

Water Oxidation Catalyst *cis*-[Ru(bpy)(5,5'-dcbpy)(H₂O)₂]²⁺ and Its Stabilization in Metal–Organic Framework

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the design of fast and durable water oxidation catalysts that can be incorporated into future sunlight-to-chemical-fuels assemblies. Here we report on the simple and readily synthetically accessible *cis*- $[Ru(bpy)(5,5'-dcbpy)(H_2O)_2]^{2+}$ (1) (bpy = 2,2'-bipyridine, 5,5'dcbpy = 2,2'-bipyridine-5,5'-dicarboxylic acid) water oxidation



catalyst. Its O₂ evolution has first-order dependence on the catalyst following the water nucleophilic attack mechanism. The *cis*- $[Ru^V=O,-OH(bpy)(5,5'-dcbpy)]^{2+}$ intermediate was detected in the reaction mixtures by X-ray absorption and resonance Raman spectroscopy in agreement with the proposed mechanism and DFT calculations. To avoid a deactivating dimerization, the catalyst was postsynthetically incorporated into the UIO-67 metal–organic framework with retention of water oxidation activity. Similar results were obtained via the incorporation of *cis*- $[Ru(bpy)(5,5'-dcbpy)]Cl_2$, a chemical precursor of 1, to UIO-67 followed by hydrolysis. Postsynthetic doping of the UIO-67 thin film on a FTO glass electrode with 1 leads to an increase of the catalytic current by two orders of magnitude. Thus, $[Ru(bpy)(5,5'-dcbpy)(H_2O)_2]^{2+}$ –UIO-67 is a promising building block for integrated photosynthetic systems.

KEYWORDS: water splitting, ruthenium, metal-organic frameworks, thin films, reactive intermediates

INTRODUCTION

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Solar energy has enormous potential as a clean, abundant, and economical energy source if it can be captured and converted into useful forms of energy such as chemical fuels.^{1,2} Hydrogen from water is an optimal energy carrier, and considerable efforts have been devoted to developing artificial photosynthetic systems for water splitting, including the water oxidation reaction (WOR) step $2H_2O \rightarrow O_2 + 4e + 4H^+$ with 4-electron cascade transformations, which is considered as an obstacle for artificial photosynthesis.³ Many WOR catalysts (WOCs) have been described, mostly based on transitionmetal (Fe, Co, Ni, Cu, Ru, Ir) coordination complexes.⁴⁻⁶ Among them, Ru-bearing complexes with rich coordination chemistry and tunable properties are the most investigated catalysts and could serve as model compounds for the design of economically viable WOCs based on Earth-abundant metals. Two main types of mechanisms are proposed for WORs catalyzed by Ru complexes in high oxidation states: a bimolecular mechanism coupling two Ru=O fragments⁷ and a monomolecular mechanism with a water nucleophilic attack on the Ru=O group, followed by sequential oxidation of the intermediates.⁸ In the group following the radical coupling pathway, Ru 2,2'-bipyridine-6,6'-dicarboxylate derivatives (Rubda) are the most active.⁹ However, such a mechanism is not operational when catalysts are immobilized on an electrode surface. One of the main challenges of assembling an artificial photosynthesis system is to design an efficient, functional device from individual components, including a water oxidation compartment. Therefore, an immobilization of Rubda-based catalysts on an electrode surface for electrocatalysis or insertion into molecular devices is not promising since presence of the second molecule of WOC is needed for their catalytic activity.

In search of WOCs active in variety of devices, effective Ru complexes capable of monomolecular WOR should be developed.^{8,10,11} Among them, polypirydyl Ru complexes have drawn considerable attention due to their high catalytic activity, ligand environment tunability, and relatively simple structure. Polypyridyl complexes with Ru are stable to ligand displacement under acidic or alkaline conditions, but for water oxidation catalysis, at least one water molecule should be coordinated with the Ru atom. Ru species in high oxidation states (IV and V) are often postulated as necessary for WOR to occur. For mononuclear Ru-based WOCs, oxygen of the essential Ru^V-oxo species undergoes nucleophilic water attack with O-O bond formation, followed by further oxidation and O2 release. Under working conditions, these WOCs may form active μ -oxo-bridged dimers ("blue dimer" with cis,cis- $[(bpy)_2Ru^{III}(H_2O) - O - Ru^{IV}(bpy)_2(OH)]^{4+}$ moiety),^{12,13}

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whereas $Ru(tpy)(bpy)Cl_2$ (bpy = 2,2'-bipyridine, tpy = 2,2':6',6"-terpyridine) analogues become active upon hydrolysis and coordination of a water molecule in the inner coordination site.¹⁴ Coordination of the second water molecule by Ru drastically increases water oxidation activity. Previously, it was shown that, for the WOR-active cis-isomer of $[Ru(bpy)_2(H_2O)_2]^{2+}$, the decrease in catalytic activity upon the addition of Ce^{IV} (cerium (IV) ammonium nitrate) includes the formation of dimeric Ru species.¹⁵ But an introduction of electron-withdrawing carboxylic groups in bipyridyl ligands for $[\operatorname{Ru}(5,5'-\operatorname{dcbpy})_2(\operatorname{H}_2O)_2]^{2+}$ $(5,5'-\operatorname{dcbpy} = 2,2'-\operatorname{bipyridine}-5,5'-$ dicarboxylic acid) increases $E_{1/2}(\operatorname{Ru}^{3+/2+})$ half-wave electrochemical potential with considerable enhancement of the water oxidation catalysis.¹⁶ We wished to explore a catalyst possessing high water oxidation activity provided by electronwithdrawing groups in heteroaromatic system, and we made comparisons between this catalyst and other structurally similar WOCs.

Herein, we report preparation of the easily synthetically accessible ruthenium complex cis-[Ru(bpy)(5,5'-dcbpy)- (H_2O) ²⁺ (1) and its water oxidation activity. We provided its chemical stabilization by postsynthetic doping of metalorganic framework (MOF) UIO-67 powder and studied its WOR using an external oxidizer Ce^{IV} and immobilization on UIO-67 thin film on a surface of a fluorine-doped tin oxide (FTO)-coated glass electrode. Although 1 is structurally similar to known water oxidation catalysts cis-[Ru- $(bpy)_2(H_2O)_2]^{2+}$ and $[Ru(5,5'-dcbpy)_2(H_2O)_2]^{2+}$, it demonstrated significantly enhanced water oxidation catalysis at low pH. The complex and its oxidized reactive intermediates have been studied by electrochemical measurements, UV-visible spectrophotometry, XAS, resonance Raman spectroscopy, NMR, and EPR techniques. Using XANES and EXAFS spectroscopy, we observed the formation of a Ru^V intermediate with a $Ru^{V} = O$ bond length of ~1.72 Å. Formation of $Ru^{V} = O$ was also confirmed using Raman (~810 cm⁻¹ wavenumber and ~40 cm^{-1 16}O/¹⁸O isotope shift) and EPR spectroscopy.

We demonstrated the efficiency of this new catalyst embedded in UIO-67 MOF in WOR and studied the possibility of its repeated use for water oxidation. Oxidation catalysts immobilized in MOFs have been extensively studied over the past several years due to the versatility of applications and tunability of their physical properties.¹⁷⁻¹⁹ Zr-based MOFs are among the most studied MOFs due to their relative stability $^{20-22}$ and ability to exchange isostructural organic linkers, including transition-metal-bearing complexes.^{17,19,23,24} Supporting Ru complexes in MOFs was used in WOR to preclude common degradation pathways, including dimerization, and it was also applicable for mononuclear Rucatalysts.^{19,24} Although incorporation of similar to 1 complexes inside the MOF using solvothermal synthesis was reported earlier, 19,23,25 the same approach did not work for *cis*-Ru(2,2'bpy)(5,5'-dcbpy)Cl₂, because it led to formation of an amorphous material. This problem was resolved using postsynthetic doping of UIO-67 with 1 or cis-Ru(2,2'bpy)(5,5'-dcbpy)Cl₂ followed by 12 h hydrolysis. Oxidation of 1-UIO-67 with an external oxidizer (Ce^{IV}) also leads to formation of Ru^V=O, confirmed using resonance Raman and EPR spectroscopy techniques.

Doping of UIO-67 thin film grown on an FTO-glass electrode surface with 1 leads to an increase in water oxidation catalytic current (pH = 1) by 2 orders of magnitude. This

drastic enhancement makes 1 applicable for electrochemical water oxidation in the artificial photosynthetic devices.

Results of density functional theory (DFT) calculations are in agreement with the suggestion that WOR catalyzed by 1 follows a monomolecular proton-coupled electron transfer (PCET) pathway with the formation of the *cis*-[Ru^V=O,– OH(bpy)(5,5'-dcbpy)]²⁺ intermediate, followed by water nucleophilic attack with further oxidation and oxygen release.

RESULTS AND DISCUSSION

1. Synthesis and Characterization. Complex 1 was prepared by hydrolysis of its precursor 1'' which, in turn, was obtained by ligand exchange reaction of $\text{Ru}(p\text{-cymene})(5,5'-\text{dcbpy})\text{Cl}_2^{26}$ with 1 equiv of bpy in DMF at 140 °C (Figure 1).²⁷ After the removal of DMF, the product was triturated



Figure 1. Preparation of *cis*- $[Ru(bpy)(5,5'-dcbpy)(H_2O)_2]^{2+}$ (1) and 1-UIO-67: (a) DMF, reflux; (b) AgNO₃, water; (c) UIO-67 in water.

with EtOH under an argon atmosphere and quickly filtered through a glass-sintered funnel in argon flow to obtain black crystals. NMR of crystalline product 1" (see Materials and Methods in the Supporting Information) demonstrated its high susceptibility to air due to possible oxidation to paramagnetic Ru^{III}. Thus, the compound should be kept in an Ar atmosphere and stored at -20 °C so the ¹H NMR spectrum might be taken without its peaks broadening. ¹H NMR showed formation of only one isomer in a p-cymene substitution reaction. For preparation of 1 mM solution of 1, the compound 1" was first dissolved in 50 μ L of trifluoroethanol. Then an appropriate amount of deionized (DI) water was added, and the solution was stirred overnight. After the addition of 2 equiv of AgNO₃ in water to remove the Cl⁻ ions, the solution was filtered through a 0.2 μ m syringe filter. Earlier, it was noted that structurally related systems cis-[Ru(5,5' $dcbpy)_2(H_2O)_2]^{2+}$ and $cis-[Ru(bpy)_2(H_2O)_2]^{2+}$ may undergo trans- isomerization under ambient light with a reduction of catalytic activity,^{16,28} so precautions were taken to keep the product and its solutions in darkness.

2. Spectral and Redox Properties of 1. Figure 2 shows the absorption spectrum of 1 mM solution of 1 in DI water with a maximum at $\lambda_{max} = 496$ nm. This spectral band can be associated with the $d_{\pi}(\text{Ru}) \rightarrow \pi^* (5,5'\text{-bipyridyl dicarboxylic acid) transition.¹⁶ This feature is in between the absorption maximums for the similar compounds <math>cis$ -[Ru(bpy)₂(H₂O)₂]²⁺ and cis-[Ru(5,5'-dcbpy)₂(H₂O)₂]²⁺ ($\lambda_{max} = 480$ nm and $\lambda_{max} = 550$ nm, respectively) and indicates lower energy of the ligand-



Figure 2. UV–visible absorption spectrum of 1 mM solution of 1 at pH = 1.

acceptor orbitals (5,5'-dcbpy) due to presence of electronwithdrawing -COOH groups.

The cyclic voltammogram of 0.5 mM 1 in a 0.1 M aqueous solution of CF₃SO₃H with an FTO-glass slide working electrode and an Ag/AgCl reference electrode is shown in Figure 3a. Two consecutive oxidation processes of Ru^{II} \rightarrow Ru^{III}



Figure 3. Cyclic voltammograms of 0.5 mM solution of 1 (solid line) vs Ag/AgCl with scan rate 100 mV/s at (a) pH = 1, (b) pH = 7. FTO-glass slide electrode as working electrode; dashed line is blank solution.

and Ru^{III} \rightarrow Ru^{IV} are accessible in a narrow potential range $E_{1/2} \sim 0.68$ V vs Ag/AgCl at pH = 1. Separation between these processes is smaller than in the case of *cis*-[Ru(bpy)₂(H₂O)₂]²⁺ ($\Delta E_{1/2} \sim 0.24$ V), while only one peak was reported in the CV of *cis*-[Ru(5,5'-dcbpy)₂(H₂O)₂]^{2+,16} For all three compounds, redox potentials of Ru^{II} \rightarrow Ru^{III} and Ru^{III} \rightarrow Ru^{IV} conversions are very similar (Table 1). Onset of a catalytic current likely corresponds to the formation of an Ru^V intermediate at ~1.4 V vs Ag/AgCl. At pH = 7, a reversible wave for Ru^{II}/Ru^{IV} transition shifts to lower potential at 0.66 V vs Ag/AgCl (Figure 3b), which is in agreement with a proton-coupled

Table 1. Summary of $E_{1/2}$ vs NHE for 1 and Its Structural Analogues at pH = 1, in Volts^{*a*}

	${\rm Ru}^{\rm III}/{\rm Ru}^{\rm II}$	${\rm Ru}^{\rm III}/{\rm Ru}^{\rm IV}$	Ru ^{IV} /Ru ^V			
1	0.92					
cis-[Ru(bpy) ₂ (H ₂ O) ₂] ²⁺	0.95	1.19	1.4			
cis - $[Ru(5,5'-dcbpy)_2(H_2O)_2]^{2+}$	1.08					
^a From Inorg. Chem., 1988, 27 (19), 3283–3291.						

electron transfer (PCET) process. Complex pH dependence of the potentials for analogous $[Ru(bpy)_2(H_2O)_2]^{2+}$ complex was reported earlier.²⁹

Also, for higher potentials, an electrocatalytic current for 1 is higher than for its analogue *cis*- $[Ru(bpy)_2(H_2O)_2]^{2+}$ (Figure 4).



Figure 4. Cyclic voltammograms of 0.5 mM solution of 1 (solid line) vs *cis*- $[Ru(bpy)_2(H_2O)_2]^{2+}$ (dashed line) vs Ag/AgCl at pH = 1 (FTO-glass slide electrode as working electrode).

3. Water Oxidation Catalysis. Water oxidation activity accompanied by oxygen evolution was assessed using an oxygraph with a Clark electrode at pH = 1 (0.1 M HNO₃) using 20 equiv of Ce^{IV} at different concentrations of 1 in a range of 0.1–1.0 mM (Figure 5). The initial rate was determined within the first 10 s of oxygen evolution. For a 0.2 mM solution of 1, the oxygen-releasing rate was found to be 23 nmol/s, comparable to $[Ru(ROtpy)(bpy)(H_2O)]^{2+}$ (R = Et, Me) and $Ru(tpy)(2,2'-bipyridine N-oxide)(H_2O)^{2+}$ WOCs.^{30,31} Additionally, the water oxidation activity of this complex was more than 1 order of magnitude higher than that



Figure 5. Oxygen evolution rates for different concentrations of 1 (black squares) vs *cis*- $[Ru(bpy)_2(H_2O)_2]^{2+}$ (triangles)¹⁵ at pH = 1 (0.1 M HNO₃) by addition of excess (20 equiv) of Ce^{IV}. The dashed line shows a first-order reaction profile. The green and turquoise squares are oxygen evolution rates for fresh 1-UIO-67 in 200 mM solution of Ce^{IV}. The red square is recycled 1-UIO-67 in 200 mM solution of Ce^{IV}.

of its analogue cis- $[Ru(bpy)_2(H_2O)_2]^{2+}$ at the same conditions.¹⁵ Unlike cis- $[Ru(bpy)_2(H_2O)_2]^{2+}$, there was no delay between the injection of Ce^{IV} and oxygen evolution.¹⁵

4. Doping of UIO-67 MOF with 1 and Its Water Oxidation Activity. Doping of UIO-67 MOF with 1 was accomplished using the postsynthetic procedure by stirring of the solution of 1 or *cis*- $[Ru(bpy)(5,5'-dcbpy)]Cl_2$ with UIO-67 in DI water^{24,32,33} in 1:12 molar ratio relative to biphenyl 4,4'-dicarboxylic linker in the MOF structure (Figure 1c).³⁴ The solution became less colored, indicating some absorption of 1 into the MOF while the MOF crystals became slightly violet. Powder X-ray diffraction (PXRD) of the obtained system corresponds to the original UIO-67 MOF (Figure 6a, red



Figure 6. (a) PXRD pattern of postsynthetically incorporated 1-UIO-67 (red) in comparison with undoped UIO-67 MOF (black) and with recycled 1-UIO-67 (violet), respectively; poor signal-to-noise of recycled material is due to small amounts of catalyst recovered from the reaction mixture, while most intense peaks show preserved crystallinity. (b) X-ray powder diffraction pattern of solvothermally assynthetized 1-UIO-67.

curve). An attempt to perform solvothermal $[Ru(bpy)(5,5'-dcbpy)]Cl_2-UIO-67$ synthesis resulted in a material with low crystallinity, (Figure 6b). Postsynthetic introduction of the complex in higher molar proportion to dicarboxy-4,4'-biphenyl linkers than the 1:12 molar ratio gave a similar result of crystallinity loss (data not shown). This is different from the structurally similar $Ru(bpy)_2(5,5'-dcbpy)Cl_2$ and may be

explained as a consequence of the smaller size of the Ru(bpy)(5,5'-dcbpy)Cl₂ molecule relative to that of Ru-(bpy)₂(5,5'-dcbpy)Cl₂ (on average 9 Å).¹⁷ Since UIO-67 has two types of cavities, a tetrahedral 11.5 Å in diameter and octahedral 23 Å in diameter,^{35,36} the molecule attempting to fit inside the smaller cavity may distort the tetrahedral Zr–O nodes and prevent the formation of a crystalline structure.

Stirring of $[Ru(bpy)(5,5'-dcbpy)]Cl_2-UIO-67$ with water for 12 h leads to a substitution of Cl ligands with water molecules with formation of the 1-UIO-67. This was confirmed by EXAFS (Figure 9b) showing the disappearance of the Ru-Cl peak at approximately 2 Å distance.³⁷ Thus, this method of UIO-67 doping should be considered equivalent to doping using 1. Loading for 1-UIO-67 was determined using both the ICP MS method and UV-vis spectrophotometry. In UV-vis the change in the 1 concentration in solution was measured before and after stirring with UIO-67 MOF. Both methods demonstrated similar results.

Reusability of 1-UIO-67 has been studied via a catalytic experiment using a recycled sample. After addition of the excess of Ce^{IV} as-synthesized 1-UIO-67 evolved oxygen with an average initial rate of 6.5 nmol/s (3 measurements were performed, Figure 5, green square). Then, the MOF was recovered by filtration and washing with 0.1 M HNO₃ and DI water. The PXRD pattern of the sample after the reaction (Figure 6a, violet curve) confirmed structural similarity with the original UIO-67 MOF, in agreement with previous results for the similar Ru(tpy)(5,5'-dcbpy)Cl₂ containing UIO-67 MOF.³⁸ ICP MS of the recovered sample showed almost three times less Ru content, and MOF showed an initial rate of oxygen evolution of 2.2 nmol/s (Figure 5, red square). We attribute loss of the catalyst from the surface to harsh conditions of the reaction, namely the acidic pH and excess of strong oxidant.

5. Resonance Raman Spectroscopy. Resonance Raman spectroscopy was conducted to shed light on the structures of 1, 1-UIO-67 MOF, and their reactive species relevant to the water oxidation. The Raman spectra of WOR catalyzed by the 1 mM solution of 1 or 20 mg of 1-UIO-67 were recorded using a 532 nm laser, Figure 7. Oxidation with an excess of Ce^T resulted in pronounced spectral changes. Previous studies in Ru-promoted WOR conditions reported the appearance of a peak around 810 cm⁻¹ which was assigned to the Ru^V=O bond.^{39,40} Upon the addition of 20 equiv of Ce^{IV} to the solution of 1 at pH = 1, we also observed a major band around 810 cm⁻¹ (Figure 7). Conducting the reaction in $H_2^{18}O$ causes a band shift of ~ -44 cm⁻¹ (Figure 7a, insert), that is consistent with previous findings.^{39,41,42} The resonance Raman spectrum of WOR catalyzed by 1 embedded in the MOF (1-UIO-67) is shown in Figure 7b (orange line) as well as data for undoped UIO-67 and 1-UIO-67 after the oxidation with Ce^{IV}. A band around 810 cm⁻¹ arises upon the addition of Ce^{IV}. That band was not present in undoped UIO-67 and 1-UIO-67 before oxidation. The appearance of this band suggests water oxidation activity of 1-UIO-67 via formation of RuV=O intermediate.

6. EPR Spectroscopy. The initial **1** is EPR silent due to the Ru^{II} spin state, S = 0. However, the addition of Ce^{IV} leads to the formation of Ru^{III} and Ru^V, both with the spin S = 1/2. Figure 8 shows the EPR of a solution of 1 and 1-UIO-67 oxidized by Ce^{IV}. The addition of 1 equiv of Ce^{IV} to the initial Ru^{II} sample results in Ru^{III} intermediates whereas 20 equiv of the Ce^{IV} generates a considerable amount of Ru^V species in



Figure 7. (a) Resonance Raman spectrum for WOR catalyzed by 1 in $H_2^{16}O$ (orange) and $H_2^{18}O$ (blue), recorded within 5 min after addition of 20 equiv of Ce^{IV} (room temperature, laser excitation 532 nm). A wavelength shift $\Delta = -44$ cm⁻¹. (b) Resonance Raman spectrum for WOR catalyzed by 1-UIO-67. Red star marks a new peak at ~810 cm⁻¹.



Figure 8. X-band EPR spectra (20 K) for the species generated by oxidation of solution of 1 (orange and green curves) and 1-UIO-67 (red and purple curves) at pH = 1 with different amounts of Ce^{IV}. The ranges for *g*-factors corresponding to Ru^{III} and Ru^V (S = 1/2) are shown as dashed lines with arrows.

both solution and MOF (Figure 8). Also g-factors $g_{xx} \sim 2.50$, $g_{yy} \sim 2.36$, $g_{zz} \sim 1.75$ were within the range for Ru^{III} reported earlier.^{42–45} The g-factor $g_{xx} \sim 2.05$, $g_{yy} \sim 1.99$, $g_{zz} \sim 1.86$ corresponding to the formation of Ru^V was observed in both 1-UIO-67 and 1 solution (Figure 8).¹⁵ These g-factors are in agreement with the data obtained for other Ru^V complexes, for example 7-coordinate [Ru^V=O(bda)(isoq)₂]⁺ (g-factors $g_{xx} = 2.07$ and $g_{yy} = 2.00$)⁷ or 7-coordinate [Ru^V=O(pic)₂(dpp)]³⁺ ($g_{xx} = 2.08$, $g_{yy} = 2.01$, $g_{zz} = 1.90$).⁴⁰

7. XAS Analysis of Water Oxidation Reaction. Ru Kedges XANES of 1 oxidized with 20 equiv of Ce^{IV} and immediately frozen are close to the Ru^V K-edge of the reference compound (tetra-*N*-propylammonium bis-2-hydroxy-2-ethylbutyrato(oxo)ruthenate^V)⁴² (Figure 9a). This



Figure 9. (a) Ru K-edge XANES of water oxidation reaction of 1 frozen in 30 s after addition of Ce^{IV} excess in comparison with XANES of Ru^{V} reference compound.⁴² Also Ru K-edge XANES of 1 immobilized on an electrode surface is shown (dashed line). (b) Fourier transforms of k^{3} -weighted Ru EXAFS of 1 before (blue line) and after addition of Ce^{IV} (green line) in 0.1 M HNO₃ solution.

observation confirms the formation of Ru^V intermediates. From Fourier-transformed EXAFS (Figure 9b), it is clear that a coordination sphere of 1 after oxidation with Ce^{IV} underwent only minor changes. Moreover, Ru-N and Ru-C bonds remain virtually unaffected whereas the presence of Ru-O at ~1.72 Å is in agreement with the formation of $Ru^V=O$ (Table 2).⁴⁶ A prominent peak corresponding to the first coordination sphere reflects the Ru-N and R-O interaction (Figure 9b).

8. Electrochemical Behavior of 1-UIO-67 Thin Film on FTO-Glass Electrode. To verify the usability of **1** in water oxidation catalysis in an artificial photosynthetic assembly, electrochemical measurements were performed for **1-UIO-67**

Table 2. EXAFS Fits for 1 oxidized with 20 equiv of Ce^{IVa}

fit	shell, N	<i>R,</i> Å	$\sigma^2 \times 10^3$	R-factor	reduced χ^2
1	Ru–N, 6	2.04	3.2	0.31	4194
2	Ru–N, 6	2.05	3.5		
	Ru-C, 8	2.92	6.4	0.08	1595
3	Ru–O, 1	1.72	32		
	Ru–N, 5	2.07	32	0.029	760
	Ru–C, 8	2.97	69		

^{*a*}N, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor. Amplitude reduction factor S_0^2 was set to 1.

MOF deposited on the surface of a FTO-glass electrode. This preparation was performed according to UIO-67 thin film fabrication on a self-assembled biphenyl-4,4'-dicarboxylic acid monolayer (SAM) followed by postsynthetic exchange.³³ First, cleaned FTO slides were immersed in 6.6 mM bpdc solution in N,N-dimethylformamide, then UIO-67 thin film was grown using a slightly adjusted procedure. After that the bpdc linkers of UIO-67 were postsynthetically exchanged with the dcbpy moieties of 1. Color change of the electrodes from white to pinkish after incubation in 1 mM water solution of 1 for 24 h indicated the immobilization of 1 onto UIO-67 MOF thin film (Figure 11). A cyclic voltammogram (CV) of a 1-UIO-67electrode at pH = 1 (0.1 M nitric acid solution) with a scan rate of 0.1 V/s measured after obtaining steady CV cycles showed a prominent electrocatalytic current relative to an undoped UIO-67-electrode (Figure 10a). The electrochemically active surface density of 1 on the electrode is quantified by analyzing CV charge transfer in the Ru^{II}/Ru^{III} and Ru^{III}/ Ru^{IV} waves (Figure 10a) and is equal to 1.16×10^{-10} mol/



Figure 10. Comparison of electrochemical behavior of undoped UIO-67 thin film FTO-glass electrode (dash line) and 1-UIO-67-electrode (solid line): (a) cyclic voltammogram at pH = 1 (0.1 M nitric acid) and scan rate 0.1 V/s; (b) amperometric i-t curve at pH = 1 (0.1 M nitric acid) and 1.4 V versus Ag/AgCl applied potential.

 cm^{2} .^{47,48} XANES of the electrode immersed in 0.1 M solution of nitric acid showed Ru in the oxidation state 3+ (Figure 9a). Both methods indicate incorporation of 1 into the MOF layer on the electrode.

Electrocatalytic water oxidation at pH = 1 was performed using 1-UIO-67-electrode immersed in 0.1 M nitric acid solution in water at 1.4 V vs Ag/AgCl applied potential for about 6 h. The initial current of the 1-UIO-67-electrode exceeded the undoped UIO-67 electrode by 2 orders of magnitude (Figure 10b). A TOF for 1 incorporated into the 1-UIO-67-electrode was calculated to be 0.26 s⁻¹ over 6 h of bulk electrolysis.

9. Density Functional Theory Calculations. DFT calculations were performed to understand the water oxidation catalytic mechanism, associated reactive intermediates and the vibrations of **1**. As shown in Table 3, formation of oxidized

Table 3. Summary of DFT Calculations for Transformations in WOR Catalyzed by 1 and Its Analogs; Comparison between the Calculated and Experimentally Observed Redox Potentials

reaction	E_0/V calcd	E_0/V measd
$\text{Ru}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})_2^{3+} + 1e^- \rightarrow \text{Ru}^{\text{II}}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$	1.04	+1.04
$\begin{array}{l} Ru^{III}(bpy)(dcbpy)(H_2O)_2{}^{3+} + 1e^- \rightarrow Ru^{II}(bpy) \\ (dcbpy)(H_2O)_2{}^{2+} \end{array}$	+1.02	
$\text{Ru}^{\text{III}}(\text{dcbpy})_2(\text{H}_2\text{O})_2^{3+} + 1e^- \rightarrow \text{Ru}^{\text{II}}(\text{dcbpy})_2(\text{H}_2\text{O})_2^{2+}$	+1.15	
$\operatorname{Ru}^{\operatorname{IV}}(\operatorname{bpy})_{2}(\operatorname{OH})_{2}^{2+}+1e^{-}+2H^{+} \rightarrow$ $\operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy})_{2}(H_{2}O)_{2}^{3+}$	+1.18	+1.19
$\begin{array}{l} \operatorname{Ru}^{\mathrm{IV}}(\mathrm{bpy})(\mathrm{dcbpy})(\mathrm{OH})_2{}^{2^+} + 1\mathrm{e}^- + 2\mathrm{H}^+ \to \operatorname{Ru}^{\mathrm{III}}(\mathrm{bpy}) \\ (\mathrm{dcbpy})(\mathrm{H}_2\mathrm{O})_2{}^{3^+} \end{array}$	+1.09	+0.92
$Ru^{IV}(dcbpy)_2(OH)_2^{2+} + 1e^{-} + 2 H^+ → Ru^{III}(dcbpy)_2(H_2O)_2^{3+}$	+1.04	+1.08 ¹⁶
$\frac{\operatorname{Ru}^{V}(\operatorname{bpy})_{2}(O)(OH)^{2+}}{\operatorname{Ru}^{V}(\operatorname{bpy})_{2}(OH)^{2+}} + 1e^{-} + H^{+} \rightarrow$	+1.47	+1.33
$\begin{array}{l} \operatorname{Ru}^{V}(bpy)(dcbpy)(O)(OH)^{2+} + 1e^{-} + H^{+} \rightarrow \operatorname{Ru}^{IV}(bpy) \\ (dcbpy)(OH)_{2}^{2+} \end{array}$	+1.53	
$\operatorname{Ru}^{V}(\operatorname{dcbpy})_{2}(O)(OH)^{2+}+1e^{-} + H^{+} \rightarrow \operatorname{Ru}^{V}(\operatorname{dcbpy})_{2}(OH)^{2+}_{2}$	+1.58	
$\begin{array}{l} \operatorname{Ru}^{V}(\operatorname{bpy})_{2}(\operatorname{O})(\operatorname{OH})^{2+} + \operatorname{H}_{2}\operatorname{O} \to \operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy})_{2}(\operatorname{OOH}) \\ (\operatorname{H}_{2}\operatorname{O})^{2+} \end{array}$	$\Delta G =$	-0.3
$\begin{array}{l} Ru^{V}(bpy)(dcbpy)(O)(OH)^{2+} + H_{2}O \rightarrow Ru^{III}(bpy) \\ (dcbpy)(OOH)(H_{2}O)^{2+} \end{array}$	$\Delta G =$	-0.33
$\operatorname{Ru}^{V}(\operatorname{dcbpy})_{2}(O)(OH)^{2+} + H_{2}O \rightarrow$ $\operatorname{Ru}^{III}(\operatorname{dcbpy})_{2}(OOH)(H_{2}O)^{2+}$	$\Delta G =$	-0.47
$\begin{array}{l} 2\text{Ru}^{\text{V}}(\text{bpy})(\text{dcbpy})(\text{O})(\text{OH})^{2+} \rightarrow [\text{Ru}^{\text{IV}}(\text{bpy})(\text{dcbpy}) \\ (\text{OH})_2]_2(\text{O}-\text{O})^{4+} \end{array}$	$\Delta G =$	-0.56

species of 1 according to the monomolecular pathway occurs at ~1.09 V vs NHE which is in relative agreement with experimental redox potential 0.92 V, showing lesser potential than for two other structural analogues. These Ru^{IV} intermediates supposedly undergo further oxidation following a sequential water nucleophilic attack pathway, further oxidizing and releasing oxygen (Figure 11). The calculated potential for Ru^V formation is 1.53 V, although the experimental Ru^{IV} \rightarrow Ru^V redox transition is masked by the catalytic current on CV of the complex at different pH values (Figure 3). Water nucleophilic attack results in conversion of Ru^V to Ru^{III} peroxo-intermediate with calculated $\Delta G = -0.33$ eV.

It is clear from Figure 5 that WOR promoted by 1 follows predominantly a monomolecular pathway, while a radical coupling mechanism was observed for the *cis*-[Ru-(bpy)₂(H₂O)₂]²⁺ analogue.¹⁵ Dimerization of the Ru^V



Figure 11. Reaction pathway for WOR of 1 according to monomolecular mechanism.



Figure 12. Reaction pathway for WOR of 1 via dimerization mechanism.

intermediate in (1) has $\Delta G = -0.27$ eV which is in agreement with dimerization energy for other Ru-based WOCs.⁴⁹ From this Ru^V dimer, Ru^{IV} peroxo-dimer formation has $\Delta G = -0.56$ eV (Figure 12). A bimolecular transformation of the complex following oxygen evolution may include the formation of μ oxo-bridges between two Ru centers.¹⁵ Formed dimers are catalytically less active, resulting in a decrease of O₂ evolution at higher catalyst concentrations (Figure 5).

DISCUSSION

When searching for catalysts to convert solar energy to chemical fuels, the following criteria should be considered: (1) high activity at low pH to promote H_2 formation in photosynthetic assembly; (2) durability in harsh oxidative media and stability over a prolonged time with satisfactory turnover numbers; (3) preparation from easily available synthetic precursors; (4) the ability to incorporate onto solid support for an artificial photosynthetic apparatus; (5) low toxicity to minimize environmental damage; (6) understandable mechanism of activity for further development.

Here we present the simple and accessible water oxidation catalyst 1 with an elevated oxygen-evolution rate. The catalyst was further incorporated into UIO-67 MOF using postsynthetic exchange of MOF's ligand with retention of catalytic activity. The introduction of electron-withdrawing groups (-COOH) to a ligand was found to increase the catalytic activity of this Ru-complex in much the same way as of Fe-TAML complexes bearing the halogens in their macrocyclic ligands.⁵⁰ This behavior is opposite to the substituted [Ru(Rtpy)(R'-bpy)(H₂O)]²⁺ family of water oxidation catalysts (R, R'-different substituents).³¹ Their activity increases with the introduction of electron-donating groups in both tpy and bpy moieties.^{30,51-53} Increased WOR activity of 1 can be attributed to a favorability of highly electrophilic Ru^V center formation along with its steric accessibility to water nucleophilic attack and the instability of the Ru^V intermediate due to electronwithdrawing substituents present in the 5,5'-dcbpy ligand. An isotopic shift ~ 40 cm⁻¹ in the Raman spectra of the H2¹⁶O-H2¹⁸O WOR mixture at room temperature along

with XAS spectroscopy confirmed the formation of highly active Ru^V=O key species, with no considerable changes in the Ru ligand environment (Figures 7, 9). In addition, the formation of Ru^V has been confirmed by EPR (Figure 8). This, along with the oxygen evolution profile (Figure 5) and DFT calculations (Table 3), provided mechanistic insight into water oxidation and lead to the conclusion that WOR catalysis follows preferentially a water nucleophilic attack mechanism (Figure 11). The formation of Ru^V intermediate in the UIO-67 framework was observed in both Raman spectra (the new peak at ~810 nm after the addition of the Ce^{IV} oxidizer (Figure 7)) and EPR spectra, showing g-factors typical for Ru^{V} intermediates ($g_{xx} \sim 2.05, g_{yy} \sim 1.99, g_{zz} \sim 1.86$). This implies that incorporation of the catalyst into the framework does not change the mechanism of water oxidation for this complex. Stability of the Ru-doped MOF was confirmed by comparing PXRD patterns before and after the water oxidation reaction. Although formations of Ru^V states were observed both in a solution and in MOF, a water oxidation ability of the latter was lower (Figure 5). Thus, the transition from homo- to heterogeneous catalysis upon immobilization of WOC in a framework decreased the rate of oxygen evolution. This could be due to limiting electron transfer to a Ce^{IV} oxidant that cannot penetrate into the UIO-67 pores or due to an increase in the activation energy of WNA inside the pore. We plan to further investigate this effect in the future and learn how to overcome this limitation.

We can assess the distribution of the complex in UIO-67 MOF by EPR spectra of MOF oxidized with excess of Ce^{IV}. Since Ce^{IV} does not penetrate the UIO-67 crystalline structure, the surface distribution of Ru complex will result in a prevalence of Ru^V over Ru^{III} as we indeed observed in EPR spectra. Thus, we can conclude that the Ru complex is distributed on the surface of UIO-67 MOF (Figure 13). This is in agreement with previous observations that the complexes of the Ru(bpy)₂ family are too large to easily penetrate through the 11 Å pores of UIO-67 MOF.^{24,38}

Solution of 1 at pH = 1 demonstrated an electrocatalytic current higher than structurally similar $[Ru(bpy)_2(H_2O)_2]^{2+}$







(Figure 4). A wave at 1.4 V potential can be attributed to the formation of Ru^V species in solution. An electrochemical water oxidation using Ru-doped UIO-67 thin films deposited on the FTO electrodes has been described earlier.^{33,37} Nevertheless, a drastic improvement of electrocatalytic WOR at low pH has not been observed so far. For the electrode with deposited 1-UIO-67 thin film prepared by postsynthetic doping of UIO-67 with 1, we observed a significant (~2 orders of magnitude) increase in catalytic current at 1.4 V vs Ag/AgCl potential at pH = 1 (Figure 10). This improvement can be attributed to catalytic activity of 1 immobilized on a thin (about 2 μ m³³) UIO-67 layer with surface area ~0.6 cm⁻¹. Since UIO-67 itself is not conductive,¹⁹ it is also important to minimize the thickness of this MOF for an improvement of water oxidation activity.

CONCLUSIONS

Active water oxidation catalyst 1 is reported and incorporated into UIO-67 MOF using postsynthetic modification of the framework. The introduction of electron-withdrawing groups (-COOH) was found to increase catalytic activity. XAS, EPR, and Raman spectroscopy confirmed the formation of the highly active Ru^V=O key intermediate in both solutions and 1-UIO-67 MOF. Spectroscopic analysis and DFT calculations provided mechanistic insight into water oxidation and lead to the conclusion that the reaction proceeds mostly via a water nucleophilic attack mechanism. On-electrode activity makes 1-UIO-67 MOF suitable for incorporation into artificial solar energy utilization systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c00488.

Experimental methods and synthetic procedures; oxygen evolution measurements; XAS and EXAFS data (PDF)

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Notes

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