

Evaluation of Ce-MOFs as Photoanode Materials for the Water Oxidation Reaction: The Effect of Doping with $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ Catalyst

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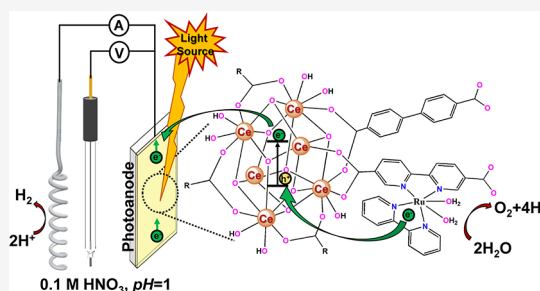


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Supporting Information

ABSTRACT: Artificial photosynthesis stands out as a highly effective method for harnessing sunlight to produce clean and renewable energy. The light-absorbing properties, chemical stability, and high redox activity of Ce-based metal–organic frameworks (MOFs) make them attractive materials for visible-light-driven water splitting. Currently, Ce-based MOFs remain a relatively underexplored system for photocatalytic water oxidation in acidic media. In this study, we synthesized a Ce-MOF with different linkers (1,4-benzenedicarboxylic acid, tetrafluoroterephthalic acid, 2-nitroterephthalic acid, 2,2'-bipyridine-5,5'-dicarboxylic acid, and 4,4'-biphenyldicarboxylic acid), which exhibit light-absorbing capability. Ce-based MOFs doped with $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ (MOF-1 and MOF-2) water oxidation catalyst showed an enhanced photoelectrocatalytic current of $\sim 10^{-4} \text{ A}\cdot\text{cm}^{-2}$ at $\text{pH} = 1$, which is comparable with the $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ -doped MIL-126 Fe-based MOF. We also demonstrated the long-term durability of Ru-doped Ce-MOFs for photoelectrocatalytic water oxidation under acidic conditions. The as-synthesized MOFs were analyzed with powder X-ray diffraction (PXRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), UV–visible diffuse reflectance spectroscopy, scanning electron microscopy (SEM), and electric conductivity measurements. This study contributes to the development of cost-effective materials for sustainable photocatalytic water splitting processes.



INTRODUCTION

The increasing global population and growing economy have led to a significant increase in energy demand. To meet this demand, we have primarily relied on fossil fuels; however, the consumption of fossil fuels increases greenhouse gas emissions, notably carbon dioxide (CO_2), introducing the foreboding presence of global warming and climate change. Therefore, there is an urgent need for green and clean energy sources as replacements for fossil fuels.^{1–5} Harnessing sunlight through artificial photosynthesis has emerged as a highly effective approach for producing carbon-free and environmentally friendly fuel. Specifically, water splitting represents the most promising pathway for advancing the development of clean and renewable energy.^{1,2} The main challenge in hydrogen production through water splitting is the complex multi-electron water oxidation reaction (WOR). To efficiently convert sunlight into chemical energy, we need photocatalytic materials that can absorb visible light photons, generate charge-separated states with suitable redox potentials, have high activity for water splitting and are high durable in the harsh chemical conditions of WOR. Currently, iridium and ruthenium oxide-based water oxidation catalysts (WOCs) are among the most active and stable electrocatalysts for water oxidation at low pH, but their high cost motivates the pursuit of more cost-effective alternatives with fewer limitations.^{6–8}

Furthermore, the development of photoelectrocatalysts is challenging because it necessitates the dual performance of the material as a photoabsorber and as a catalyst. MOFs have emerged as a promising category of porous materials with tremendous potential for innovative applications in photocatalysis.^{9,10} Their unique crystalline structures, characterized by metal ions or clusters linked by organic ligands, provide remarkable surface area and tunable properties.^{11–13}

In the past decade, Zr-based MOFs have been studied for their photocatalytic performance under UV-light.^{14,15} However, the wide band gap of Zr-based MOFs ($\sim 3.7 \text{ eV}$) does not allow for photoactivity in the visible range.^{16,17} Fe-based MOFs (Fe-MIL-101, Fe-MIL-126, Fe-MIL-100, Fe-MIL-88, and Fe-MIL-53), all containing Fe_3O units with carboxylate ligands, are capable of absorbing the visible light.^{18,19} Our group recently reported the incorporation of catalytically active $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ WOC into an Fe-based MIL-126, demonstrating the efficient photoelectrochemical water

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oxidation at pH = 1.⁶ While being photoactive, Fe-based MOFs, such as Fe-MIL-101, Fe-MIL-126, Fe-MIL-100, Fe-MIL-88, and Fe-MIL-53, have low electrical conductivity, which possibly limits the overall performance of the photoanodes. Hence, this study analyzes the effect of the replacement of the Fe-based MOFs with Fe₃O₄ photoactive units with a variety of Ce-based MOFs with all Ce^{IV} Ce₆-nodes while using the same [Ru(bpy)(dcbpy)(H₂O)₂]²⁺ WOC. The electrical conductivity of the Ce-MOFs was systematically assessed in the study but was also found to be low.

Motivation to evaluate Ce-based MOFs²⁰ is compelling, as interest in these materials has witnessed rapid growth in recent years due to their unique advantages, such as their relatively low cost, high redox activity, photoabsorbing properties, and environmentally friendly synthesis.^{21–29} The appeal of Ce-MOFs lies in their combination of microporosity, the Ce^{III/IV} redox properties, and the presence of low-energy 4f orbitals, granting them the capability to exhibit exceptional photo/electrocatalytic properties.^{29–31} The ability to tailor Ce-MOFs with different functional groups, control their bandgap, and prevent the recombination of photogenerated electrons and holes makes them an interesting material for efficient visible light-responsive catalysts.^{22,23,31} For instance, Meicheng Wen et al. found that cerium-ion-doped chromium-based amine-functionalized MOF (CeMIL-101(Cr)) is suitable for H₂ production from ammonia borane under visible light irradiation.³² Pd/CeMIL-101(Cr) exhibited improved catalytic activity compared to Pd/MIL-101(Cr) under visible light irradiation due to efficient light-induced charge separation and transfer of photogenerated electrons from MOF to Pd.³² Recently, Shan Dai et al. reported different Ce-based MOFs (Ce-UiO-66-X (X = H, Br, NH₂, NO₂, COOH), Ce-DUT-67, and Ce-MOF-808) and investigated their photocatalytic activity for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) under simulated sunlight irradiation.²³ Ce-UiO-66-NH₂ and Ce-UiO-66-NO₂ showed the best HER and OER activity, respectively, at pH ~ 7.²³ Interestingly, these Ce-UiO-66-based materials were found to be more active than their zirconium analogues, likely due to the low-lying 4f orbitals of Ce⁴⁺ ions that favor the ligand-to-metal charge transfer.²³ These studies show the light-absorbing properties, chemical stability, and high redox activity of Ce-based MOFs.^{23,32}

Here, we explore Ce-based MOFs for photocatalytic water oxidation in acidic media. Ce-MOF (Ce-UiO-66 (Ce-BDC), Ce-UiO-66-F₄ (Ce-BDC-F₄), Ce-UiO-66-NO₂ (Ce-BDC-NO₂), Ce-UiO-66-dcbpy (Ce-dcbpy), and Ce-UiO-66-bpdc (Ce-bpdc), with different linkers (BDC = 1,4-benzenedicarboxylic acid, BDC-F₄ = tetrafluoroterephthalic acid, BDC-NO₂ = 2-nitroterephthalic acid, dcbpy = 2,2'-bipyridine-5,5'-dicarboxylic acid, and bpdc = 4,4'-biphenyldicarboxylic acid) were prepared (Figure 1). All materials exhibited light-absorbing capability; Ce-bpdc and Ce-bpdc-dcbpy(1:1) materials allowed the incorporation of [Ru(bpy)(dcbpy)(H₂O)₂]²⁺ using various synthetic routes (Figure 2). Ru-WOC enhanced prolonged photoelectrocatalytic activity toward water oxidation in acidic media (pH = 1). We have achieved the long-term stabilization of Ce-MOF materials on fluorine-doped tin oxide (FTO) glass electrodes for sustained photoelectrocatalytic water oxidation in acidic conditions with the use of a proton-conductive Nafion membrane. The as-synthesized Ce-MOFs were analyzed with powder X-ray diffraction (PXRD), Raman spectroscopy, Fourier transform

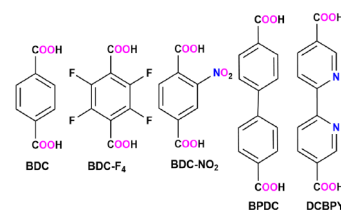


Figure 1. Chemical structures and abbreviations of the linker ligands used in this study.

infrared spectroscopy (FTIR), UV–visible diffuse reflectance spectroscopy, scanning electron microscopy (SEM), and electric conductivity measurements.

EXPERIMENTAL SECTION

Materials. All chemicals and solvents were purchased from Sigma Aldrich, AK Scientific, Fisher Scientific, and TCI America, and were used without further purification. Aqueous solutions were prepared using ultrapure (Type 1) water (resistivity 18.2 MΩ·cm at 25 °C) from the Q-POD unit of the Milli-Q integral water purification system (Millipore, Billerica, MA, USA).

Synthesis of Ce-UiO-66-NO₂ (Ce-BDC-NO₂). Ce-BDC-NO₂ was prepared with a slight modification to the reported procedures.²³ 820 mg of cerium (IV) ammonium nitrate was weighed in a glass vial. Add 3 mL of acetic acid and 8 mL of DI water into it, and magnetic stirring was performed at 600 rpm for 5 min. 1.6 mmol of 2-nitroterephthalic acid was added to the solution. The solution is then magnetically stirred at 600 rpm for 2 h at room temperature. The precipitates were then isolated *via* vacuum filtration, washed with water several times, and dried overnight under ambient conditions. The yield was ~696 mg.

Synthesis of Ce-UiO-66 (Ce-BDC). The synthesis of Ce-BDC is similar to that of Ce-BDC-NO₂. 20 mL ethanol is added to the solution before the introduction of the terephthalic acid ligands. The yield was ~430 mg.

Synthesis of Ce-UiO-66-F₄ (Ce-BDC-F₄). The synthesis of Ce-BDC-F₄ is similar to that of Ce-BDC. Tetrafluoroterephthalic acid is used instead of terephthalic acid ligands. The yield was ~495 mg.

Synthesis of Ce-UiO-66-dcbpy (Ce-dcbpy). Ce-dcbpy was prepared with a slight modification to the reported procedures.^{20,31} 104.2 mg of 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂dcbpy) was weighed in a 20 mL glass vial and dissolved with 2.5 mL of DMF. To the solution of dcbpy, an aqueous solution of cerium (IV) ammonium nitrate (800 μL, 0.533 M) was added. The glass vial was sealed and heated at 100 °C for 15 min under stirring. After cooling down to the room temperature, the yellow precipitates were collected *via* vacuum filtration, washed with DMF, and subjected to acetone washing for several times, and dried overnight under ambient conditions. The yield was ~102 mg.

Synthesis of Ce-UiO-66-bpdc (Ce-bpdc). The synthesis of Ce-bpdc is similar to that of Ce-dcbpy. 4,4'-Biphenyldicarboxylic acid (H₂bpdc) is used instead of H₂dcbpy.

Synthesis of Ce-bpdc-dcbpy(1:1). The synthesis of Ce-bpdc-dcbpy(1:1) is similar to that of Ce-dcbpy. 52.1 mg of H₂bpdc and 52.1 mg of H₂dcbpy were used for the synthesis of Ce-bpdc-dcbpy(1:1).

Synthesis of Ru-doped Ce-bpdc (MOF-1). 50 mg of Ce-bpdc and 6 mg of Ru(bpy)(dcbpy)Cl₂ were added in a 20 mL glass vial. Add 5 mL of ethanol and 5 mL of toluene into it. The mixture was heated at 90 °C for 24 h under magnetic stirring at 400 rpm.³¹ The precipitates were then collected *via* vacuum filtration, washed with ethanol and acetone for several times, and dried overnight under ambient conditions. Yield: ~47 mg.

Synthesis of Ru-doped Ce-bpdc-dcbpy(1:1) (MOF-2). 50 mg of Ce-bpdc-dcbpy(1:1) and 6 mg of Ru(bpy)(p-cymene)Cl₂ were added in a 20 mL glass vial. Add 5 mL of ethanol and 5 mL of toluene into it. The mixture was heated at 90 °C for 24 h under magnetic

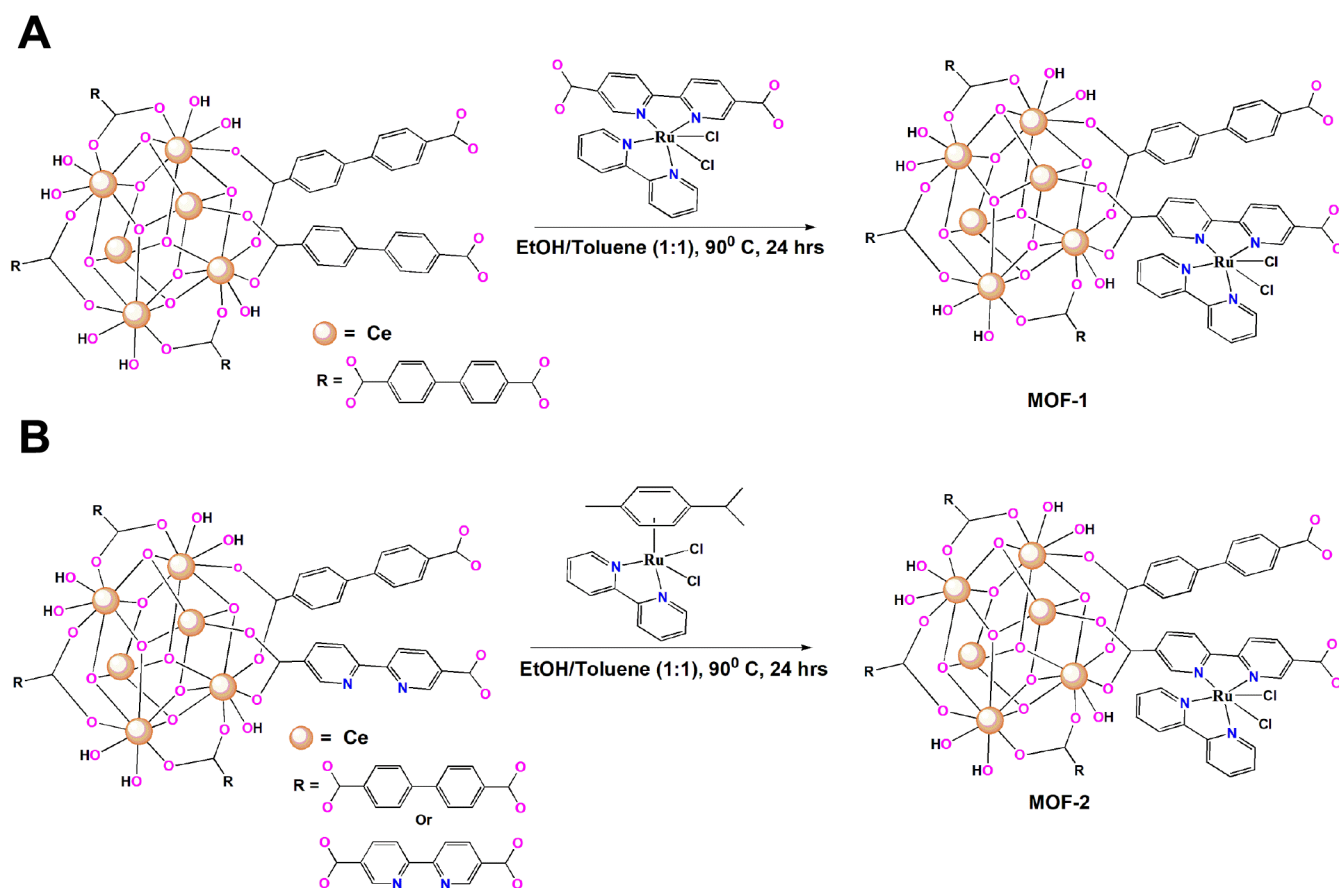


Figure 2. Synthetic scheme for the integration of a Ru catalyst into a Ce-MOF. (A) Linker exchange of Ce-bpdc with Ru(bpy)(dcbpy)Cl₂ and (B) doping of Ru(bpy)(p-cymene)Cl₂ onto Ce-bpdc-dcbpy(1:1).

stirring at 400 rpm. The precipitates were then collected *via* vacuum filtration, washed with ethanol and acetone for several times, and dried overnight under ambient conditions. The yield was ~52 mg.

Physical Mixture of Ru(bpy)(p-cymene)Cl₂ and Ce-bpdc-dcbpy(1:1) (MOF-2-PM). 50 mg of Ce-bpdc-dcbpy(1:1) and 6 mg of Ru(bpy)(p-cymene)Cl₂ were ground using a mortar and pestle for 15 min. The physical mixture was taken, and an ink solution was made for photoelectrocatalytic measurements.

Safety comment: No uncommon hazards were noted during the experiments on the synthesis of samples and their characterization.

RESULTS

The Ru(bpy)(dcbpy)Cl₂ and Ru(bpy)(p-cymene)Cl₂ precursors were synthesized by following methods reported in the literature.^{12,17} Ce-MOFs with bpdc/dcbpy linkers were synthesized by reacting ceric ammonium nitrate with the linkers with (~3:1,v/v) DMF:H₂O solution at 100 °C.^{20,31} The chemical structures and abbreviations of the ligands used for the synthesis of Ce-MOFs are shown in Figure 1.

The PXRD measurements were carried out to study the crystal structure of the as-synthesized materials. The measured PXRD patterns were compared with simulated patterns using existing crystallographic information from the Cambridge Crystallographic Data Centre (CCDC). Our synthesized Ce-bpdc, Ce-dcbpy, and Ce-bpdc-dcbpy(1:1) have crystalline structures (Figure S1), which are in agreement with the simulated PXRD patterns of Ce-Uio-66-dcbpy (CCDC 1509775). The PXRD patterns of Ce-BDC, Ce-BDC-F₄, and Ce-BDC-NO₂ are given in Figure S2, which show the crystalline nature of the materials and match the simulated

PXRD patterns of Ce-Uio-66. The experimental PXRD patterns of Ce-MOFs with different linkers were in agreement with the simulated patterns, suggesting a relatively high purity and crystallinity of the synthesized Ce-MOFs.

The catalyst [Ru(bpy)(dcbpy)(H₂O)₂]²⁺ was introduced into the Ce-MOFs *via* two different methods: i) using a presynthesized Ru(bpy)(dcbpy)Cl₂ catalyst for ligand exchange (dcbpy of Ru-catalyst) with the Ce-bpdc MOF (MOF-1) (Figure 2A) or ii) using the precursor Ru(bpy)(p-cymene)Cl₂, allowing its reaction with the dcbpy-linker in the Ce-bpdc-dcbpy(1:1) (MOF-2) (Figure 2B). Incorporating Ru-catalysts into the Ce-bpdc-dcbpy(1:1) MOF is facilitated by the presence of dcbpy, which effectively coordinates the Ru-catalysts as compared to other single-ring BDC-based linkers. Both methods result in the incorporation of [Ru(bpy)(dcbpy)(H₂O)₂]²⁺ into Ce-MOF, enhancing the catalytic activity in water oxidation. The Ce-Uio-66 has an average pore diameter of ~15 Å³³ and [Ru(bpy)] moiety has a size of ~10 Å,⁶ which should potentially allow the [Ru(bpy)] moiety to get inside the MOF pores during the synthesis. The crystalline nature of the Ce-MOFs remains the same after doping of the Ru catalyst into Ce-MOFs (Figure S3). The ratio of Ru precursor (Ru(bpy)(p-cymene)Cl₂ or Ru(bpy)(dcbpy)Cl₂) to the linker was kept at ~1:12 based on our earlier findings for Fe MIL-126 MOF that such a ratio maintains the MOF crystalline structure.⁶

The electric conductivities of the as-synthesized Ce-MOFs were determined using a custom-made conductivity setup (Figure S4) and are tabulated in Tables 1 and S1. The Ce-

Table 1. The Electric Conductivity, Bandgap, and Photocatalytic Current Measured for Ce-MOFs

material	electric conductivity, σ (S/cm)		direct bandgap (eV)	photocatalytic current ($\text{A}\cdot\text{cm}^{-2}$)	
	dark	light		pH = 1	pH = 7
Ce-BDC	2.44×10^{-11}	3.00×10^{-11}	2.96	1.0×10^{-5}	9.26×10^{-6}
Ce-BDC- F_4	5.57×10^{-6}	5.81×10^{-6}	2.82	4.7×10^{-5}	4.27×10^{-5}
Ce-BDC- NO_2	1.10×10^{-7}	1.19×10^{-7}	3.06	5.5×10^{-5}	1.47×10^{-5}
Ce-bpdc	1.40×10^{-7}	1.62×10^{-7}	2.98	5.4×10^{-5}	2.85×10^{-6}
Ce-dcbpy	1.73×10^{-7}	1.94×10^{-7}	2.98	9.6×10^{-5}	9.15×10^{-6}
Ce-bpdc-dcbpy(1:1)	0.91×10^{-7}	1.10×10^{-7}	2.98	1.7×10^{-5}	7.57×10^{-6}

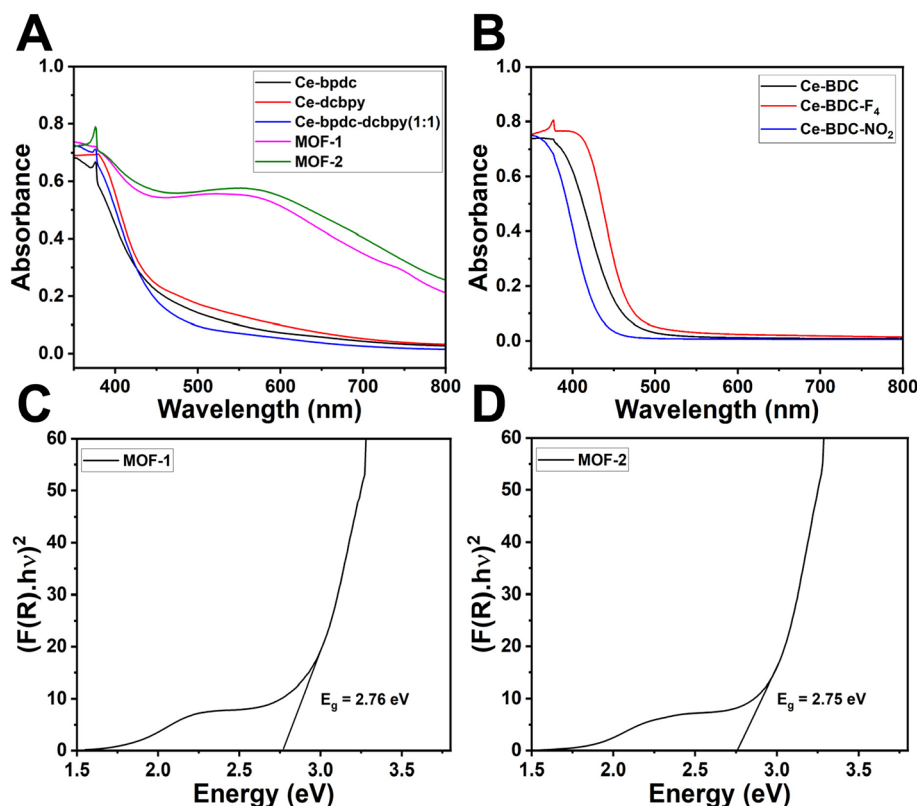


Figure 3. UV-vis diffuse reflectance spectra of (A) Ce-bpdc, Ce-dcbpy, Ce-bpdc-dcbpy(1:1), MOF-1, and MOF-2, and (B) Ce-BDC, Ce-BDC- F_4 , and Ce-BDC- NO_2 MOFs. Kubelka–Munk transformed reflectance spectra for (C) MOF-1 and (D) MOF-2. E_g is a bandgap energy.

bpdc, Ce-dcbpy, and Ce-bpdc-dcbpy(1:1) samples show an electric conductivity $\sim 10^{-7}$ S/cm, which is two orders of magnitude better than the reported Fe MIL-126 MOF (3.3×10^{-9} S/cm).⁶ The electric conductivity of Ce-MOFs increased slightly under illumination (Tables 1 and S1).

Fourier transform infrared spectroscopy (FTIR) was used to measure the interaction between the Ce ions and the ligands. The FTIR spectra of Ce-bpdc, Ce-dcbpy, and Ce-bpdc-dcbpy(1:1) are given in Figure S5A, which show the presence of carbonyl group vibrations in the $1300\text{--}1700\text{ cm}^{-1}$ range and other bands characteristic of bpdc and dcbpy ligands (Table S2).^{6,20} Meanwhile, for Ce-bpdc-dcbpy(1:1), the prominent two peaks observed at $\sim 1592\text{ cm}^{-1}$ and $\sim 1395\text{ cm}^{-1}$ are ascribed to the asymmetric and symmetric stretching vibrations of the coordinated carboxylic groups, respectively.^{6,20} Figure S5B represents the FTIR spectra of Ce-BDC, Ce-BDC- F_4 , and Ce-BDC- NO_2 . The two prominent peaks at $\sim 1500\text{ cm}^{-1}$ and $\sim 1380\text{ cm}^{-1}$ are vibrations of the terephthalate ion and carboxylate ions and the peak visible at 1538 cm^{-1} for Ce-BDC- NO_2 is assigned to asymmetric vibration of the nitro group (N-O).²³ Additionally, the low-intensity bands observed

at 600 cm^{-1} to 800 cm^{-1} of the as-synthesized Ce-MOFs are due to the stretching vibrations of Ce–O.²² The FTIR spectra of MOF-1 and MOF-2 are similar with those of the Ce-bpdc and Ce-bpdc-dcbpy(1:1), respectively (Figure S5C,D), which indicates that the MOFs remain unchanged with the doping of the Ru catalyst. Further, we carried out Raman spectroscopy of the as-synthesized MOFs at an excitation wavelength of 532 nm. The Raman spectra of the as-synthesized Ce-MOFs and Ru-doped Ce-MOFs are shown in Figure S6A–C. The Raman peaks at 300 cm^{-1} to 600 cm^{-1} are attributed to metal–ligand vibration of Ce-MOFs, and the Raman peak at 1100 cm^{-1} to 1700 cm^{-1} are corresponding to the vibrations associated with the organic ligands of Ce-MOFs.⁶ The Raman spectra of MOF-1 show the peaks of Ce-bpdc and Ru(bpy)(dcbpy) Cl_2 and those of the MOF-2 show the peaks of Ce-bpdc-dcbpy(1:1) and Ru(bpy)(dcbpy) Cl_2 (Figure S6C), which indicates the successful incorporation of [Ru(bpy)(dcbpy)-(H₂O)₂]²⁺ water oxidation catalyst into the Ce-MOF. The slight changes in the Raman spectra of MOF-1 and MOF-2 are mainly due to color differences and hence different enhancement in resonance Raman.

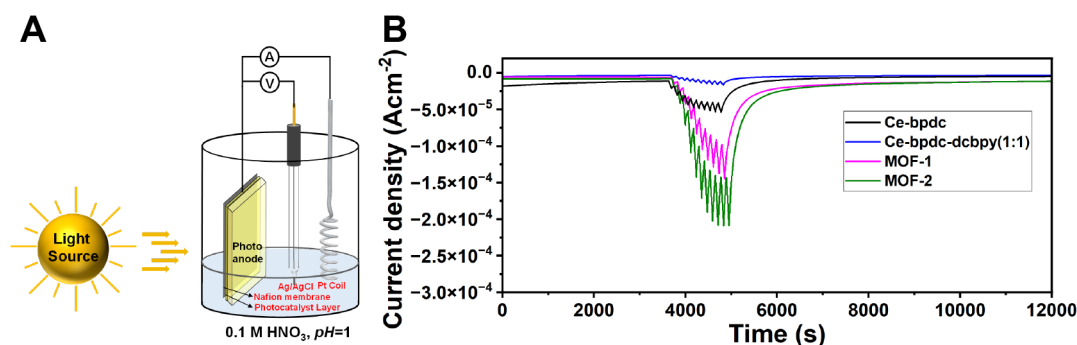


Figure 4. (A) Photoelectrochemical three-electrode setup with drop-casted MOF on FTO confined with the Nafion membrane, Ag/AgCl electrode, and Pt coil as working, reference, and counter electrodes, respectively, in 0.1 M HNO₃ electrolyte (pH = 1). (B) Chronoamperometry plots of Ce-bpdc, Ce-bpdc-dcbpy(1:1), MOF-1, and MOF-2 photoanodes at +1.4 V vs Ag/AgCl in 0.1 M HNO₃ (pH = 1). 10 light/dark cycles (1 min light/1 min dark) were applied after 60 min of the applied potential.

UV–vis diffuse reflectance spectroscopy is used to investigate the light absorption property of the as-synthesized materials. Figure 3A,B represents the UV–vis diffuse reflectance spectra of Ce-MOFs and Ru-doped Ce-MOFs, which illustrate the absorbance bands extending to the visible light region for all MOFs, with the intensity of absorbance increasing in the presence of Ru catalysts. The bandgaps of the MOFs were determined by converting the UV–vis diffuse reflectance spectra to Kubelka–Munk plots (detailed calculations are given in Supporting Information). The Kubelka–Munk plots of MOF-1 and MOF-2 are shown in Figure 3C,D, respectively. The Kubelka–Munk plots of all the Ce-MOFs in this study are given in Figure S7, and the bandgap of the MOFs are tabulated in Tables 1 and S3. The bandgap energy of the Ce-MOFs reported in this work matches that reported in the literature.^{21–23,25} The UV–vis diffuse reflectance spectra of control samples; Zr-based UiO-67-dcbpy and Ru-doped UiO-67-dcbpy, are given in Figure S8. UiO-67-dcbpy lacks photoabsorbing ability to visible light,⁶ but for Ru-doped UiO-67-dcbpy, the absorption band extended to visible light and the intensity of absorbance increased in the presence of the Ru catalyst, similar to Ce-MOFs (Figure S8). For optimal utilization of visible light for water splitting, a photocatalyst should have a typical bandgap in the range of 2 to 3 eV.²³ All prepared Ce-MOFs satisfy this condition.^{23,25} The bandgap for MOF-1 is 2.76 eV, and for MOF-2 is 2.75 eV due to the presence of a brightly colored (due to MLCT band) Ru^{II} complex. However, under catalytic conditions, Ru is converted into a higher oxidation states of Ru^{III} and Ru^{IV}, which are lightly colored. Thus, we do not consider the Ru center to participate as a chromophore, and the Ce-based node remains the photoabsorber in MOFs 1–2 passing the holes to the Ru-based WOC. The same effect was established in Ru-containing Fe-based MOFs.⁶ We expect that when photoanodes are illuminated under an applied potential of +1.4 V vs Ag/AgCl, cerium nodes interconnected by ligands would effectively serve as a photoabsorber and Ru WOC would act as a catalyst for water oxidation at pH = 1.

An electrode was fabricated by drop-casting the ink prepared from Ce-MOFs or Ru-doped Ce-MOFs with Nafion solution as a binder on the FTO. To prepare a water splitting device, the electrode was firmly covered by a proton-conductive Nafion membrane (Figure 4A). Controlled electrocatalytic measurements were carried out using a three-electrode setup in 0.1 M HNO₃ (pH = 1). The Ce-MOFs, MOF-1, and MOF-2 with a proton-conductive Nafion membrane used as a

photoanode, and Ag/AgCl and Pt coil were used as reference and counter electrodes, respectively. The chemical and structural stability of the photoanode in the electrolyte is essential for ensuring its electrocatalytic activity toward prolonged electrolysis. To minimize dissolution effects, photoelectrochemical measurements are carried out by submerging the bottom of the photoanode in 0.1 M HNO₃. Chronoamperometry was used for recording the photoactivity of the MOFs as the working anodes at the applied potential. Further, the activation process of drop-casted MOFs and saturation of the Nafion film was done at +1.4 V vs Ag/AgCl for 60 min. The photoelectrocatalytic performance of the MOFs was investigated with 1 min light on/off for 10 cycles, after 1 h of activation and ~24 h from the start of applied potential. Initially, we used a control study to examine the photoelectrocatalytic performance of Ce-MOFs without a Ru catalyst. The chronoamperometry plots of Ce-bpdc, Ce-dcbpy, Ce-bpdc-dcbpy(1:1), Ce-BDC, Ce-BDC-F₄, and Ce-BDC-NO₂ photoanodes at +1.4 V vs Ag/AgCl at pH = 1 are shown in Figure S9, and the photocatalytic current of the Ce-MOFs are tabulated in Tables 1 and S4. All of the Ce-MOFs showed photoelectrocatalytic activity toward water oxidation with photocatalytic current in the order of $\sim 10^{-5}$ A·cm⁻². The low current of Ce-MOFs photoanodes is likely due to the low catalytic activity of Ce-MOFs in water oxidation at pH = 1. Zhixiong Guo et al. reported the photoinduced phase transition of Ce-UiO-66 observed *via* the color change of the Ce-UiO-66 suspensions from pale yellow (Ce^{IV}) to brown (Ce^{III}) during extended light exposure.¹³ Herein, we did not observe any color change of the Ce-MOFs drop cast on the FTO electrode before and after the photoelectrocatalytic measurement, which indicated the stability of the material.

Further, in order to improve the photoelectrocatalytic activity, we incorporated the Ru catalyst into Ce-MOFs using two different methods using Ru(bpy)(dcbpy)Cl₂ and Ru(bpy)(p-cymene)Cl₂ precursors. Ru-doped Ce-MOFs showed enhanced photoelectrocatalytic activity for water oxidation in acidic conditions. The photocatalytic current increased by more than 1 order of magnitude for MOF-1 and MOF-2 under illumination, with MOF-1 and MOF-2 displaying a photocatalytic current of $\sim 1.4 \times 10^{-4}$ A·cm⁻² and 2.1×10^{-4} A·cm⁻², respectively, at +1.4 V vs Ag/AgCl in 0.1 M HNO₃ (Figures 4B, S10). To examine the stability of the photoelectrocatalyst, a prolonged electrolysis was conducted and photoelectrocatalytic activity was investigated again after ~24 h from the start of the applied potential. The MOF-1

and **MOF-2** exhibited a photocatalytic current of $\sim 1.3 \times 10^{-4}$ A·cm $^{-2}$ and 2.3×10^{-4} A·cm $^{-2}$, respectively, which showed the long-term durability of the materials even after ~ 24 h of chronoamperometry test without any significant loss of photocurrent (Figure S10). As a control study, the physical mixture of Ce-bpdc-dcbpy(1:1) and Ru(bpy)(p-cymene)Cl $_2$ was made (**MOF-2-PM**) and photoelectrocatalytic measurement was carried out under the same conditions as those of Ce-MOFs. **MOF-2-PM** showed a photocatalytic current of $\sim 6.5 \times 10^{-5}$ A·cm $^{-2}$ at +1.4 V vs Ag/AgCl in 0.1 M HNO $_3$ (Figure S11), which is lower as compared to the **MOF-2**. This indicates that the physical mixing of the samples does not enhance the photoelectrocatalytic activity due to the lack of a formed electrocatalyst in the photoabsorbing material. Further, we studied the photoelectrocatalytic performance of **MOF-1** and **MOF-2** under pH = 7 in a three-electrode setup without a proton-conductive Nafion membrane. Both **MOF-1** and **MOF-2** showed the current density of $\sim 10^{-4}$ A·cm $^{-2}$ at +1.4 V vs Ag/AgCl in 0.1 M phosphate buffer (pH = 7) (Figure S12).

“Thus, no activity improvement was found at pH = 7. This is similar to the earlier observations that an Fe-based MOF with [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ catalyst did not show improvement in current at pH = 7.⁶ This is likely due to the limitations of the Ru catalyst or local acidification of the pores with a catalyst at pH = 7.

Further, we performed a control study of chronoamperometry measurement on [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ -doped UiO-67-dcbpy ($\sim 1:12$ ratio of Ru catalyst to the dcbpy linker) with 1 min light on/off for 10 cycles, after 1 h of activation at +1.4 V vs Ag/AgCl in 0.1 M HNO $_3$. UiO-67-dcbpy lacks photoabsorption in the visible light owing to its wide band gap energy. The measured photoelectrocatalytic current of Ru(bpy)(dcbpy)-doped UiO-67-dcbpy is notably lower as compared to **MOF-2** (Figure S13), which suggests that the [Ru(bpy)(dcbpy)] part in Ru-doped UiO-67-dcbpy cannot function as an effective light absorbing unit for photoelectrochemical water splitting.⁶

To examine the structural stability of the catalyst during photoelectrocatalysis, we carried out the post-catalysis characterizations (FTIR and SEM) for **MOF-1** and **MOF-2**. Figure S14 displays the SEM images of **MOF-1** and **MOF-2** before and after the 24 h photoelectrocatalytic chronoamperometry test in acidic media. Remarkably, the morphology of **MOF-1** and **MOF-2** remains largely unchanged even after the 24 h stability test, suggesting the structural stability of the materials. Figure S15 illustrates the FTIR spectra of **MOF-1** and **MOF-2** before and after the 24 h stability test in acidic media. There was no significant change in the FTIR peak position of **MOF-1** and **MOF-2** after the photoelectrocatalysis, further indicating the material stability.

DISCUSSION

Metal–organic frameworks (MOFs) have emerged as a platform for the realization of integrated devices for artificial photosynthesis,^{15,18,34–43} because of their large surface areas, adaptability, stability, and, in some instances, photocatalytic properties.⁴⁴ Notably, certain WOCs based on Ir and Ru have been incorporated into UiO-67 and NU-1000 (NU = Northwestern University)^{17,44–46} MOFs, enhancing electrocatalytic water oxidation activity. However, these systems currently lack light absorption capabilities.^{44,47–49} Developing cost-effective and highly efficient photoelectrocatalysts for water splitting under light activation is yet challenging. A few

Ce-based MOFs have been reported for photocatalytic water splitting and photocatalytic water splitting with CO $_2$ reduction at moderate pH.^{23,31} Water oxidation in MOFs under illumination can be investigated as a multistep process similar to the mechanisms observed in natural photosynthesis. Generally, the first step for photocatalytic water oxidation is the absorption of incident photons by the photoactive material followed by the splitting of water by an catalytically active center. If the bandgap energy of the photoactive material is lower than the energy of the incident photon, it generates the electron–hole pair.⁶ Holes are expected to migrate to the catalytic sites to drive the water splitting reaction.⁶ However, one prominent challenge is the occurrence of charge recombination, which diminishes the overall efficiency of photocatalytic systems. Ce-based MOFs were shown to be efficient in preventing the recombination of photogenerated electrons and holes, making them an ideal candidate for photoelectrocatalysis.^{22,23}

The substitution of the benzene moiety with a bipyridine ligand proved crucial, enabling the development of a chelating framework capable of binding transition metal coordination compounds.⁶ This immobilization of active WOC within the MOF significantly enhances its catalytic activity.⁶ The incorporation of [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ catalytic unit into Fe-MOFs either by linker exchange or doping of the precursor (Ru(bpy)(p-cymene)Cl $_2$) was reported earlier.⁶ The doping strategy is designed to achieve an enhanced photocatalytic water oxidation activity by facilitating the transfer of electrons from immobilized Ru-catalysts to light-activated Fe-nodes of the MOF.⁶ In this study, we found that the incorporation of [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ in Ce-based MOFs (**MOF-1** and **MOF-2**) increases the activity in photocatalytic water oxidation.

The band position for the UiO-66-dcbpy Ce-MOF is reported by Karmakar et al.³¹ In our study, as the Ce-MOF cluster is the same as reported by Karmakar et al., we have taken the value of the conduction band position and calculated the valence band position for our MOF from the band gap value (Tables 1 and S3). The energy diagram of the Ce-MOF is given in Figure S8. In our previous study, we reported the electrochemistry of the [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ WOC.¹⁷ The oxidation potentials of [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ are ~ 1.02 V, ~ 1.09 V, and ~ 1.53 V vs NHE for Ru II /Ru III , Ru III /Ru IV , and Ru IV /Ru V redox couple, respectively, at pH = 1, and Ru V is the active intermediate for water splitting. Herein, we performed the photoelectrocatalysis using Ru(bpy)(dcbpy)-doped Ce-MOFs at the applied potential of +1.6 V vs NHE at pH = 1, which is high enough to convert the Ru-catalyst to Ru V species to ease the water oxidation reaction. Hence [Ru(bpy)(dcbpy)(H $_2$ O) $_2$] $^{2+}$ acts as a WOC and not as a photosensitizer. According to the literature, we found that Ce-MOFs (without catalyst) are capable of absorbing visible light and generating electron–hole pairs. Following this, the electron is transferred from the catalytic Ru center to electron vacancies (holes) in the Ce-MOFs and later to the electrode, which further facilitates the water splitting process (Figure 5).

MOF-1 and **MOF-2** exhibit high current densities for water oxidation in acidic conditions under illumination. This indicates the enhanced photocatalytic water oxidation activity of Ru-WOC Ce-MOFs, which is also comparable with the reported Fe-based MOFs (Table 2).⁶ We calculated theoretically the amount of hydrogen evolved from the chronoamperometry plot during light illumination. Ce-bpdc-dcbpy(1:1)

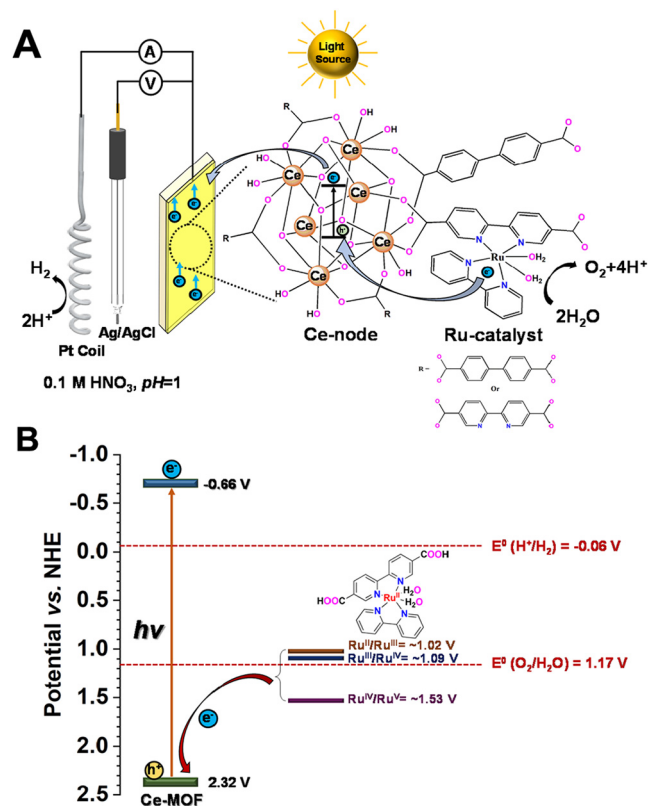


Figure 5. (A) Schematic representation of the proposed photoelectrocatalytic water oxidation mechanism of Ru-doped Ce-MOFs and (B) energy level diagram of Ce-MOFs showing a possible charge transfer mechanism. Required potential for the HER or OER vs NHE at pH = 1 is marked in the figure. The oxidation potentials of $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ are ~ 1.02 V, ~ 1.09 V, and ~ 1.53 V vs NHE for $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$, $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$, and $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{V}}$ redox couple, respectively at pH = 1.

exhibits a low photocatalytic hydrogen evolution of $4.1 \mu\text{mol h}^{-1}$ at pH = 1 (8 mg of MOF having a geometrical area of 1 cm^2). In contrast, MOF-1 and MOF-2 show higher photocatalytic hydrogen evolution of $25.8 \mu\text{mol h}^{-1}$ and $40.4 \mu\text{mol h}^{-1}$, respectively at pH = 1, which is better than that of the reported Pt/Ce-Uio-66-NH₂ system.²³

The cost-effective and catalytically active Ru-WOC Ce-MOFs are promising candidates for light-driven water oxidation, particularly under acidic conditions. This development opens a new pathway for the advancement of such systems designed for sustainable water-splitting processes.

CONCLUSION

In conclusion, the $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ catalytic unit was successfully incorporated into Ce-based MOFs (MOF-1 and MOF-2). The strategic substitution of benzene moieties with bipyridine ligands allowed the immobilization of an active water oxidation catalyst, enhancing the catalytic activity. Ru-doped Ce-MOFs exhibit a high current density comparable with the reported $[\text{Ru}(\text{bpy})(\text{dcbpy})(\text{H}_2\text{O})_2]^{2+}$ @ Fe MIL-126 MOF for water oxidation under acidic conditions. This study marks a significant milestone in advancing the sustainable energy technologies, offering promising options for environmentally conscious and economically viable photoelectrocatalysts. The success of Ru-WOC Ce-MOFs positions them as key contributors to a cleaner and more sustainable energy future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.3c04632>.

PXRD patterns, conductivity measurements, FTIR spectra, Raman spectra, UV-vis diffuse reflectance spectra, chronoamperometry plot and SEM images (PDF)

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Notes

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Table 2. Comparison of the Current Densities Shown by Different Mononuclear Ru Complex-Doped MOFs

type of system	potential (V vs Ag/AgCl)	current density ($\text{A}\cdot\text{cm}^{-2}$)	pH	references
Uio-67@[Ru(tpy)(dcbpy)(H ₂ O)] ²⁺	1.5	7.1×10^{-5}	~ 7	36
Uio-67@[Ru(tpy)(dcbpy)(H ₂ O)] ²⁺	1.5	1.1×10^{-5}	~ 8	45
Uio-67@[Ru(bpy)(dcbpy)(H ₂ O)] ²⁺	1.4	2.5×10^{-5}	1	17
MIL-126@[Ru(bpy)(dcbpy)(H ₂ O)] ²⁺	1.4	^a 6.5×10^{-4}	1	6
NU-1000@[Ru(tda)(py(PhCOOH) ₂)]	1.1	1.8×10^{-4}	7	46
MOF-1	1.4	^a 1.4×10^{-4}	1	this work
MOF-2	1.4	^a 2.1×10^{-4}	1	
MOF-1	1.4	^a 1.0×10^{-4}	7	
MOF-2	1.4	^a 1.0×10^{-4}	7	

^aPhotoelectrocatalytic current measured under illumination.

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