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Supplementary Information

Electrocatalytic Water Oxidation by a Molecular Catalyst Incorporated into a Metal-Organic Framework Thin Film

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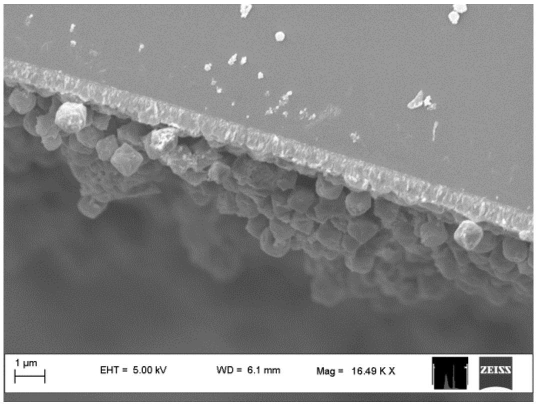


Figure S1. Cross-sectional SEM image of UiO67@FTO.

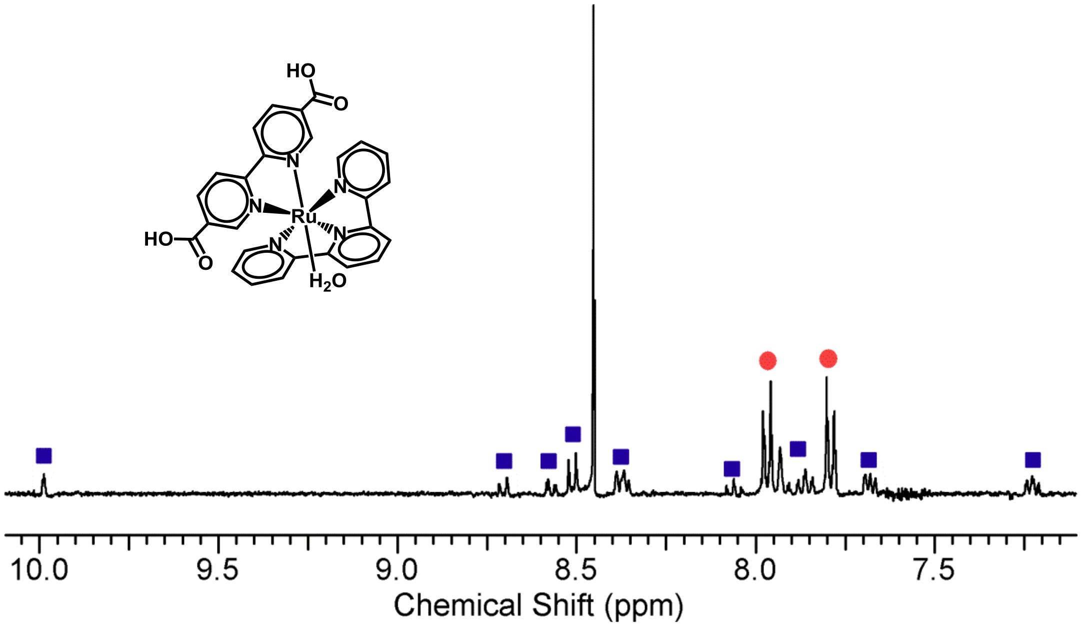


Figure S2. ^{1}H NMR (D_2O/NaOD) at 298K of supernatant liquid after PSE of [**1**] with bulk UiO67 material. Red circles correspond to bpdc, and blue squares indicate peaks assigned to [**1**].

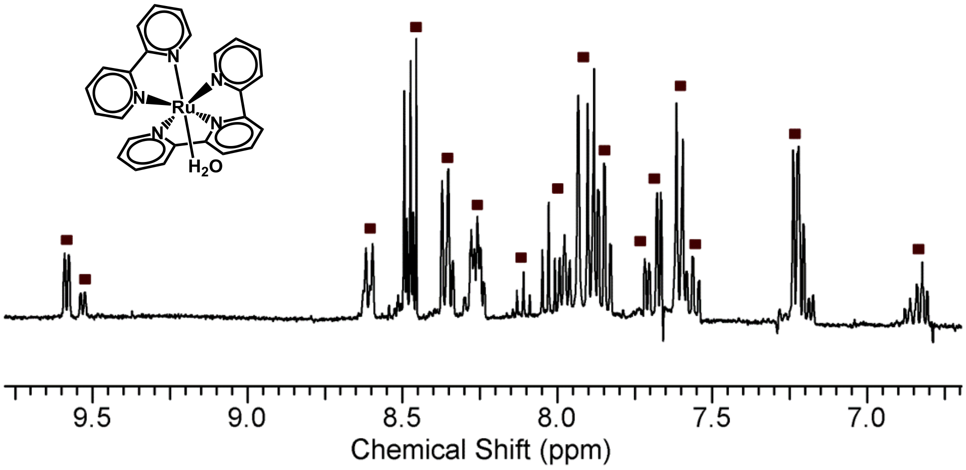


Figure S3. ^{1}H NMR (D_2O/NaOD) at 298K of supernatant liquid after PSE of $[Ru(tpy)(bpy)(OH_2)]^{2+}$ with bulk UiO67 material. Brown squares indicate peaks assigned to $[Ru(tpy)(bpy)(OH_2)]^{2+}$ or $[Ru(tpy)(bpy)(OH)]^{+}$. No resonances for the bpdc linker can be observed.

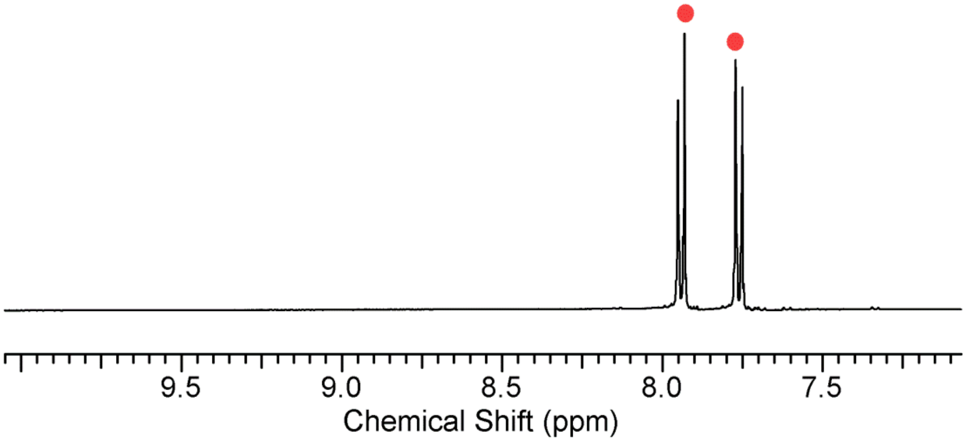


Figure S4. ^{1}H NMR (D_2O/NaOD) at 298K of bpdc (red circles).

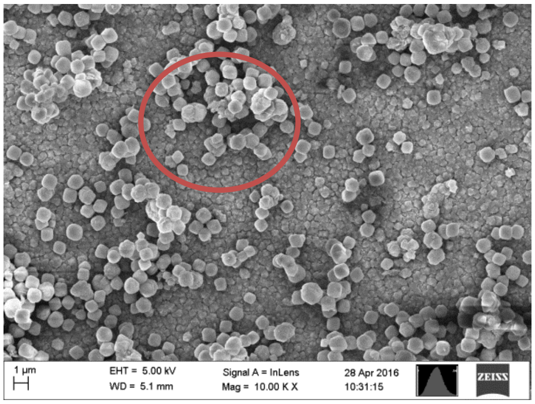


Figure S5. SEM image of UiO67-[RuOH$_2$]@FTO taken after measuring multiple CVs in 0.1M KCl (pH = 6.2). Red circle shows weakly adhered UiO67 particles.

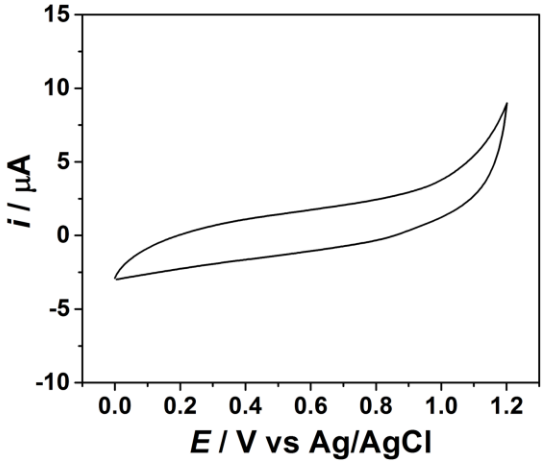


Figure S6. CV at 100 mV s^{-1} of solution phase using an auxiliary glassy carbon electrode (0.071 cm^2) between scans of UiO67-[RuOH$_2$]@FTO in 0.1M KCl (pH = 6.2).

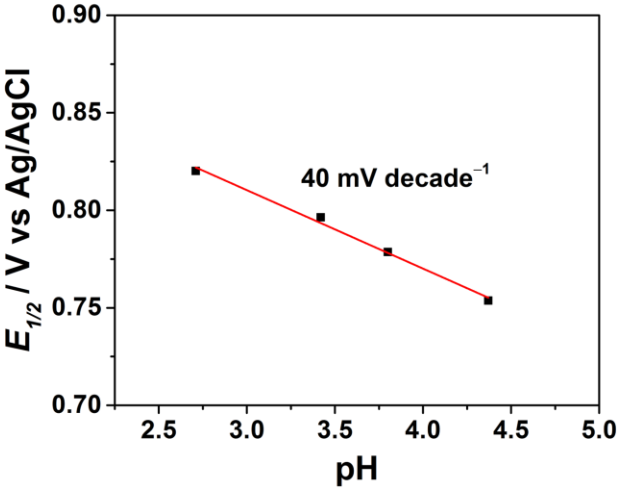


Figure S7. Dependence of $E_{1/2}$ of the $Ru^{III/II}$ couple on pH. Measured at 100 mV s^{-1} in 1M KNO_3 titrated with 1M HNO_3 to obtain a range of pH values.

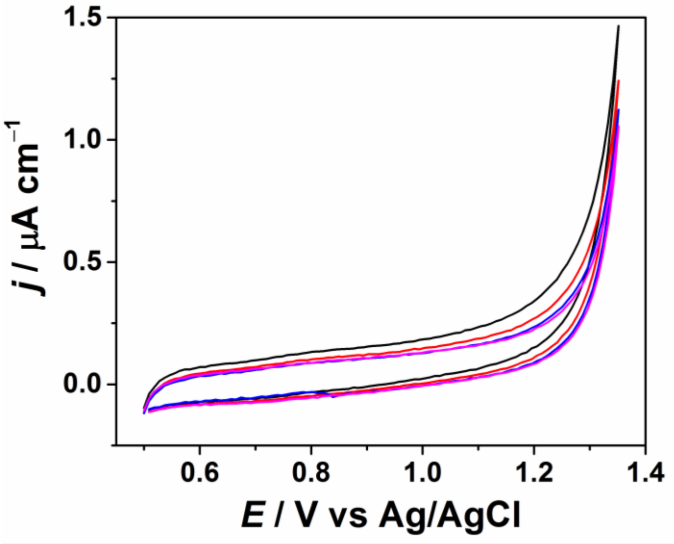


Figure S8. CVs showing multiple anodic scans of SAM-coated FTO slides treated under identical conditions as UiO67@FTO during PSE, measured in 0.1M KCl (pH = 6.2) at 100 mV s^{-1}.

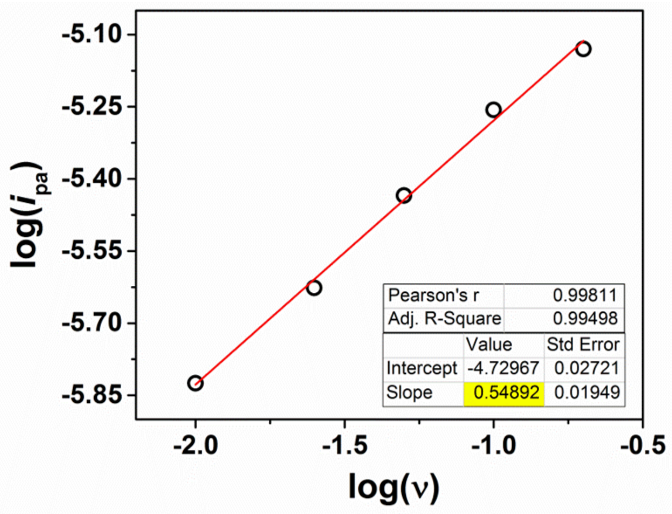


Figure S9. Plot of log(i_{pa}) vs. log(v) from CVs of UiO67-[RuOH$_2$]@FTO in 0.1M KCl (pH = 6.2) at scan rate from 10 mV s^{-1} to 200 mV s^{-1}. Highlighted portion of inset shows a linear fit to this data and the slope = 0.55, indicating $i_{pa} \propto v^{1/2}$.

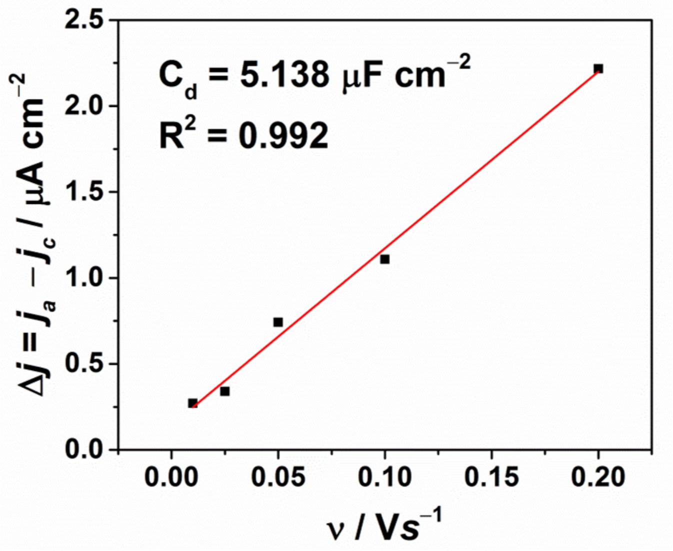


Figure S10a. Charging current densities (Δ*j*) plotted against scan rates taken from CVs of UiO67-[$RuOH_2$]@FTO in 0.1M KCl (pH = 6.2) at scan rates from 10 mV s^{-1} to 200 mV s^{-1} at 0.1 V vs. Ag/AgCl. The double layer capacitance (C_d) was determined from the slope of Δ*j* vs. *v*.

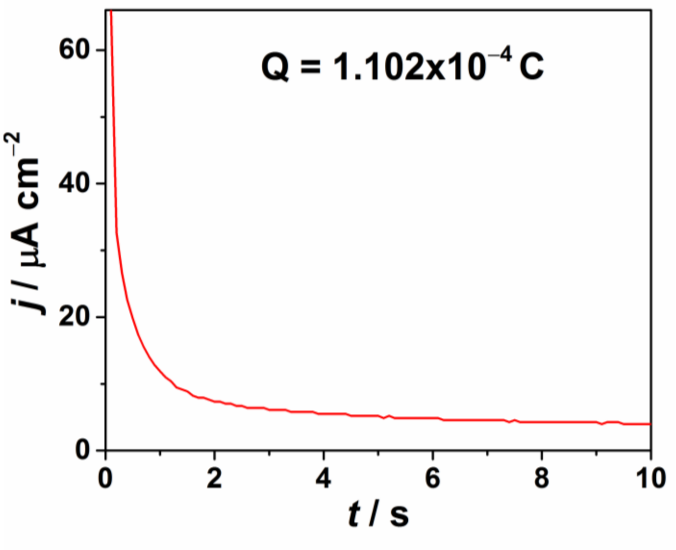


Figure S10b. CPE of UiO67-[$RuOH_2$]@FTO at 1.2 V vs. Ag/AgCl in 0.1M KCl (pH = 6.2) for determining the total charge passed (Q) during electrolysis.

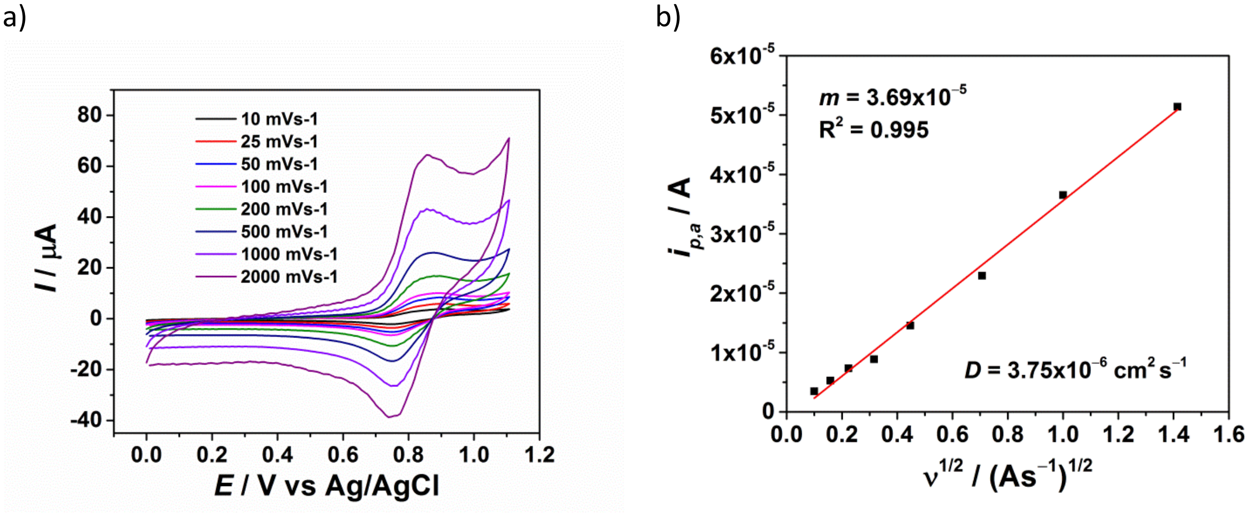


Figure S11. a) CVs of **[1]** in 0.1 M KCl with 10% acetone (pH = 7.1) at scan rates from 10 to 2000 mV s^{-1} and b) plot of i_{pa} vs. $\nu^{1/2}$ giving the diffusion coefficient, *D.*

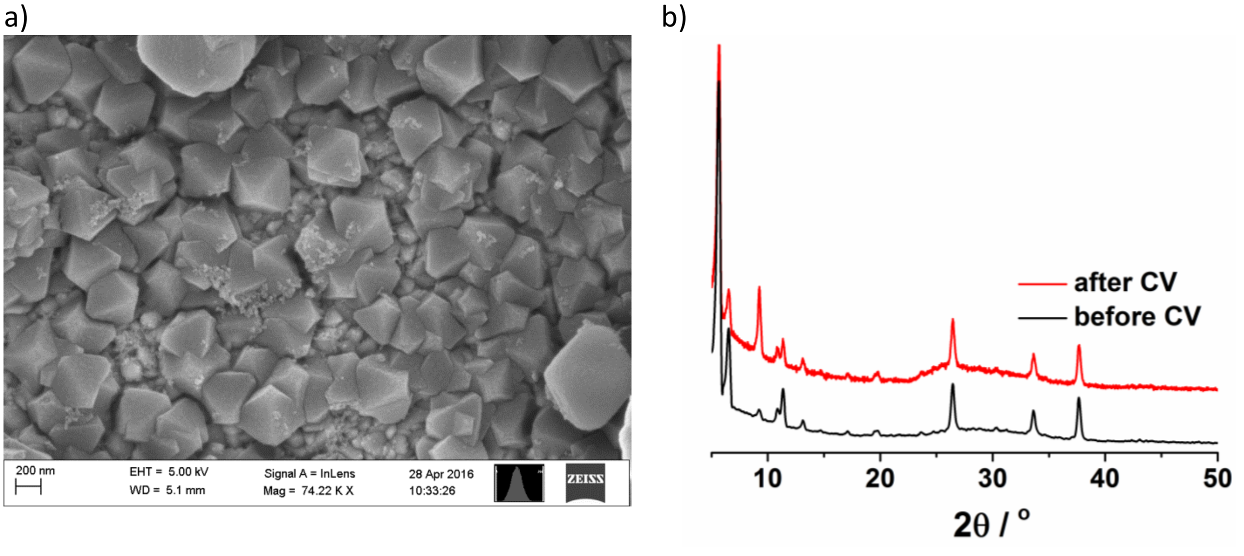


Figure S12. a) SEM of UiO67-[$RuOH_2$]@FTO after measuring multiple CVs and b) PXRD of UiO67-[$RuOH_2$]@FTO before (black) and after (red) measuring CVs.

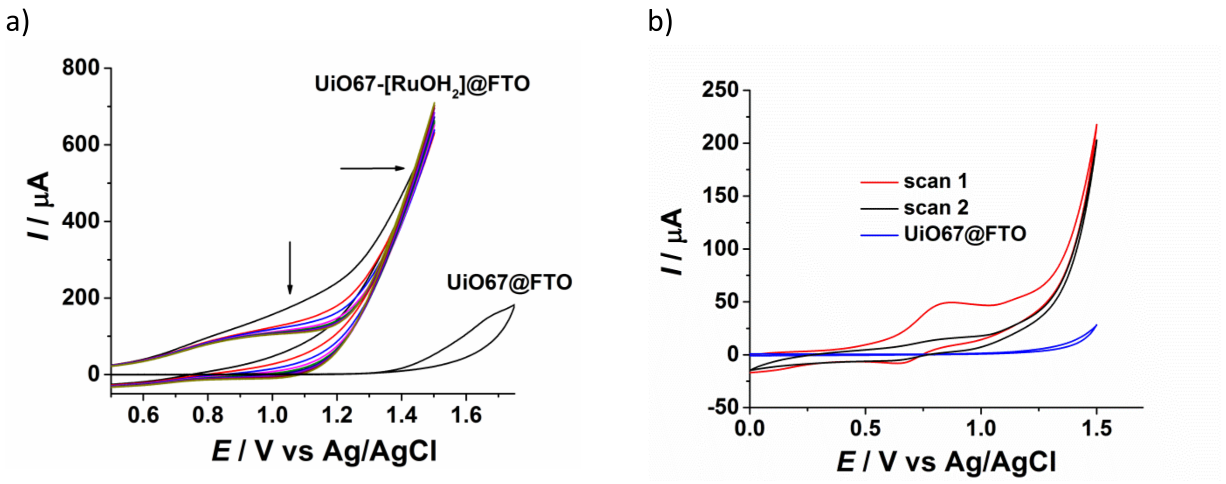


Figure S13. CVs of UiO67-[$RuOH_2$]@FTO (1 cm^2) at a) pH = 7 in 1M phosphate buffer and at b) pH = 8.4 in 0.1M carbonate buffer.

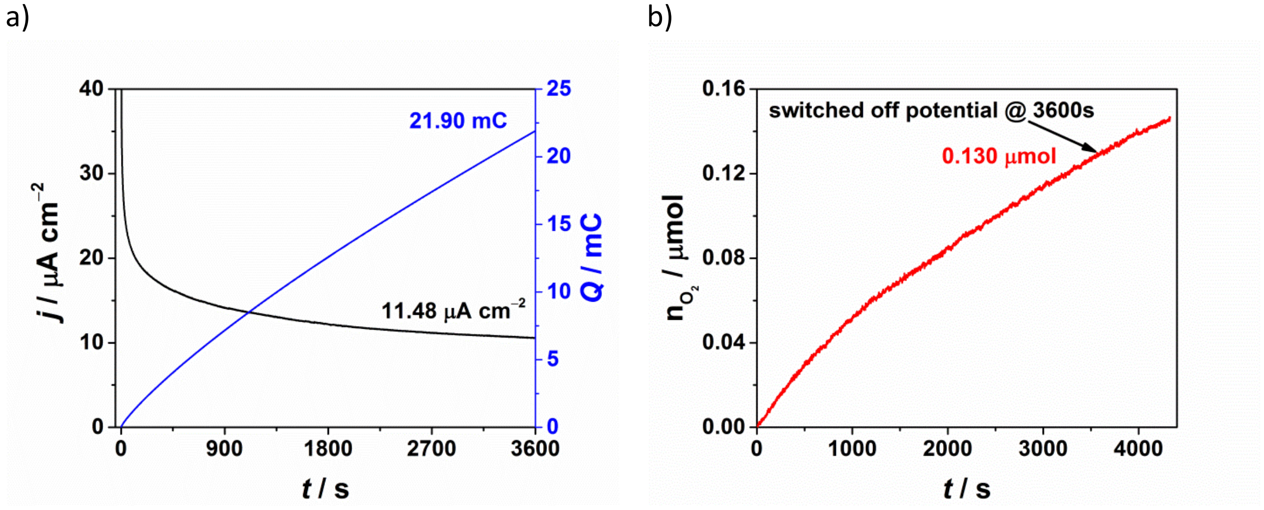


Figure S14. a) CPE of UiO67-[$RuOH_2$]@FTO (0.46 cm^2) at 1.5 V vs. Ag/AgCl in pH = 8.4 borate buffer (0.1 M) showing current density (black) and total charge passed (blue) over 1 hour and b) corresponding O_2 level, measured in solution, where a total of 0.130 μmol of O_2 accumulated (including contamination from air) after 3600 s (see below for O_2 evolution and FE calculations).

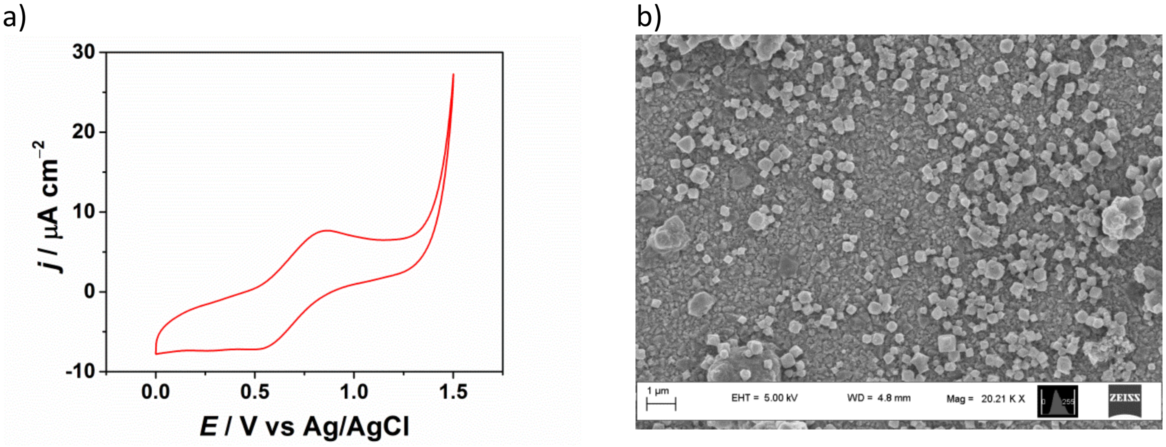
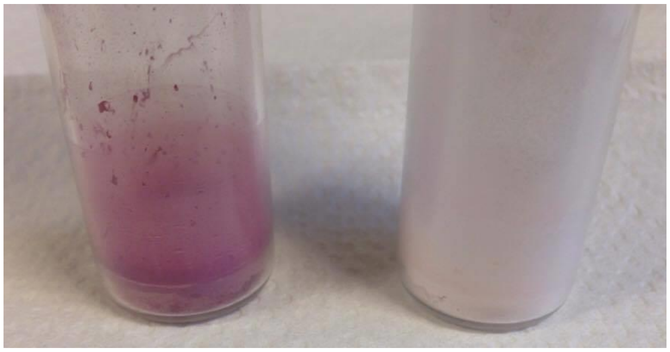


Figure S15. a) CV of UiO67-[RuOH$_2$]@FTO after a 1 hour CPE at 1.5 V vs. Ag/AgCl in pH = 8.4 borate buffer (0.1 M) showing presence of Ru$^{III/II}$ couple and b) corresponding SEM image of the UiO67-[RuOH$_2$]@FTO film after CPE.

Post Synthetic Exchange Procedure Using Bulk UiO67.

PSE: In a 20 mL vial, 100 mg of bulk UiO67 powder was combined with 10 mg of [**1**] or [Ru(tpy)(bpy)(OH_2)](PF_6)$_2$ to which a 4 mL solution of 3:1 H_2O/acetone with 20 µL of acetic acid was added. The resulting suspensions were sonicated for 10 min. and then incubated at room temperature for 3 days. The solids were collected by centrifugation, and washed with 3:1 H_2O/acetone (5 x 5 mL) followed by acetone (5 x 5 mL). The supernatant liquids from each wash were combined and reserved for ^{1}H NMR. Finally, the solids were incubated in acetone for 24h before being washed a final time with Et_2O (3 x 5 mL). Then the resulting UiO67 powders were dried under vacuum at 80°C for 24 h.



Photograph of UiO67 powders after PSE (right) using [**1**], which retains the color of the complex after washing and (left) using [Ru(tpy)(bpy)(OH_2)]$^{2+}$, which returns to the white color of pristine UiO67 after washing.

^{1}H NMR: The supernatant liquids obtained from each separate PSE were evaporated under reduced pressure to which 2 mL of D_2O was added. The solutions were treated with 2 drops of NaOD, filtered, and finally 0.6 mL was used to acquire the ^{1}H NMR spectra in Figures S2 and S3. 10 mg of bpdc was treated under the same conditions to obtain the reference spectrum in Figure S4.

Total Surface Concentration Calculations.

ICP	**Ru**	**Zr**
µg/mL	0.57	7.99

$$\mathbf{Zr_6O_4(OH)_4(C_{14}H_8O_4)_{5.614}(C_{27}H_{19}Cl_2N_5O_{13}Ru)_{0.386}}$$

Molecular Weight: 2334.2

A_{2D} = geometric surface area (A_{2D} = 1 cm^2); SBU = secondary binding unit

**Total amount of UiO67-[RuOH$_2$] on Film:*

(digested using 5 ml of conc. HNO_3)

$$7.99\frac{\mu g\ \mathrm{Zr}}{ml}\times 5\ ml = 39.95\ \mu g\ \mathrm{Zr}$$

$$39.95\ \mu g\ Zr\ \times\frac{1}{91.224}\ \frac{mol\ \mathrm{Zr}}{g\ \mathrm{Zr}}\times\frac{1\ g}{1\times 10^6\mu g} = 4.38\times 10^{-7} mol\ \mathrm{Zr}$$

$$4.38\times 10^{-7} mol\ \mathrm{Zr}\ \times\frac{1\ \mathrm{mol\ Zr_6\ SBU}}{6\ mol\ \mathrm{Zr}}\times\frac{1\ mol\ \mathrm{UiO67Ru@FTO}}{1\ \mathrm{mol\ Zr_6\ SBU}}\times\frac{2334.2\ g\ \mathrm{UiO67Ru@FTO}}{1\ mol\ \mathrm{UiO67Ru@FTO}}$$

$$= 1.70\times 10^{-4} g\ \mathrm{UiO67Ru@FTO} = 0.170\ mg\ \mathrm{UiO67Ru@FTO\ on\ 1\ cm^2\ FTO\ slide}$$

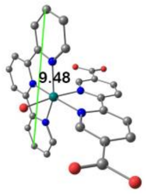
**Total amount of [RuOH$_2$] in Film:*

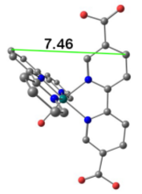
$$0.57\frac{\mu g\ \mathrm{Ru}}{ml}\times 5\ ml = 2.85\ \mu g\ \mathrm{Ru}$$

$$2.85\ \mu g\ \mathrm{Ru}\ \times\frac{1}{101.07}\ \frac{mol\ \mathrm{Ru}}{g\ \mathrm{Ru}}\times\frac{1\ g}{1\times 10^6\mu g} = 2.820\times 10^{-8}\ mol\ [\mathrm{RuOH_2}]$$

$$Total\ Surface\ Concentration = \frac{mol\ [RuOH_2]}{A_{2D}} = \frac{2.820\times 10^{-8}\ mol\ [\mathrm{RuOH_2}]}{1\ cm^2} = 2.820\times 10^{-8}\ mol\ cm^{-2}$$

**Adsorbed monolayer:*





Using DFT optimized structure of [**1**] [B3LYP/6-31G*/LANL2DZ/Gas phase] and 1 cm^2 FTO area:

$$\text{Projected Area} = 7.46\text{Å}\ width\times 9.48\text{Å}\ length = 70.7\ \text{Å}^2 = 7.07\times 10^{-15}\ \frac{cm^2}{molecule}$$
$$= 1.42\times 10^{14}\ \frac{molecule}{cm^2}$$

$$1.42\times 10^{14}\ \frac{molecule}{cm^2}\times\frac{1}{6.022\times 10^{23}}\frac{mol}{molecule} = 2.35\times 10^{-10}\ mol\ cm^{-2}$$

Electroactive Surface Concentration (Γ) Calculation.[1]

$\Delta j = 2\nu C_d A_{2D}$

$slope = 2C_d A_{2D} = 1.027 \times 10^{-5}$ (see Figure S5a)

$C_d = 5.138\,\mu F\ cm^{-2}$

$Q = Q_{dl} + Q_{Ru^{II/III}} = A_{2D} C_d (E_i - E_f) + nFA\Gamma$

$Q = 1.102 \times 10^{-4}\ C;\ E_i - E_f = 1.2V$ (see Figure S5b)

$\Gamma = 1.08 \times 10^{-9}\ mol\ cm^{-2}$

Diffusion Coefficient (*D*) and Concentration (*C*) Calculations.[1c]

$$C = \frac{\Gamma \times A_{2D}}{total\ volume}$$

Experimental pore volume of UiO67[2] $= 0.95\ cm^3 g^{-1}$

$total\ volume = 0.95\frac{cm^3}{g} \times 1.704 \times 10^{-4} g\ \mathrm{UiO67Ru@FTO} = 1.619 \times 10^{-4}\ cm^3$

$C = \frac{1.08 \times 10^{-9}\ mol\ cm^{-2} \times 1\ cm^2}{1.619 \times 10^{-4}\ cm^3}$

$C = 6.66 \times 10^{-6} mol\ cm^{-3}$ assuming an equal distribution of [**1**] throughout the film.

$$i_p = 0.4463 nFA_{2D}C\left(\frac{nF\upsilon D}{RT}\right)^{\frac{1}{2}}$$

(see Figure 4b in main text)

$slope = 1.7489 \times 10^{-5} = 0.4463 nFA_{2D}C\left(\frac{nFD}{RT}\right)^{\frac{1}{2}}$

$D = \left(\frac{slope}{0.4463 nFA_{2D}C}\right)^2 \left(\frac{RT}{nF}\right)$

$D = 9.56 \times 10^{-11}\ cm^2\ s^{-1}$

O_2 Evolution and Faradaic Efficiency (FE) Caculation.

A CPE was performed in a stirred solution of 0.1 M borate buffer (pH = 8.4) at 1.5 V vs. Ag/AgCl. Over 1 hour at total charge of 21.90 mC passed (Figure S10a), and of 0.130 µmol of O_2 ($n_{O_2}^{Total}$) was detected using an *in-situ* O_2 sensor (Figure S10b). After 1 hour the potential was returned to 0 V and the amount of dissolved O_2 continued to be monitored. From the increase in dissolved O_2 as a result of air contamination after the potential was switched off the amount of O_2 contamination ($n_{O_2}^{air}$) entering into the cell per unit time could be determined where

$$n_{O_2}^{air}\ rate = \frac{16.9\ nmol}{727\ s} = 0.023\ nmol\ s^{-1}$$

This was used to subtract the O_2 from air contamination ($n_{O_2}^{air}$) from the total O_2 detected to obtain the O_2 produced during the experiment ($n_{O_2}^{Exp}$).

$$n_{O_2}^{air} = 0.023\ nmol\ s^{-1} \times 3600\ s = 83.5\ nmol$$

$$n_{O_2}^{Exp} = n_{O_2}^{Total} - n_{O_2}^{air}$$

$$n_{O_2}^{Exp} = 130 - 83.5 = 46.5\ nmol$$

The Faradaic efficency (FE) was calculated by determining the theoretical amount of O_2 produced during the experiment using Fraday's Law,

$$n_{O_2}^{Theor} = Q/nF = 56.7\ nmol$$

where *Q* is the total charge passed during the CPE, *F* is Faraday's constant, and *n* is the number of electrons transferred (*n* = 4).

$$\mathrm{FE} = n_{O_2}^{Exp}/n_{O_2}^{Theor} = 46.5/56.7 = 82\%$$

References

[1] a) P. Manna, J. Debgupta, S. Bose, S. K. Das, *Angew. Chem. Int. Ed.* **2016**, *55*, 2425-2430; b) I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha, J. T. Hupp, *ACS Catal.* **2015**, *5*, 6302-6309; c) L. R. F. Allen J. Bard, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley & Sons, Inc, **2010**.

[2] S. Chavan, J. G. Vitillo, D. Gianolio, O. Zavorotynska, B. Civalleri, S. Jakobsen, M. H. Nilsen, L. Valenzano, C. Lamberti, K. P. Lillerud, S. Bordiga, *PCCP* **2012**, *14*, 1614-1626.