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Cobalt-Based Metal–Organic Cages for Visible-Light-Driven Water Oxidation

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sable but a challenge for splitting H₂O. In this work, a series of Cobased metal–organic cages (MOCs) for photoinduced water oxidation were prepared. MOC-1 with both bis(μ -oxo) bridged dicobalt and Co–O (O from H₂O) displays catalytic activity with an initial oxygen evolution rate of 80.4 mmol/g/h and a TOF of 7.49 × 10⁻³ s⁻¹ in 10 min. In contrast, MOC-2 containing only Co–O (O from H₂O) in the structure results in a lower oxygen evolution rate (40.8 mmol/g/h, 4.78 × 10⁻³ s⁻¹), while the



amount of oxygen evolved from the solution of MOC-4 without both active sites is undetectable. Isotope experiments with or without $H_2^{18}O$ as the reactant successfully demonstrate that the molecular oxygen was produced from water oxidation. Photophysical and electrochemical studies reveal that photoinduced water oxidation initializes via electron transfer from the excited $[Ru(bpy)_3]^{2+*}$ to $Na_2S_2O_8$, and then, the cobalt active sites further donate electrons to the oxidized $[Ru(bpy)_3]^{3+}$ to drive water oxidation. This proof-of-concept study indicates that MOCs can work as potential efficient catalysts for photoinduced water oxidation.

INTRODUCTION

Photoinduced water splitting into hydrogen and oxygen has been perceived as one of the most promising pathways for solving the energy crisis and environmental problems. Water oxidation to molecular oxygen providing electrons needed for the reduction of the proton is regarded as a challenge, as this reaction involves a four-electron process, with very sluggish kinetics.¹ Despite precious metal oxides (e.g., IrO₂ and RuO₂) being active for water oxidation, exploring efficient water oxidation catalysts based on low-cost earth-abundant metals is urgent and a big challenge.^{2–10}

Metal-organic cages (MOCs), constructed from organic linkers and metal nodes, are a kind of porous supramolecular coordination complexes, similar to those of the well-known metal-organic frameworks (MOFs).¹¹ Especially, the MOC exists as a discrete cage on the molecular scale, and its every vertex was coordinated by terminal groups. In terms of their confined coordination space, guest-selective windows, modifiable organic linkers/metal nodes, MOCs have been widely used for separation, stabilizing active species, catalysis, chemical sensor, and so forth.¹²⁻¹⁸ Although lots of MOCs have been designed and fabricated, they have drawn little attention to artificial photosynthesis. Up to now, only a few MOCs have been reported to show potential photoinduced application and no MOC for photoinduced water oxidation was reported.¹⁸⁻²² In contrast, artificial photosynthesis including photoinduced water oxidation by MOFs has been widely studied in the past few years.^{23–31}

In natural photosynthesis, the Mn_4CaO_5 cluster had been proved to be the heart of photosystem II (from green plants and bacteria) by single-crystal X-ray crystallography.³² Bis(μ oxo) and mono(μ -oxo) bridged metal atoms in this cluster had been recognized as the water oxidation catalytic sites.²⁹ In the case of the artificial photosystem, both bis(μ -oxo) bridged dicobalt and Co–O (O from OH or H₂O) on the surface of an abundant metal-oxide catalyst (Co₃O₄) had also been identified to be the active sites by using time-resolved Fourier-transform infrared spectroscopy.³³ Especially, the bis(μ -oxo) bridged dicobalt unit was proved to be the fast catalytic site. Inspired by the active sites in Mn₄CaO₅ cluster and Co₃O₄, we can hypothesize that MOCs containing bis(μ oxo) bridged dicobalt or Co–O (O from H₂O) are potential catalysts for photodriven water oxidation.

Previously, we utilized a subcomponent self-assembly strategy to design and synthesize a series of MOCs.^{14,34–38} In this article, we employ four MOCs based on cobalt ions and imidazolate ligands to study their capacity on photodriven water oxidation. In those MOCs, MOC-1 contains both bis(μ -oxo) bridged dicobalt and Co–O (O from H₂O) active sites,

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while MOC-2 only contains Co–O (O from H₂O).^{35,36} For MOC-3 and MOC-4, all the cobalt ions were coordinated by anions (NO₃⁻ and Br⁻ for MOC-3 and MOC-4, respectively) or nitrogen atoms from the ligands. As a result, no such active sites exist.³⁴ Indeed, as expected, MOC-1 showed the highest activity in those MOCs, while MOCs 2–4 showed lower or no activity. Isotope experiments proved that molecular oxygen was produced from water oxidation. Photophysical and electrochemical studies reveal that photoinduced water oxidation in MOC-1 initiates via electron transfer from the excited [Ru(bpy)₃]²⁺* to Na₂S₂O₈, and the oxidized [Ru(bpy)₃]³⁺ further accepts electrons from the bis(μ -oxo)dicobalt sites and Co–O sites of MOC-1 to drive water oxidation.

EXPERIMENTAL SECTION

Synthesis of MOC-1. MOC-1 was synthesized based on our previously published paper.³⁵ A mixture of $Co(BF_4)_2 \cdot 6H_2O$ (17.0 mg, 0.05 mmol), 2-methyl-1*H*-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), tetraethylammonium perchlorate (45.9 mg, 0.2 mmol), *N*,*N*-dimethylformamide (DMF, 2.0 mL), and methanol (1.0 mL) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 3 days. Then, the mixture was cooled down to room temperature at a rate of 5 °C h⁻¹. Deep red polyhedron-like crystals were obtained, and the isolated yield was 63.4%, based on $Co(BF_4)_2 \cdot 6H_2O$. MOC-1 was formulated as $[Co_{20}L1_{12}(OH)_{12}(H_2O)_4] \cdot (CIO_4)_8$ $(H_2L1 = 1,3-bis[(2-methyl-1$ *H*-imidazole-4-yl)methyleneaminomethyl]benzene).

Synthesis of MOC-2. MOC-2 was synthesized based on our previously published paper.³⁶ A mixture of $Co(BF_4)_2 \cdot 6H_2O$ (13.6 mg, 0.04 mmol), 5-methyl-1*H*-imidazole-4-carbaldehyde (6.6 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), *N*,*N*-dimethylace-tamide (DMA) (2.0 mL), and ethanol (1.0 mL) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 3 days. Then, the mixture was cooled down to room temperature at a rate of 5 °C h⁻¹. Dark red polyhedron-like crystals were obtained, and the isolated yield was 30.5%, based on $Co(BF_4)_2 \cdot 6H_2O$. MOC-2 was formulated as $[Co_8L2_6(H_2O)_6] \cdot (BF_4)_6$, $(H_2L2 = 1,3-bis[(5-methyl-1$ *H*-imidazole-4-yl)methyleneaminomethyl]benzene).

Synthesis of MOC-3. MOC-3 was synthesized based on our previously published paper.³⁵ A mixture of $Co(NO_3)_2$ ·6H₂O (11.6 mg, 0.04 mmol), 1H-imidazole-4-carbaldehyde (5.8 mg, 0.06 mmol), *m*-xylylenediamine (4.1 mg, 0.03 mmol), DMA (2.0 mL), and methanol (1.0 mL) was sealed in a Pyrex glass tube and heated in an oven at 100 °C for 3 days. Then, the mixture was cooled down to room temperature at a rate of 5 °C h⁻¹. Deep red block crystals were obtained, and the isolated yield was 32.4%, based on $Co(NO_3)_2$ ·6H₂O. MOC-3 was formulated as $[Co_8L3_6(NO_3)_6]$, (H₂L3 = 1,3-bis[(1H-imidazole-4-yl)methyleneaminomethyl]benzene).

Synthesis of MOC-4. MOC-4 was synthesized based on our previously published paper.³⁴ A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.08 mmol, 23.3 mg), sodium bromide (0.20 mmol, 20.6 mg), 5-methylimidazole-4-carboxaldehyde (0.12 mmol, 13.2 mg), 4-methylbenzylamine (0.12 mmol, 14.5 mg), *N*,*N*-diethylformamide (DEF, 0.8 mL), and EtOH (1.6 mL) was sealed in a Pyrex glass tube and heated in an oven at 120 °C for 3 days. Then, the mixture was cooled down to room temperature at a rate of 5 °C h⁻¹. Black green block-like crystals were obtained, and the isolated yield was 54.7%, based on $Co(NO_3)_2$. $6H_2O$. MOC-4 was formulated as $[(Co^{III}_4Co^{II}_4L4_{12}Br_4)] \cdot (Br)_3$. (NO_3) , $(H_2L4 = N-((5-methyl-1H-imidazole-4-yl)methylene)$ (4methylphenyl)-methanamine).

Photoinduced Oxygen Evolution Measurement. The photoinduced oxygen evolution experiments were carried out on WP-TEC-1020H with a quartz tube. In detail, a mixture of 2.0 mg of photocatalyst, 37.4 mg of $[Ru(bpy)_3]Cl_2$ (50 μ mol, working as photosensitizer), 95.2 mg of $Na_2S_2O_8$ (400 μ mol, working as sacrificial agent), and 10 mL of borate solution (0.2 M, pH = 9.0) was added into a quartz transparent tube. The above mixture was then stirred and bubbled with Argon for 30 min under room temperature by using circulating water. After that, the photoinduced oxygen evolution started by turning on a 470 nm LED lamp and the generated oxygen was detected by a gas chromatography (GC9790II) with a TCD detector.

Isotope-Labeling Experiment. The isotope-labeling experiment was also carried out on WP-TEC-1020H with a quartz tube. In detail, a mixture of 2.0 mg of photocatalyst, 3.7 mg $[Ru(bpy)_3]Cl_2$ (5 μ mol, working as photosensitizer), 9.5 mg of Na₂S₂O₈ (40 μ mol, working as the sacrificial agent), 0.1 mL of 97% H₂¹⁸O, and 0.9 mL of borate solution (0.2 M, pH = 9.0) was added into a quartz transparent tube. The above mixture was then stirred and bubbled with Argon for 30 min under room temperature by using circulating water. After that, the photoinduced oxygen evolution started by turning on a 470 nm LED lamp and the generated oxygen was detected by gas chromatography–mass spectrometry (Agilent 5977B).

Electrochemical Measurements. The cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometric i-t experiments were conducted under the heterogeneous condition by dropcasting the MOC materials onto the carbon paper electrode. In detail, 4 mg of MOC material (MOC-1, 2, 3, or 4) was grinded first and dispersed into 1 mL of ethanol solution containing 25 μ L of Nafion D-520 dispersion (5% w/w solution) under sonification to form a homogeneous mixture. Then 50 μ L of the mixture was dripped on a carbon paper electrode with a geometrical surface area of 0.72 cm² to prepare the working electrode. After that, the CV, LSV, and chronoamperometric i-t curves were recorded on the CHI760E electrochemical workstation with a standard three-electrode system, in which MOC-modified carbon paper electrode worked as the working electrode, platinum wire as the counter electrode, and the saturated calomel electrode as a reference electrode. A 0.2 M borate solution (pH = 9.0) was used as the electrolyte.

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterization. MOC-1 was synthesized according to our previously reported subcomponent self-assembly strategy, formulated as $[Co_{20}L1_{12}(OH)_{12}(H_2O)_4] \cdot (ClO_4)_8 (H_2L1 = 1,3-bis[(2-meth$ yl-1*H*-imidazole-4-yl)methyleneaminomethyl]benzene).³⁵ It features a 20-nucleus Co-based tetartoidal (tetragonal pentagonal dodecahedral) structure and contains two types of geometrically independent mononuclear cobalt centers (Co1 and Co2) and one type of $bis(\mu-oxo)$ dicobalt (Figures 1, S1, and Table S1). Co1 (CoN₆) is octahedrally coordinated by six nitrogen atoms from three L1 ligands with Co-N bond lengths ranging from 1.946 to 1.986 Å, indicating +3 valence of the Co ion in Co1 (Figure S1). Co2 (CoN₃O) is tetrahedrally coordinated by three nitrogen atoms from three imidazolyl groups and one oxygen atom from the aqua ligand (Figure S1). The bis(μ -oxo)dicobalt is coordinated to six nitrogen atoms from four L1 ligands (Figure S1). Compared with Co1, the Co-N bond lengths in Co2 and $bis(\mu$ -oxo)dicobalt ranging from 2.001 to 2.185 Å are longer, indicating +2 valence of Co ions. The Co-Co distance of $bis(\mu$ -oxo)dicobalt is only 3.0511(26) Å, which benefits the synergistic catalysis of the water oxidation. Twelve L1, four Co1, four Co2, and 6 bis(μ oxo)dicobalt construct this unusual 20-nucleus Co-based MOC. The structure and high purity of the synthesized MOC-1 were confirmed by the powder X-ray diffraction (PXRD) measurements (Figure 2a) and scanning electron microscopy (SEM) images (Figure S5). Furthermore, the FT-IR spectrum with obvious C=N specific absorbance bands at around 1620 cm⁻¹ suggested that the L1 was in situ-generated successfully during the synthesis process of MOC-1 (Figure S13).

Photocatalysis. The photoinduced water oxidation of MOC-1 was conducted with $[Ru(bpy)_3]Cl_2$ as the photo-



Figure 1. Subcomponent self-assembly of MOC-1, MOC-2, MOC-3, and MOC-4. The network topology (the first column) and crystal structure (the second column) of MOC-1, MOC-2, MOC-3, and MOC-4. The large yellow balls represent the cavity in the cages. Color codes for elements: Co turquoise, N blue, C gray, O red, Br dark yellow, and hydrogen atoms are omitted for clarity.

sensitizer and Na₂S₂O₈ as the electron scavenger. This condition is widely used in the previous literature related to photoinduced water oxidation.²⁹ Visible light was achieved by using a 470 nm LED lamp. The evolved oxygen was analyzed by gas chromatography equipped with a thermal conductivity detector. Oxygen was immediately generated under visible light irradiation, and the initial evolution rate even reached 84.6 mmol/g/h in the first 5 min (TOF = $7.88 \times 10^{-3} \text{ s}^{-1}$). The evolution rate slightly decreased to 80.4 mmol/g/h with a TOF of $7.49 \times 10^{-3} \text{ s}^{-1}$ in 10 min and then gradually stopped in 1 h, which is due to both decomposition and consumption of the photosensitizer and electron scavenger (persulfate) (Figure 2b and Tables 1 and S6).^{28,39} The catalytic

Table 1. Photoinduced Water Oxidation Catalyzed by Various Cobalt-Based MOCs Catalysts^a

entry	catalyst	O_2 evolution rate $\left[mmol/g/h\right]$	TOF $[\times 10^{-3} s^{-1}]$
1	MOC-1	80.4	7.49
2	MOC-2	40.8	4.78
3	MOC-3	20.0	2.40
4	MOC-4	0	0

"Conditions: catalyst (2 mg), 5 mM $[Ru(bpy)_3]^{2+}$ aq. 40 mM $Na_2S_2O_8$ aq. 0.2 M borate buffer (10.0 mL, pH = 9.0), and a 470 nm LED lamp light source, reaction for 10 min.

performance of MOC-1 is comparable with the state-of-theart water oxidation photocatalysts, such as $P_2W_{18}Co_4@MOF-545$ (4.00 × 10^{-2} s⁻¹),²⁸ CoPOM/MIL-101 (7.10 × 10^{-3} s⁻¹),⁴⁰ Co₃O₄ nanocages (3.20 × 10^{-4} s⁻¹),⁴¹ and MnCo₂O₄ (1.23 × 10^{-4} s⁻¹)⁴² (Table S7). Interestingly, after the removal of MOC-1 by a filter during a reaction, the resulted solution



Figure 2. (a) PXRD patterns of simulated and as-synthesized MOC-1. (b) Time-resolved O₂ evolution with MOC-1, MOC-2, MOC-3, and MOC-4 as photocatalysts, respectively. Reaction conditions: photocatalysts (2.0 mg), $[Ru(bpy)_3]Cl_2$ (50 μ mol), Na₂S₂O₈ (400 μ mol), borate buffer (10.0 mL, 0.2 M, initial pH = 9.0), LED light (λ = 470 nm). (c) GC–MS spectrum of product when using H₂¹⁸O (10% enriched) as the solvent. (d) GC–MS spectrum of product when using H₂¹⁶O as the solvent.



Figure 3. (a) CV curve of MOC-1 in 0.2 M borate buffer (pH = 9.0) (scan rate, 50 mV/s). The inset picture in a in the enlarged CV curve with current density from -1 to 1 mA/cm². (b) LSV curve of MOC-1 in 0.2 M borate buffer (pH = 9.0) (scan rate, 5 mV/s).

cannot produce molecular oxygen any more under light irradiation, indicating the heterogeneous catalysis nature (Figure 2b). On the other hand, we reused the recycled MOC-1 under same reaction condition. The evolution of oxygen did not decrease significantly in the recycle runs (Figure S18). Those observations demonstrate that MOC-1 works as a relatively stable heterogeneous catalyst for efficient water oxidation. The morphology study of MOC-1 showed that the tetrahedral crystals changed to microsized uniform particles after catalysis (Figure S6), while FT-IR, Raman, UV– vis absorption, and XPS showed that its spectra were identical to the original one (Figures S17, S29, S31, S32).⁴³ ICP–MS data for solution after photoinduced reaction showed that only 1.85% Co species leached and further indicated the high stability of MOC-1 (Table S4).

Control experiments further indicated that the MOC-1, light, photosensitizer, and sacrificial electron acceptor are indispensable for water oxidation (Table S5). The oxygen evolution rate was also affected by the pH value of the solution obviously, and pH = 9.0 is the optimal condition (Figure S19). Additionally, to prove that the evolved O₂ resulted from the photocatalyzed oxidation of water, an isotope experiment was performed with MOC-1 as the catalyst. The produced gas was then analyzed by GC–MS. As shown in Figure 2c, both ¹⁶O¹⁸O and ¹⁸O¹⁸O were detected when using H₂¹⁸O (10% enriched) as the solvent. In comparison, only ¹⁶O¹⁶O could be detected if only using H₂¹⁶O (Figure 2d). The isotope experiments successfully demonstrate that molecular oxygen is produced from water oxidation.

To further study the interplay between the structure and catalytic performance, another three Co-based MOCs with a cubic structure were also synthesized for comparison (Figure 1): (i) MOC-2 with only Co–O (O from H_2O) active site; (ii) MOC-3 with only Co-N active site (N from NO₃⁻, which coordinated on trigonal bipyramidal Co); (iii) MOC-4 without both active sites (Br⁻ coordinated on tetrahedral Co). Crystal structural details can be found in the Supporting Information (Section II in Supporting Information, Figures S7-12, S14-16). The photoinduced water oxidation experiments of MOC-2, MOC-3, and MOC-4 were conducted under the same condition as MOC-1. The oxygen evolution rate in 10 min is as follows: MOC-1 (80.4 mmol/g/h) > MOC-2 (40.8 mmol/ g/h > MOC-3 (20.0 mmol/g/h) > MOC-4 (0 mmol/g/h) (Figure 2b and Table 1). The TOFs of those MOCs also follow the same order of the oxygen evolution rate, that is, $\begin{array}{l} \text{MOC-1} \ (7.49 \times 10^{-3} \ \text{s}^{-1}) > \ \text{MOC-2} \ (4.78 \times 10^{-3} \ \text{s}^{-1}) > \\ \text{MOC-3} \ (2.40 \ \times \ 10^{-3} \ \text{s}^{-1}) > \ \text{MOC-4} \ (0 \ \times \ 10^{-3} \ \text{s}^{-1}). \end{array}$ Interestingly, MOC-1 with both $bis(\mu$ -oxo) bridged dicobalt

and Co–O (O from H₂O) displayed the best catalytic performance among those MOCs. MOC-2 possessing only Co–O (O from H₂O) without $bis(\mu$ -oxo) bridged dicobalt was shown with a lower activity, while MOC-4 without both active sites displayed undetectable activity. MOC-3 containing no $bis(\mu$ -oxo) bridged dicobalt or Co–O (O from H₂O) showed a little catalysis effect for water oxidation, which may be ascribed to the easier exchange of NO₃⁻ with hydroxyl than Br⁻. Therefore, we speculate that both $bis(\mu$ -oxo) bridged dicobalt and Co–O (O from H₂O) on the Co-MOCs would promote the reaction rate.

The electrochemical catalytic water oxidation performance of MOCs in 0.2 M borate buffer at pH 9.0 were also conducted to further study the influence of structure on catalytic performance. In this three-electrode cell, platinum wire acted as the counter electrode, while the MOC-modified carbon paper electrode and saturated calomel electrode (SCE) were employed as the working electrode and reference electrode, respectively. The CV curve of MOC-1 showed an oxidation wave at 0.628 V versus SCE, which is attributed to the valence state transformation of Co sites (Figure 3a).²⁹ The intensities of this oxidation waves were dramatically decreased for other three MOCs, especially for MOC-4 (Figures S21-23). Consider that if the materials are claimed to work with the photogenerated $[Ru(bpy)_3]^{3+}$ oxidant, the onset potential of the water oxidation waves should be lower or comparable to the potential of the Ru(III/II) couple, that is, 1.02 V versus SCE. As shown in Figure 3b, the onset potential of the water oxidation waves of MOC-1 obtained from the LSV curves is 0.800 V versus SCE, which is much lower than 1.02 V (Table S3). With the same method, the onset potentials of the water oxidation waves of other three MOCs were also obtained, which showed an order of MOC-1 < MOC-2 < MOC-3 < MOC-4 (Table S3). This order is consistent with the results of photoinduced oxygen evolution experiments. The over potential of MOC-1 is estimated to be 463 mV at a current density of 1 mA/cm^2 . For comparison, other three MOCs shows a similar LSV curve but with lower current density and higher over potential (Table S3). The turnover frequency of MOCs under electrochemical conditions at a potential of 1.02 V versus SCE (the oxide potential of $[Ru(bpy)_3]^{3+}$) were also analyzed, which showed a similar trend but a higher efficiency compared with photoinduced water oxidation (Table S2). Furthermore, multi-cycle CV and chronoamperometric i-t curves indicated the stability of MOC-1 in electrochemical conditions. Raman and XPS spectra of MOC-1 also demonstrated that no CoOx species was produced during the electrocatalysis process (Figures S30 and S33).⁴



Figure 4. Photodriven water oxidation mechanism by MOC-1 with $[Ru(bpy)_3]Cl_2$ as the photosensitizer and $Na_2S_2O_8$ as the electron scavenger (a). Water oxidation mechanism for the bis(μ -oxo)dicobalt site (b) and Co–O site (c).

Mechanistic Studies. Combined with our experiments and previous reports,³³ the proposed mechanism of MOC-1 for visible-light-driven water oxidation is shown in Figure 4. Photoinduced water oxidation in MOC-1 initiates via electron transfer from the excited $[Ru(bpy)_3]^{2+*}$ to $Na_2S_2O_8$, and the oxidized $[Ru(bpy)_3]^{3+}$ further accepts electrons from the bis(μ -oxo)dicobalt sites and Co2 (CoN₃O) sites of MOC-1 to drive water oxidation (Figures 4, S20).⁴⁴ It should be noted that the short Co–Co distance of 3.05 Å and the distorted dissymmetry coordination geometry in bis(μ -oxo)dicobalt will probably facilitate the critical structural motifs (oxygen ligands) to be involved in the proton-coupled electron transfer (PCET) processes during water oxidation (Figure 4b).²⁹

CONCLUSIONS

In summary, we have demonstrated the cobalt-based MOCs are a kind of promising photocatalysts for photodriven water oxidation under visible light for the first time. Based on the structure-activity relationship, MOC-1 containing both Co-O and $bis(\mu$ -oxo)dicobalt active sites was found to display high catalytic activity to other MOCs, which have only Co-O sites (MOC-2) or no active site (MOC-3 and MOC-4). The isotope experiments successfully demonstrate that molecular oxygen is produced from water oxidation. Photophysical and electrochemical studies reveal that photoinduced water oxidation initializes via electron transfer from the excited $[Ru(bpy)_3]^{2+*}$ to Na₂S₂O₈, and then, the bis(μ -oxo)dicobalt and Co2 (CoN₃O) active sites in MOC-1 further donate electrons to the oxidized $[Ru(bpy)_3]^{3+}$ to drive water oxidation. This study not only paves a way for using MOCs for water oxidation but also illustrates the structure-activity relationships for designing future highly efficient water oxidation catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00907.

Chemicals, characterization methods, detailed structural information (MOC-2, MOC-3, and MOC-4), TOF

calculation, and supplementary figures and tables (Figures S1–S33, Tables S1–S7) (PDF)

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Notes

The authors declare no competing financial interest.

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