_2$ , whereas the  $\{Cu_{24}^I(\mu_3-Cl)_8(\mu_4-Cl)_6\}$  clusters of the cationic framework can act as photoelectron generators to improve the activity of  $H_2$  generation.

### EXPERIMENTAL SECTION

Materials and Methods. All chemical reagents were obtained from the merchant channels and utilized without any treatment. Elemental analysis (EA) experiments were performed with an elemental analyzer (Flash EA 1112 series) after total combustion at 900 °C under an O<sub>2</sub> atmosphere. Thermogravimetric analysis (TGA) was measured by a PerkinElmer Pyris Diamond DTA/TG thermal system under a N<sub>2</sub> environment. Powder X-ray diffraction (PXRD) diffractograms were obtained on a Rigaku D/Max-2500 X-ray diffractometer using a graphite monochromator and a copper-target tube. Solid-state IR spectra were obtained by a Bruker Tensor 27 spectrometer. Optical diffuse-reflectance spectra were recorded on a Hitachi UH4150 spectrophotometer. UV-vis absorption spectra were measured by a Hitachi UH4150 spectrophotometer. Photoluminescence spectra were obtained by a Cary Eclipse fluorescence spectrophotometer (Agilent G9800A). Cyclic voltammetry (CV) measurements were performed on a ModuLab XM electrochemical system of the standard three-compartment cell. Transient photocurrent responses were obtained on a ModuLab XM electrochemical system in a standard three-compartment cell. The elemental mappings of energy-dispersive X-ray spectroscopy were determined by a JSM-7001F field-emission scanning electron microscope.

Synthesis of  $H_{48}[Cu^{1}_{24}(\mu_{3}-CI)_{8}(\mu_{4}-CI)_{6}]$ -(TPB)<sub>24</sub>[Cu<sup>II</sup>(CH<sub>3</sub>OH)]<sub>6</sub>[ $W_{12}O_{40}$ ]<sub>8</sub>[ $W_{6}O_{19}$ ]<sub>3</sub> (ZZULI-1; CCDC 1833731). A mixture of (TBA)<sub>4</sub>[ $W_{10}O_{32}$ ]<sup>12</sup> (TBA = tetrabutylammonium; 33.2 mg, 0.01 mmol), 5'-(4-(4H-1,2,4-triazol-4-yl)phenyl)-4''-(4H-1,2,4-triazol-4-yl)-[1,1':3',1''-terpheny]-4-carboxylic acid (TPC;12.1 mg, 0.025 mmol), 1,3,5-tris(3-(1,3,4-triazol-1-yl)phenyl)benzene (TPB; 2.5 mg, 0.005 mmol), and CuCl<sub>2</sub>·2H<sub>2</sub>O (34.1 mg, 0.20 mmol) in mixed solvents of N,N-dimethylformamide (DMF; 2.0 mL), methanol (0.25 mL), and acetonitrile (4.0 mL) was stirred and adjusted to pH = 2.3 using 1.0 mol L<sup>-1</sup> HCl. The above suspension was placed in a 25 mL reaction container and kept at a reaction temperature of 120 °C for 3 days. After the container was cooled to ambient temperature, dark-green block crystals of **ZZULI-1** were obtained. Yield: ca. 56% based on TPB. EA and inductively coupled plasma. Calcd for  $C_{726}H_{504}N_{192}O_{383}Cl_{14}W_{114}Cu_{30}$ : C, 20.85; H, 1.39; N, 7.24; Cu, 4.56; W, 50.12. Found: C, 20.94; H, 1.51; N, 7.16; Cu, 4.49; W, 50.08.

**Photocatalytic H<sub>2</sub> Evolution Experiments.** Visible-light-driven H<sub>2</sub> generation experiments were completed in a 25 mL quartz reaction tube. Different amounts of the dual-functionalized photocatalyst **ZZULI-1**, the sacrificial electron donor of triethanolamine (TEA) and the photosensitizer of fluorescein (Fl) in the mixed solvents of H<sub>2</sub>O/CH<sub>3</sub>CH<sub>2</sub>OH [1:1 (v/v), 3 mL], were added into the reaction tube. The specific pH value of the photocatalytic system was adjusted with a NaOH or HCl solution. After that, the reaction solution was degassed by argon for 10 min. The solution was irradiated using a 300 W xenon lamp light source at ambient temperature. The amount of H<sub>2</sub> was investigated by a GC 7900 instrument using a 5 Å molecular sieve column (0.6 m × 3 mm) as well as a thermal conductivity detector.

**Photocatalytic O<sub>2</sub> Evolution Experiments.** Visible-light-driven O<sub>2</sub> generation experiments were similar to those of photocatalytic H<sub>2</sub> evolution. Different amounts of the dual-functionalized photocatalyst **ZZULI-1**, the  $[Ru(bpy)_3]Cl_2$  photosensitizer, and the Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> electron acceptor in a sodium borate buffer (8.0 × 10<sup>-2</sup> M, 10.0 mL) were added into the reaction flask. The solution was degassed by argon for 10 min. Subsequently, the solution was irradiated by a light-emitting-diode (LED) lamp (beam diameter = 2 cm; light intensity = 16 mW;  $\lambda \ge 420$  nm) at room temperature. The amount of O<sub>2</sub> was investigated by a GC 7900 instrument using a 5 Å molecular sieve column (2 m × 3 mm) as well as a thermal conductivity detector.

#### RESULTS AND DISCUSSION

Crystal Structure and Characterizations. The darkgreen block crystals of ZZULI-1 were synthesized by the hydrothermal reaction of  $(TBA)_4[W_{10}O_{32}]$  and  $CuCl_2 \cdot 2H_2O$ with the ligands TPB and TPC in a yield of 56%. The  $[W_{10}O_{32}]^{4-}$  precursors are unstable under solvothermal conditions and favor rebuilding into steady Keggin- or Lindqvist-type polyoxoanions.<sup>13</sup> Among the hydrothermal reaction, the TPC ligand will play a very important role in the constitution of ZZULI-1 materials. PXRD and EA confirm the pure phase of ZZULI-1. Single-crystal X-ray analysis reveals that ZZULI-1 crystallizes in cubic space group  $Pm\overline{3}m$ , consisting of 26-hedral { $Cu_{24}^{I}(\mu_3-Cl)_8(\mu_4-Cl)_6$ } cages, mononuclear  $\mathbf{C}\mathbf{u}^{II}$  ions as nodal points, and rigid TPB ligands as connectors with two types of POMs,  $[W_{12}O_{40}]^{8-}$  and  $[W_6O_{19}]^{2-}$ , embedded (Figure S1). The asymmetry unit comprises two crystallographically independent Cu ions. The Cu<sup>II</sup> center and Cu<sup>I</sup> atom adopt five-coordinate squarepyramidal and four-coordinate tetrahedral geometries, respectively. Typically, 24 symmetry-equivalent Cu<sup>1</sup> ions are ligated by 8  $\mu_3$ -Cl and 6  $\mu_4$ -Cl to form a unique spherical {Cu<sup>I</sup><sub>24</sub>( $\mu_3$ - $Cl_{8}(\mu_{4}-Cl_{6})$  cluster (Figure 1a).

More interestingly, the 26-hedral { $Cu_{24}^{I}(\mu_3-Cl)_8(\mu_4-Cl)_6$ } cores and mononuclear  $Cu^{II}$  nodes are connected by TPB ligands, affording the cationic 3D framework (Figure 1c). The oxidative  $[W_{12}O_{40}]^{8-}/[W_6O_{19}]^{2-}$  polyoxoanions are further embedded in the cationic pores of cage-based MOFs via electrostatic interaction to produce a dual-functionalized POM@MOF with a 10.0 Å × 8.0 Å channel (Figure 1b,d), which remarkably has not been reported in the POM@MOF research field. Because copper(I) halide aggregates have received extensive attention in photocatalytic water reduction,<sup>8,14</sup> the coexistence of both reductive { $Cu_{24}^{I}(\mu_3-Cl)_8(\mu_4 Cl)_6$ } clusters and oxidative POM polyoxoanions would contribute to a dual oxidation–reduction POM@MOF,



**Figure 1.** Crystal structure of **ZZULI-1**: (a)  $\{Cu_{24}^{I}(\mu_3\text{-}Cl)_8(\mu_4\text{-}Cl)_6\}$  cage with an inner diameter of 8.2 Å. (b) 3D framework formed by  $\{Cu_{24}^{I}(\mu_3\text{-}Cl)_8(\mu_4\text{-}Cl)_6\}$  units,  $Cu^{II}$  nodes, and TPB linkers with two types of POMs embedded. (c) Octahedral cage generated from six  $\{Cu_{24}^{I}(\mu_3\text{-}Cl)_8(\mu_4\text{-}Cl)_6\}$  clusters. (d) Connolly surface diagrams showing the 1D channels.

which is promisingly designed for photocatalytic  $\mathrm{H}_2$  and  $\mathrm{O}_2$  generation.

Confocal fluorescence microscopy has been well applied in the bioimaging field. It can offer a new approach to investigating thick porous MOF materials because it provides the benefit of increased infiltration depth (>500 mm).<sup>15</sup> Evaluation of the guest-accessible volume in porous MOFs can be strictly tested by using a confocal fluorescence microscope with a tool probe of luminescent dyes with large sizes. Dye uptake research was tested by soaking ZZULI-1 with a methanol solution of Fl. The confocal laser scanning microscopy images (Figure 2) exhibit obvious green fluorescence ( $\lambda_{ex}$  = 488 nm), which is assigned to the emission of Fl, confirming the successful uptake of Fl dyes into the pores of ZZULI-1 materials.<sup>16</sup> Moreover, the very regular distribution of Fl dyes over the entire crystal confirms that Fl molecules penetrate deeply into the channels rather than adhering to the external surface of ZZULI-1. Taking no account of the guest solvent molecules, the effective guestaccessible volume of ZZULI-1 was evaluated as 48.3% by PLATON software.<sup>1</sup>

Compared with those of the free POMs and TPB, the UV– vis spectrum of **ZZULI-1** reveals that the adsorption band of **ZZULI-1** exhibits a significant red shift (Figure 3a). This is possibly related to the impression of coordinated Cu centers on the excited state of TPB, d–d electronic transitions of Cu atoms,  $\pi - \pi^*$  interaction of TPB, and ligand-to-metal charge transfer.<sup>18</sup> The solid-state diffuse-reflectance spectroscopy and Kubelka–Munk representation of **ZZULI-1** were also investigated (Figure S9). The band-gap energy ( $E_g$ ) of **ZZULI-1** determined from the Tauc plot is 1.90 eV. The



**Figure 2.** Confocal laser scanning microscopy images of empty (a and b) and soaked (c–l) Fl molecules. Bright-field images (a and c) and confocal micrographs (b and d–l) were explored at  $\lambda_{em} = 510-610$  nm and excited by  $\lambda_{ex} = 488$  nm. The confocal images of parts d–l show nine slices from the top down.

result reveals that **ZZULI-1** can be used as an ideal semiconductive POM@MOF and that such a low-band-gap  $E_{\rm g}$  value is very rare in MOF materials.<sup>19</sup>

Photocatalytic H<sub>2</sub> Evolution. Photocatalytic tests of dualfunctionalized ZZULI-1 for H<sub>2</sub> evolution were investigated under visible-light irradiation with TEA as the sacrificial factor and Fl as the photosensitizer. Under optimized conditions, ZZULI-1 is highly active for H<sub>2</sub> production, with a rate of H<sub>2</sub> evolution of 6614  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> (Figure 4). It should be noted that no detectable H<sub>2</sub> was detected in the absence of ZZULI-1 or in the dark under the same experimental conditions, indicating that ZZULI-1 plays a very important role in photocatalytic H<sub>2</sub> generation. Furthermore, the stability of ZZULI-1 for H<sub>2</sub> evolution could be confirmed by recycling experiments. Solids of ZZULI-1 were separated from the suspension by simple centrifugation and recycled three times (from 6614 to 6607  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup> of yield after recycling three times; Figure 3d). The PXRD patterns and Raman spectra of ZZULI-1 before and after the H<sub>2</sub> evolution reaction suggest that the crystallinity was well-maintained (Figures 3c and S20). Heretofore, the high catalytic efficiency of ZZULI-1 for splitting water into  $H_2$  is one of the highest values among MOFs,<sup>20</sup> revealing the excellent advantage of dual-functionalized ZZULI-1.

Control experiments were investigated to provide insights for the catalytic mechanism and assess the contribution of  $\{Cu_{24}^{1}(\mu_{3}-Cl)_{8}(\mu_{4}-Cl)_{6}\}$  clusters and the outer coordination sphere for H<sub>2</sub> evolution. The H<sub>2</sub> evolution efficiencies of CuCl<sub>2</sub>, TPB, POMs, and CuCl<sub>2</sub> + TPB + POMs were tested under the same measured conditions as those of ZZULI-1. The order of the catalytic photoactivity is as follows: TPB <  $CuCl_2 \approx POMs \approx CuCl_2 + TPB + POMs \ll ZZULI-1$ . The ligand TPB will be completely inactive because of the lack of photoactive sites. Neither CuCl<sub>2</sub> nor POMs nor CuCl<sub>2</sub> + TPB + POMs shows meaningful amounts of H<sub>2</sub> production. The importance of the distinct 3D framework of ZZULI-1 is confirmed by a comparison of CuCl<sub>2</sub> + TPB + POMs with **ZZULI-1**. The ordered structural arrangement of  $\{Cu_{24}^{I}(\mu_{3} Cl)_8(\mu_4-Cl)_6$  clusters in ZZULI-1 may profit from electron and energy transfer over a long distance.<sup>21</sup> The structural characteristics would promote the rapid diversion of photogenerated charges from the excited-state photosensitizer and



Figure 3. (a) Solid-state UV–vis absorption spectra of ZZULI-1. (b) Transient photocurrent profiles of ZZULI-1. (c) PXRD patterns of ZZULI-1. (d) Durability testing for  $H_2$  evolution over ZZULI-1, which was recycled from the reaction solution and used again under the same catalytic conditions three times.



**Figure 4.** Kinetics of  $H_2$  evolution over **ZZULI-1** in the photocatalytic system. Conditions: **ZZULI-1** (3 mg), Fl (5 mg), and TEA (10% v/v); a mixed solvent of  $H_2O/CH_3CH_2OH$  [1:1 (v/v), 3 mL, pH = 13.0]; with or without xenon-lamp irradiation. Inset: Proposed mechanism for photocatalytic  $H_2$  evolution.

enhance the charge separation efficiency, which would figure out the completely different activities proven by ZZULI-1 and  $CuCl_2 + TPB + POMs$ .

The CV experiment for **ZZULI-1** was investigated in a KOH solution at pH = 13.0 (Figure S10). **ZZULI-1** undergoes multiple redox processes, and the cyclic voltammogram shows the first nearly irreversible redox couple at a midpoint potential of -1.12 V (vs Ag/AgCl), which could be distributed to the Cu<sup>I</sup>/Cu<sup>0</sup> couple. The second quasi-reversible reduction curve occurs at  $E_{pc} = -0.96$  V, whereas the corresponding oxidation curve shifts to  $E_{pa} = -0.93$  V, which can be attributed to the Cu<sup>II</sup>/Cu<sup>I</sup> redox processes. Therefore, the reduction potential of the excited state of Fl\* can feasibly reduce Cu<sup>II</sup> or Cu<sup>I</sup> in **ZZULI-1** to Cu<sup>0</sup>. Furthermore, Cu<sup>I</sup>/Cu<sup>0</sup>, with a more negative reduction potential than reduction of the protons at pH = 13.0

(-0.96 V; vs Ag/AgCl), is competent of reducing protons to H<sub>2</sub>. The third quasi-reversible redox couple ( $E_{\rm pc} = -0.45$  V and  $E_{\rm pa} = -0.38$  V) is probably related to the ligand and metal. The proton likely bonds to the opened Cu sites to form copper hydride species for the release of H<sub>2</sub>.<sup>22</sup>

The transient photocurrent-time experiments under visiblelight irradiation illustrate that the electrode modified by **ZZULI-1**, **ZZULI-1** + Fl, or **ZZULI-1** +  $[Ru(bpy)_3]Cl_2$ provides the minutiae on the efficient charge separation (Figure 3b). When the xenon lamp is turned on, the photocurrent signal quickly rises to a certain value, whereas when the xenon lamp is turned off, the photocurrent signal rapidly returns to zero. Pristine ZZULI-1 has a small photocurrent response (1.0  $\mu$ A cm<sup>-2</sup>) in a KCl solution, which evidences the charge transport occurring from ZZULI-1 to the glassy carbon electrode. This result is confirmed with the relatively low photocatalytic activity without any photosensitizer. However, strong photocurrent responses were obtained with the electrode modified by ZZULI-1 + Fl (4.0  $\mu A \text{ cm}^{-2}$ ) or ZZULI-1 + [Ru(bpy)] Cl<sub>2</sub> (2.0  $\mu A \text{ cm}^{-2}$ ). These results are confirmed by the improvement of electron transfer occurring from the excited state of  $[Ru(bpy)_3]Cl_2$  or Fl to ZZULI-1 and, subsequently, to the outside of the working electrode.<sup>23</sup> In addition, when ZZULI-1 was added to a  $CH_3CH_2OH/H_2O$  [1:1 (v/v)] solution of Fl (10  $\mu$ M), emission quenching was observed (Figure S11). The quenching can be assigned to the photoinduced charge transport from the excited state of Fl to ZZULI-1, which also offers the possible excited state of Fl to activated ZZULI-1 for proton reduction. The findings of transient photocurrent tests and quenching experiments provide direct evidence of charge transport from the excited state of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> or Fl to ZZULI-1.

On the basis of the results of transient photocurrent tests and quenching experiments, a possible reaction mechanism is proposed (Figure 4, inset). Photogenerated electrons of Fl<sup>\*</sup> effectively transfer to **ZZULI-1** under visible-light irradiation, and then the conjugated packing and long-length order of TPB transfer electrons to the coordinately unsaturated { $Cu_{24}^{I}(\mu_3-Cl)_8(\mu_4-Cl)_6$ } clusters,<sup>24</sup> where H<sub>2</sub> generation reactions occur. The sacrificial agent TEA supplements the holes in Fl<sup>+\*</sup> to recover the excited state of Fl<sup>\*</sup> to the ground state. These results highlight the great importance of { $Cu_{24}^{I}(\mu_3-Cl)_8(\mu_4-Cl)_6$ } clusters, functional ligands, coordination environments, and regular solid-state structures. Notably, { $Cu_{24}^{I}(\mu_3-Cl)_8(\mu_4-Cl)_6$ } clusters provide an excellent place to improve the Cu<sup>I</sup> hydride interactions, which rapidly give H<sub>2</sub> evolution and recover the starting **ZZULI-1**.

**Photocatalytic**  $O_2$  **Evolution.** Photocatalytic tests of **ZZULI-1** for  $O_2$  generation were tested in a borate buffer solution (pH = 8.0) with [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> as the photosensitizer and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the electron acceptor. Dual-functionalized **ZZULI-1** shows a wonderfully catalytic performance for  $O_2$  generation with a rate of  $O_2$  generation of 1032  $\mu$ mol g<sup>-1</sup> calculated for the first 6 min (Figure 5). To confirm the nature



**Figure 5.** Kinetics of O<sub>2</sub> generation over **ZZULI-1** in the photocatalytic system. Conditions:  $[Ru(bpy)_3]Cl_2$  (7.7 mg), **ZZULI-1** (2 mg), and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (11.9 mg); a sodium borate buffer (8.0 × 10<sup>-2</sup> M, 10 mL, pH = 8); with or without LED-lamp irradiation. Inset: Proposed mechanism for photocatalytic O<sub>2</sub> evolution.

of heterogeneous catalysis for ZZULI-1, the supernatant solution (after separation of ZZULI-1) was carefully tested, and filtration exhibits no detection of  $O_2$  evolution at the same photocatalytic conditions (Table S3, entry 4).<sup>25</sup> Furthermore, ZZULI-1 was isolated and reused for visible-light-driven  $O_2$  evolution at least three times (Figure S21). The PXRD patterns of ZZULI-1 isolated after three cycles are similar to those of pristine ZZULI-1, which confirms that ZZULI-1 is well-maintained before and after photocatalysis (Figure S22). The photocatalytic activities of ZZULI-1 for water oxidation mainly depend on the POMs embedded in the POM@MOF materials, which is confirmed by the demand of injecting multiple electrons.

Photocatalytic  $O_2$  evolution over **ZZULI-1** was further demonstrated by control experiments. To prove that  $O_2$  was not produced from any other source such as a sodium borate buffer and an oxygen impurity in the photocatalytic system, the GC profiles of standard  $O_2$ ,  $O_2$  evolution, and air were tested (Figure S18). Also, we have performed a controlled experiment using dried acetonitrile instead of a borate buffer, which shows no detection of  $O_2$  evolution at the same photocatalytic conditions (Table S3, entry 5). No  $O_2$  will be generated in the absence of light or without the catalyst of ZZULI-1 (Table S3, entries 6 and 7). Furthermore, it could be found that the  $O_2$  evolution efficiency for (TBA)<sub>2</sub>W<sub>6</sub>O<sub>19</sub> or Na<sub>6</sub>W<sub>12</sub>O<sub>39</sub>·H<sub>2</sub>O is significantly weaker than that of ZZULI-1 (Table S3, entries 1–3). It can be concluded that the high  $O_2$  evolution efficiency is dominated by the synergistic catalysis between the two types of POMs and the spacious environment of the channels in ZZULI-1.

Photocatalytic  $O_2$  evolution with  $[Ru(bpy)_3]Cl_2$  as the photosensitizer and  $Na_2S_2O_8$  as the electron acceptor is demonstrated, which shows facile and reversible O-O bond generation (Figure 5, inset). During the photocatalytic process, two  $[Ru(bpy)_3]^{2+}$  are excited by visible light to generate two excited states of [Ru\*(bpy)<sub>3</sub>]<sup>2+</sup>, whereafter two [Ru\*(bpy)<sub>3</sub>]<sup>2+</sup> are further photooxidized to form  $[Ru(bpy)_3]^{3+}$  by the electron acceptor of  $Na_2S_2O_8$ . The course occurs via  $Na_2S_2O_8$ quenching of the accostable metal-to-ligand charge-transfer excited state of  $[Ru^*(bpy)_3]^{2+}$ , which has been well-proven.<sup>26</sup> At the same time,  $2SO_4^{\bullet-}$  in situ formation rapidly oxidizes two equivalent  $[Ru(bpy)_3]^{2+}$  to generate other  $[Ru(bpy)_3]^{3+}$ . Subsequently, ZZULI-1 is oxidized to high oxidation states by four  $[Ru(bpy)_3]^{3+}$ . During O<sub>2</sub> generation, mixed POMs of ZZULI-1 are used to promote effective charge transport from the dual-functionalized **ZZULI-1** to oxidized  $[Ru(bpy)_3]^{3+}$ , where the oxidized  $[Ru(bpy)_3]^{3+}$  are regenerated to the starting state.

#### CONCLUSION

In a word, we have successfully demonstrated the conception that photocatalytic H<sub>2</sub> and O<sub>2</sub> evolution over POM@MOFs can be performed for the first time under visible-light irradiation. **ZZULI-1** exhibits highly efficient photocatalytic H<sub>2</sub> and O<sub>2</sub> evolution. The high H<sub>2</sub> and O<sub>2</sub> evolution rate over **ZZULI-1** might be ascribed to its multiple active units derived from the excellent structural characteristics and its reduction oxidation behavior of {Cu<sup>1</sup><sub>24</sub>( $\mu_3$ -Cl)<sub>8</sub>( $\mu_4$ -Cl)<sub>6</sub>} and two types of POM components, which results in effective charge transport during photocatalytic reaction. It is noteworthy that this work promotes a perfect insight for the design of highly efficient and noble-metal-free photocatalysts that could functionally imitate both photosystems I and II of bionic water-splitting photocatalysts.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00206.

Additional crystallographic data, structural details, and experimental results, such as photocatalytic experiments, durability testing, diffuse-reflectance spectrum, and elemental mappings (PDF)

#### Accession Codes

CCDC 1833731 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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