# Water Oxidation by an Electropolymerized Catalyst on Derivatized Mesoporous Metal Oxide Electrodes

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## Contents

## Experimental

**Sample Preparation.**
*Materials.* [Ru($\eta^6$-benzene)(Cl)$_2$]$_2$,[1] 2,6-bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridine,[2] and 5,5'-divinyl-2,2'-bipyridine[3] were synthesized as previously reported. Distilled water was further purified by using a Milli-Q Ultrapure water purification system. All other reagents were ACS grade and used without further purification. Fluoride-doped tin oxide (FTO)-coated glass (Hartford Glass; sheet resistance 15 Ω cm$^{-2}$), was cut into 10 mm × 40 mm strips and used as the substrate for $TiO_2$ nanoparticle films. Microwave reactions were carried out using a CEM MARS microwave reactor. A CEM HP-500 Plus Teflon-coated microwave vessel (100 mL) was used at a power setting of 400 W. The vessel was rotated and stirred throughout the microwave procedure. The pressure of the reaction vessel was monitored throughout the reaction, and never exceeded 300 PSI.

*Metal Oxide Films.* *n*$TiO_2$ films, typically 4 - 7 $\mu$m thick (~20 nm particle diameter), with a coating area of roughly 10 mm × 15 mm, were synthesized according to a literature procedure.[4]

**Electrochemical and Photophysical Measurements**.
*Absorption spectra* were obtained by placing the dry derivatized films perpendicular to the detection beam path of the spectrophotometer. The expression, $\Gamma = A(\lambda)/\varepsilon(\lambda)/1000$, was used to calculate surface coverages.[5] Molar extinction coefficients ($\varepsilon$) in $H_2O$ were used; $A(\lambda)$ was the absorbance at the MLCT $\lambda_{max}$. All measurements were carried out of films loaded from methanol solutions of 150 $\mu$M in ruthenium complex, which gave complete surface coverage ($\Gamma = 8 \times 10^{-8}$ mol cm$^{-2}$).

*Electrochemical* measurements were conducted on a CH Instruments 660D potentiostat with a Pt-mesh or Pt-wire counter electrode, and a $Ag/AgNO_3$ (0.01 M $AgNO_3$/0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) in $CH_3CN$; -0.09 V vs. $Fc^{+/0}$)[6] or Ag/AgCl (3 M NaCl; 0.197 V vs. NHE) reference electrode. $E_{1/2}$ values were obtained from the peak currents in square wave voltammograms or from averaging cathodic and anodic potentials at peak current values ($E_{p,c}$ and $E_{p,a}$) in cyclic voltammograms. Reductive electropolymerization was carried out in anhydrous propylene carbonate (dried over $MgSO_4$) with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte under an atmosphere of argon. Solutions were degassed with argon for at least 5 minutes prior to reductive electrochemical cycling.

Surface coverages on planar FTO electrodes were calculated using Eq. S1 where Q is the integrated current under the $Ru^{III/II}$-$OH_2$ redox couple of *poly***RuOH$_2^{2+}$**, *F* is Faraday's constant (96,485 C), *n* is the number of electrons transferred (*n* = 1), and *A* is the area of the electrode (~ 1 cm$^2$).

$$\Gamma = Q/nFA \quad \text{(Eq. S1)}$$

Catalytic rate constants for the water oxidation, $k_{obs}$, were calculated using Eq. S2 where $i_{cat}$ is the catalytic current taken at 1.7 V (vs NHE), $i_{peak}$ is the current taken for the $Ru^{III}$-OH/$Ru^{II}$-$OH_2$ redox couple, $n_{cat}$ is the number of electrons involved in the catalytic step (4 for water oxidation), R is the ideal gas constant, T is the temperature, $n_p$ is the number of electrons involved in the $Ru^{III}$-OH/$Ru^{II}$-$OH_2$ redox couple (1 in this case), F is Faraday's constant, and $\nu$ is the scan rate.[7]

$$\frac{i_{cat}}{i_{peak}} = \left(\frac{4RTn_{cat}}{n_p^2F}\right)k_{obs}\left(\frac{1}{\nu}\right) \quad \text{(Eq. S2)}$$

*Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)* results were obtained on a FEI Helios 600 Nanolab Dual Beam System equipped with an Oxford instruments, INCA PentaFET-x3 detector. A cross section was taken of *n*$TiO_2$-**RuPdvb$^{2+}$** that had been reductively cycled 60, 120, and 300 times in presence of **RuOH$_2^{2+}$**. Surface images were taken at 5 kV with a 86 pA beam current. Three EDS spectra were obtained at the $TiO_2$/solution interface (top), in the bulk of $TiO_2$ nanoparticles (middle), and at the nano-$TiO_2$/FTO interface (bottom) of the cross section.

*Photostability* measurements were performed by a previously reported procedure.[8] The light from a Royal Blue (455 nm, FWHM ~30 nm, 475 mW/cm$^2$) Mounted High Power LED (Thorlabs, Inc., M455L2) powered by a T-Cube LED Driver (Thorlabs, Inc., LEDD1B) was focused to a 2.5 mm diameter spot size by a focusing beam probe (Newport Corp. 77646) outfitted with a second lens (Newport, Corp 41230). The light output was directed onto the derivatized thin film placed at 45° in a standard 10 mm path length cuvette containing 3 mL of the solution. The illumination spot was adjusted to coincide both with the thin film and the perpendicular beam path of a Varian Cary 50 UV/Vis spectrophotometer. The absorption spectrum (360 – 800 nm) of the film was taken every 15 minutes over 16 hours of illumination. The incident light intensity was measured with a thermopile detector (Newport Corp 1918-C meter and 818P-020-12 detector). The solution temperature, 22±2°C, was consistent throughout the duration of the experiment.

The absorption-time traces at 400 nm, 450 nm, and 500 nm for the pH 4.6 (0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$) could be satisfactorily fit with the biexponential function (Eq. S3). For comparison purposes, the results of the multi-exponential analysis were represented by a single rate constant by first calculating the weighted average lifetime ($<\tau>$) using Eq. S4. The three weighted average lifetimes ($<\tau>_{400nm}$, $<\tau>_{450nm}$, $<\tau>_{500nm}$) were then averaged (Eq. S5) to give a desorption rate constant $k_{des}$.

$$y = A_1e^{-(1/\tau_1)x} + A_2e^{-(1/\tau_2)x} + y_0 \quad \text{(eq S3)}$$

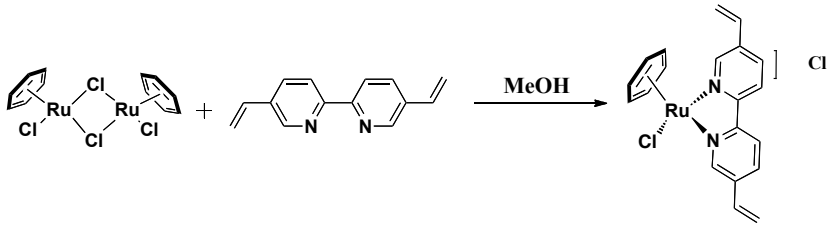
$$\langle \tau \rangle = \Sigma A_i \tau_i^2 / \Sigma A_i \tau \quad \text{(eq S4)}$$

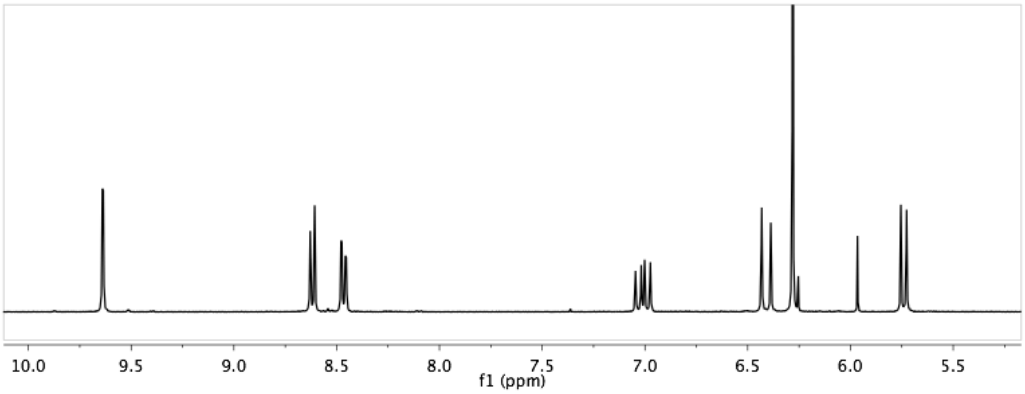
$$1/k_{des} = (\langle \tau \rangle_{400nm} + \langle \tau \rangle_{450nm} + \langle \tau \rangle_{500nm})/3 \quad \text{(Eq. S5)}$$

**Synthesis.**

[Ru(5,5'-dvb)( $\eta^6$-benzene)(Cl)](Cl)

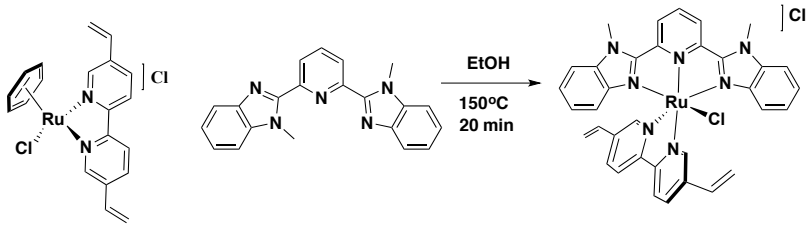
This complex was synthesized according a modified literature procedure.[9] [Ru($\eta^6$-benzene)$(Cl)_2]_2$ (0.24 g, 0.48 mmol) and 5,5'-divinyl-2,2'-bipyridine (0.2 g, 0.96 mmol) were dissolved in MeOH (~40 mL). The solution was refluxed overnight under an atmosphere of argon. The reaction was cooled, filtered, and the filtrate was taken to dryness by a rotary evaporator. The solid was triturated with ether, collected, and air-dried. This complex was used without further purification (0.42 g, 95%). $^1$H NMR (400 MHz, DMSO) $\delta$ (ppm) 9.64 (s, 2H), 8.63 (d, 2H), 8.48 (d, 2H), 7.05 (dd, 2H), 6.43 (d, 2H), 6.28 (s, 6H), 5.73 (d, 2H).

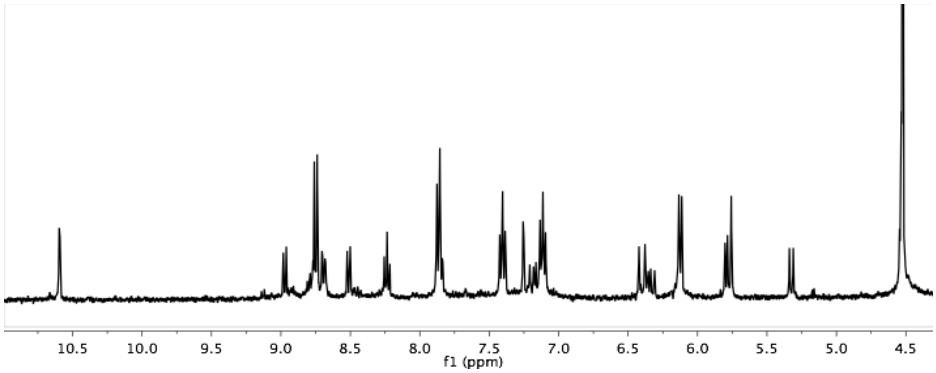



[Ru(Mebimpy)(5,5'-dvb)(Cl)](Cl)

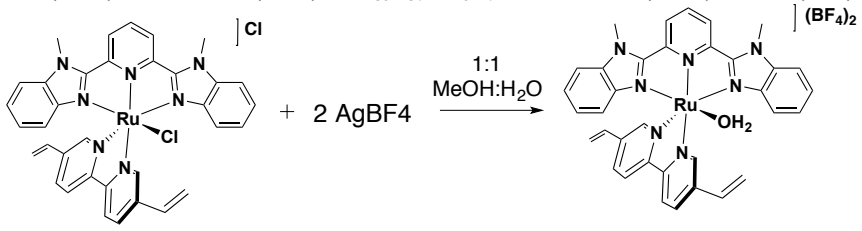
This complex was synthesized according a modified literature procedure.[10] [Ru(5,5'-dvb)( $\eta^6$-benzene)(Cl)]Cl (0.122 g, 0.27 mmol) and 2,6-bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridine (0.09 g, 0.27 mmol) were heated at reflux for 20 minutes at 150 °C in 40 mL EtOH in a microwave reactor. The solution was cooled, then filtered. A saturated solution of LiCl (~15 mL) was added along with additional $H_2O$ (15 mL), and the EtOH was removed by rotary evaporation. The dark purple precipitate was filtered, washed with water and ether, air dried and collected. This complex was used without further purification (0.169 g, 87%). $^1$H NMR (600 MHz, $d_6$-DMSO) $\delta$ (ppm) 10.6 (s, 1H), 8.98 (d, 1H), 8.76 (m, 2H), 8.70 (d, 1H), 8.50 (d, 1H), 8.24 (t, 1H), 7.87 (m, 3H), 7.40 (t, 2H), 7.26 (s, 1H), 7.11 (m, 3H), 6.42 (d, 1H), 6.32 (d, 1H), 6.11 (d, 2H), 5.79 (m, 2H), 5.32 (d, 1H), 4.53 (s, 6H).

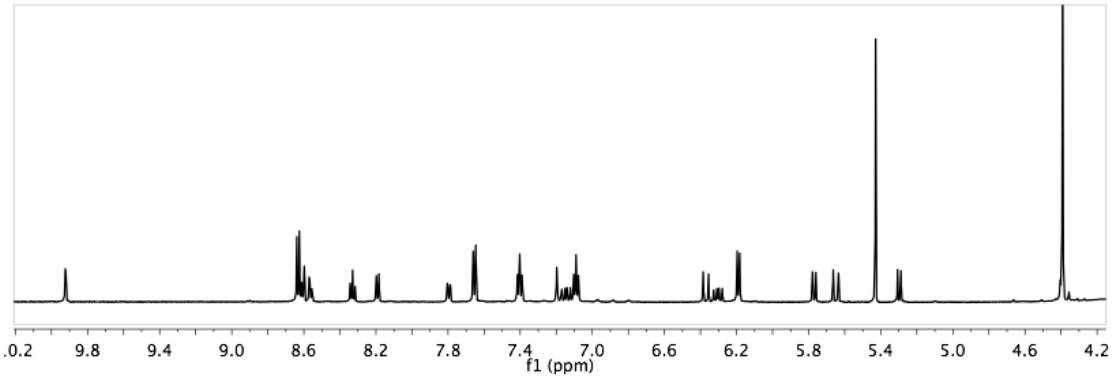





[Ru(Mebimpy)(5,5'-dvb)($OH_2$)]($BF_4$)$_2$ (**$RuOH_2^{2+}$**)

[Ru(Mebimpy)(5,5'-dvb)(Cl)](Cl) (0.344 g, 0.48 mmol) was dissolved in 1:1 MeOH:$H_2O$ (~ 30 mL) under an atmosphere of argon. A solution of $AgBF_4$ (0.189 g, 0.97 mmol) in $H_2O$ (~10 mL) was added. The solution was refluxed in the dark overnight under an atmosphere of argon. The solution was cooled, filtered through Celite, and the filtrate was taken to dryness using a rotary evaporator. The crude product was then purified by size-exclusion chromatography (Sephadex LH-20) with 1:1 MeOH:$H_2O$ as eluent. Similar fractions (based of UV-Vis spectra) were combined, and the solvent was removed by rotary evaporation. The dark red solid was triturated with ether and collected (0.29 g, 73%). $^1$H NMR (600 MHz, $CD_3CN$) $\delta$ (ppm) 9.97 (s, 1H), 8.60 (m, 4H), 8.34 (t, 1H), 8.19 (d, 1H), 7.82 (dd, 1H), 7.67 (d, 2H), 7.44 (t, 2H), 7.22 (d, 1H), 7.18 (dd, 1H), 7.12 (t, 2H), 6.42 (d, 1H), 6.36 (dd, 1H), 6.23 (d, 2H), 5.80 (d, 1H), 5.69 (d, 1H), 5.33 (d, 1H), 4.41 (s, 6H). Anal. Found (Calc.) for $C_{35}H_{37}B_2F_8N_7O_4Ru$: C 46.83 (47.00), H 3.72 (4.17), N 10.96 (10.96).



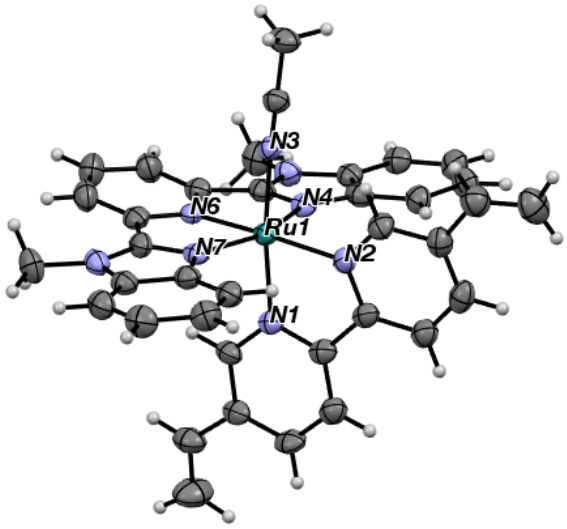



**Figure S1**. Crystal structure of **Ru-NCCH$_3$**$^{2+}$ grown by slow diffusion of diethyl ether into a solution of **RuOH$_2$**$^{2+}$ in $CH_3CN$. Structural details are listed at the end of Supporting Information.

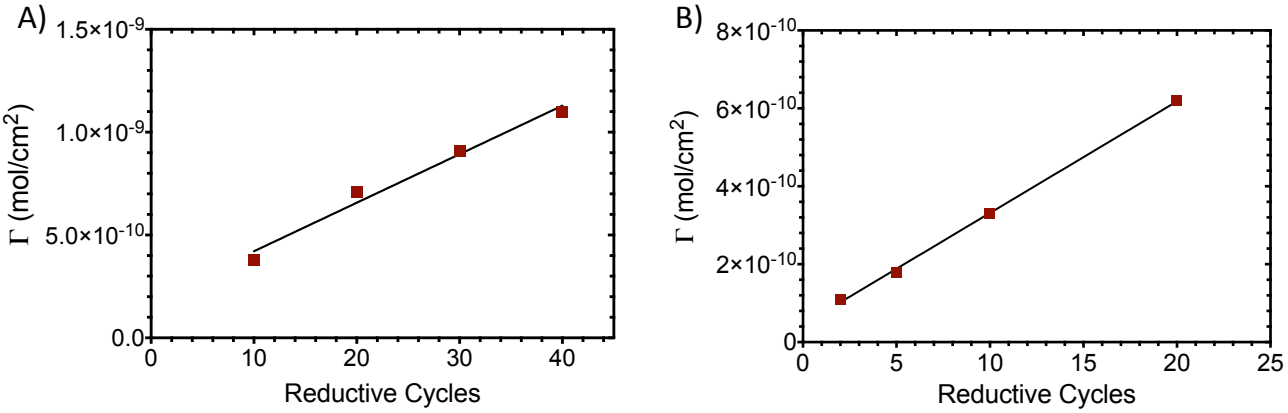



**Figure S2**. *Poly***RuOH$_2$**$^{2+}$ surface coverage on (A) bare *p*FTO and (B) *p*FTO-**RuPdvb**$^{2+}$ versus the number of reductive cycles in dry PC solution of **RuOH$_2$**$^{2+}$ (0.5 mM, 0.1 M $TBAPF_6$), cycling form 0 to -1.8 V (vs. $Ag/AgNO_3$), Pt counter, and $Ag/AgNO_3$ reference electrode.

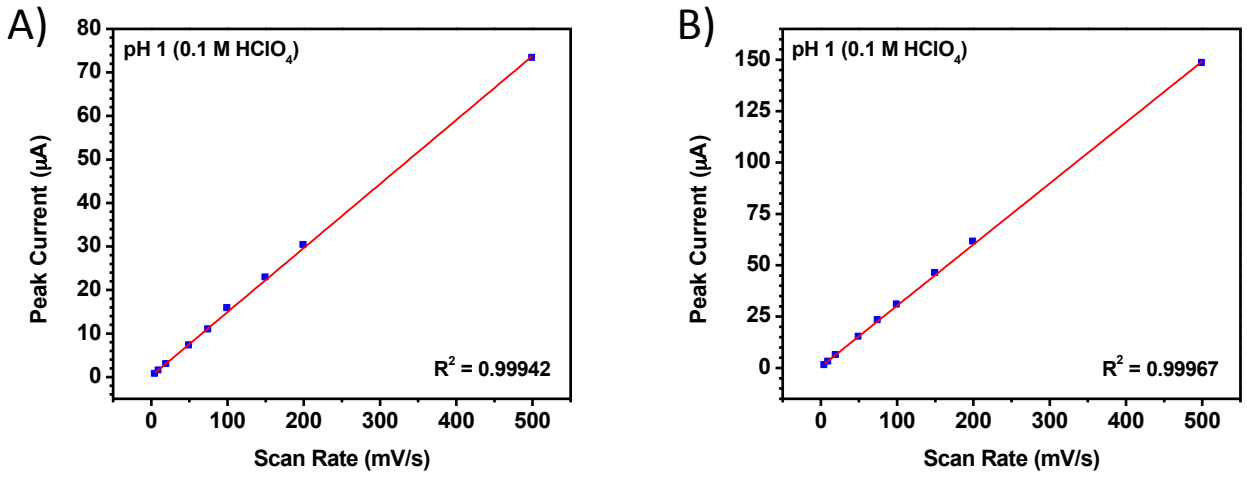



**Figure S3**. Peak current for the *poly*$Ru^{III/II}OH_2$ redox couple versus the scan rate for *p*FTO-**RuPdvb**$^{2+}$-*poly***RuOH**$_2^{2+}$ with 5 (A) and 20 (B) monolayers of *poly***RuOH**$_2^{2+}$ in aqueous 0.1 M $HClO_4$, Pt-wire counter electrode, and Ag/AgCl reference electrode.

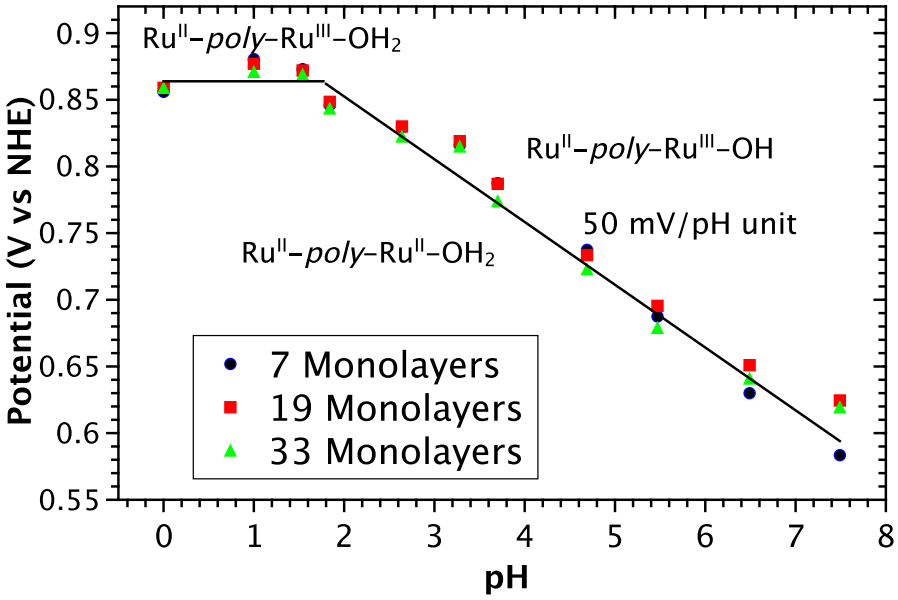



**Figure S4**. $E_{1/2}$ versus pH diagram of *p*FTO-**RuPdvb**$^{2+}$-*poly***RuOH**$_2^{2+}$ with 7 (blue circles), 19 (red squares) and 33 (green triangles) monolayer equivalents of **RuOH**$_2^{2+}$ deposited onto *p*FTO-**RuPdvb**$^{2+}$. $E_{1/2}$ values were obtained at peak current maxima in square wave voltammograms. The solid lines are best fits of the variation in $E_{1/2}$ values with pH for the $Ru^{III}$-$OH_2$/$Ru^{II}$-$OH_2$ and $Ru^{III}$-OH/$Ru^{II}$-$OH_2$ redox couples at 23 °C in aqueous 0.5 M $NaClO_4$ and 0.1 M buffer.

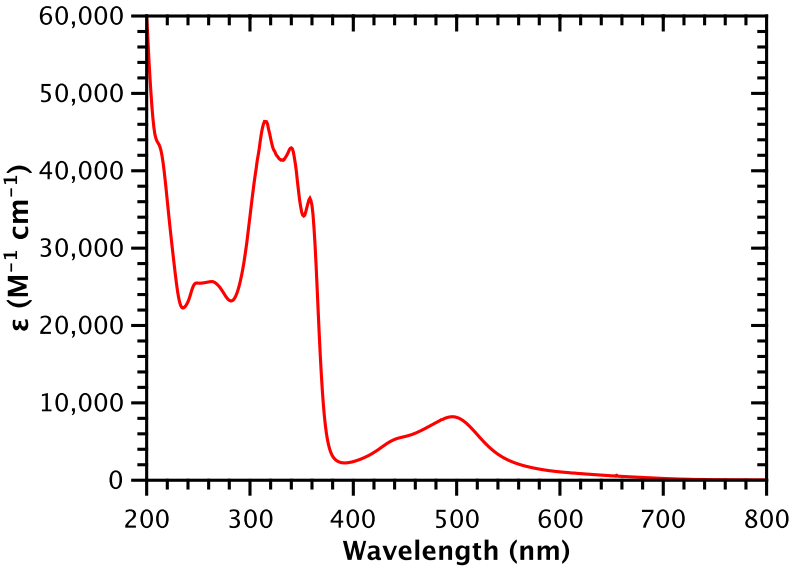



**Figure S5**. Absorption spectrum of $\mathbf{RuOH_2^{2+}}$ at room temperature in $H_2O$.

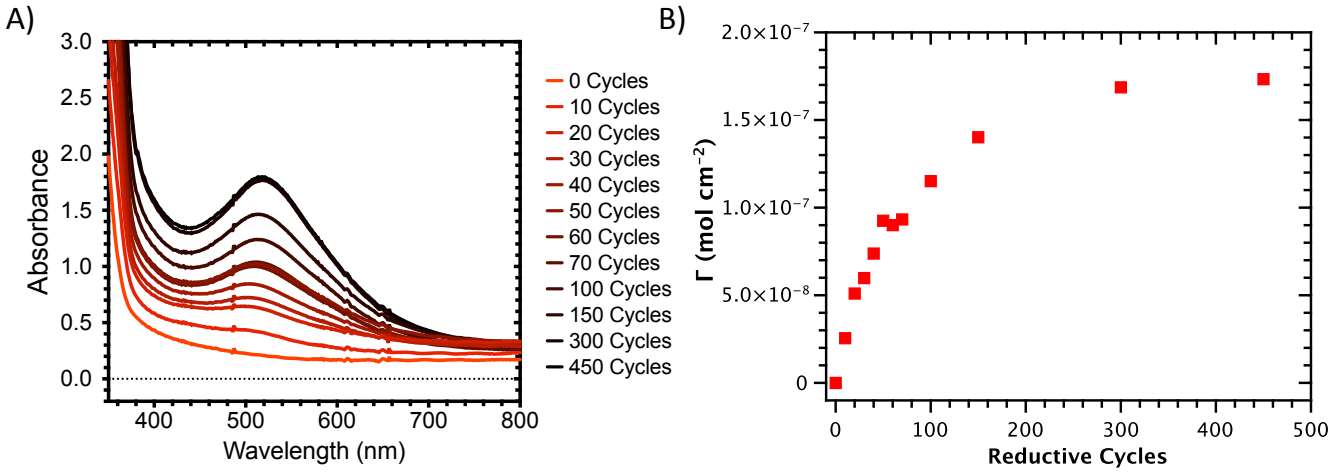



**Figure S6**. (A) Changes in UV/visible absorption spectra for *n*$TiO_2$ with increasing number of reductive cycles from 0 to -1.8 V (vs $Ag/AgNO_3$) in PC solution (0.1 M $TBAPF_6$) of $\mathbf{RuOH_2^{2+}}$ (0.5 mM), Pt counter, and $Ag/AgNO_3$ reference. (B) Surface coverage of *poly*$\mathbf{RuOH_2^{2+}}$ versus the number of reductive cycles.

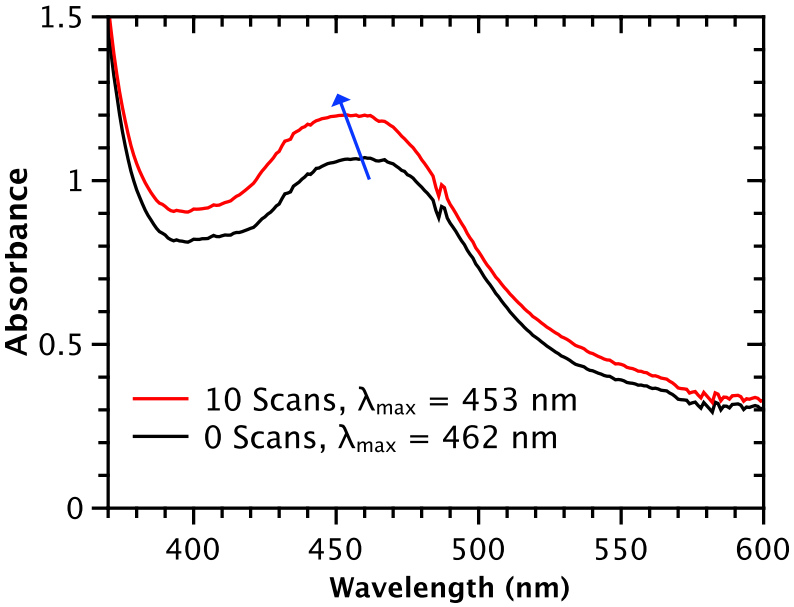



**Figure S7**. UV/visible absorption spectra of *n*$TiO_2$-**RuPdvb**$^{2+}$ before (black) and after (red) 10 reductive cycles from 0 to -1.8 V (vs $Ag/AgNO_3$) in a PC solution of 0.5 mM **RuOH$_2$**$^{2+}$, Pt counter, and $Ag/AgNO_3$ reference electrode.

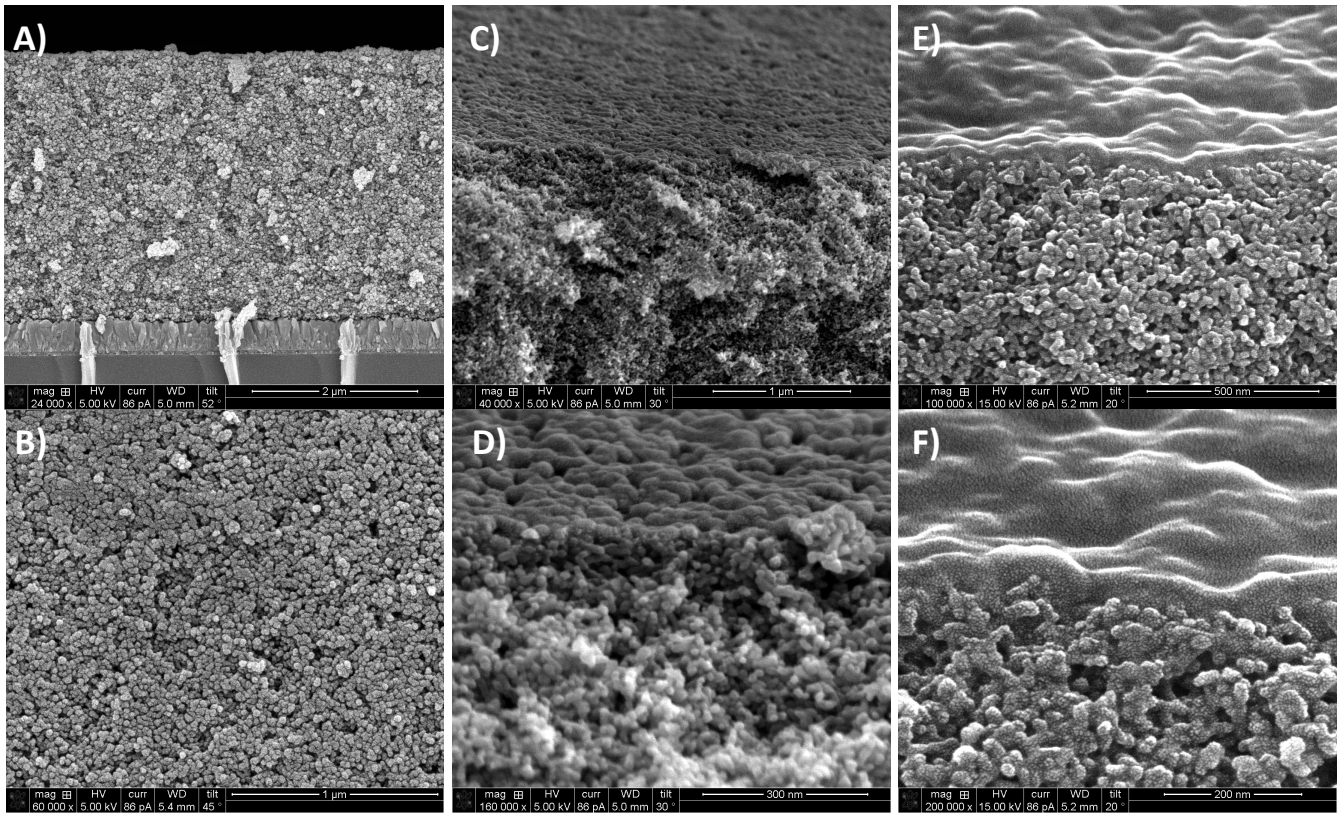



**Figure S8**. Cross-sectional SEM images of the *n*$TiO_2$-**RuPdvb**$^{2+}$ films following 60 (A and B), 120 (C and D), and 450 (E and F) reductive cycles in a PC solution containing 0.5 mM **RuOH$_2$**$^{2+}$.

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 12.07 | 19.68 |
| O K | 54.70 | 66.98 |
| Ti K | 32.03 | 13.10 |
| Ru L | 1.19 | 0.23 |
| | | |
| Totals | 100.00 | |

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 7.64 | 14.27 |
| O K | 46.42 | 65.14 |
| Ca K | 0.42 | 0.23 |
| Ti K | 41.90 | 19.64 |
| Ru L | 1.06 | 0.24 |
| Sn L | 2.56 | 0.48 |
| | | |
| Totals | 100.00 | |

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 5.44 | 11.44 |
| O K | 40.44 | 63.91 |
| Si K | 1.81 | 1.63 |
| Ti K | 37.62 | 19.85 |
| Ru L | 0.91 | 0.23 |
| Sn L | 13.78 | 2.93 |
| | | |
| Totals | 100.00 | |

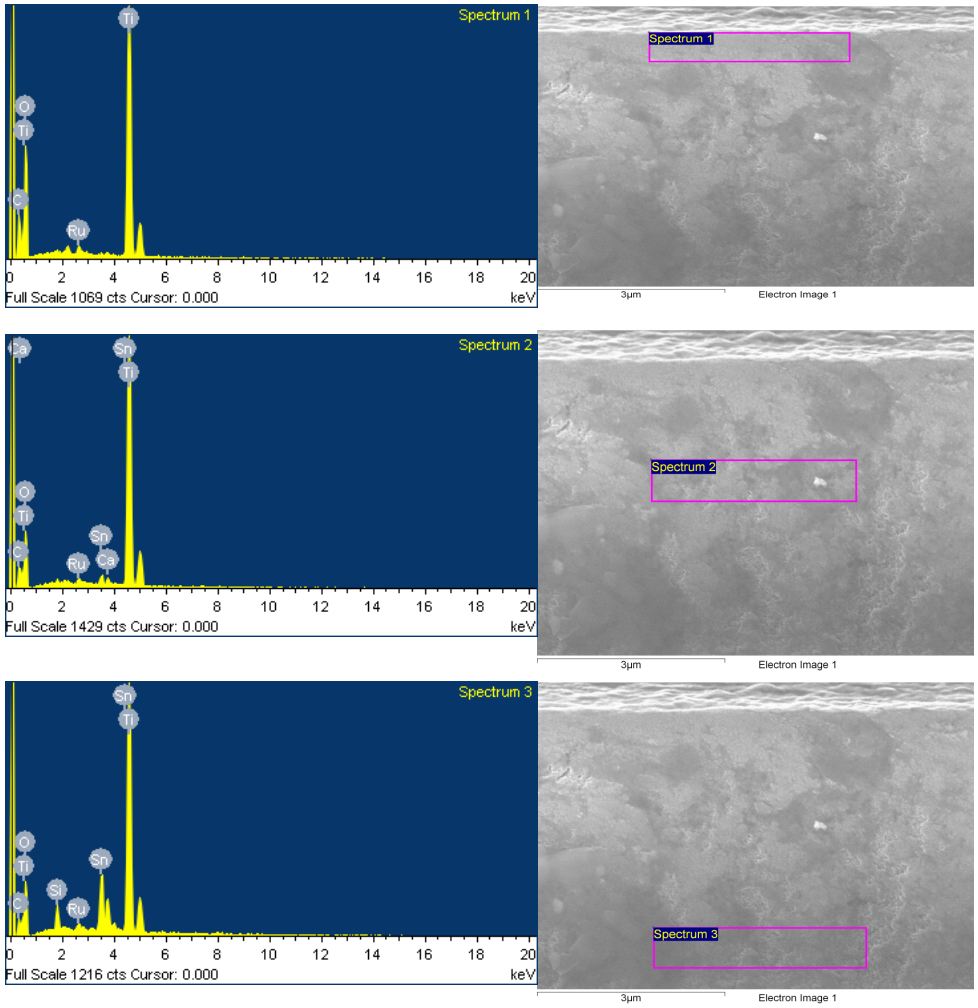



**Figure S9**. EDS spectra (middle) and the tabulated results (left) obtained for *n*$TiO_2$-**RuPdvb$^{2+}$**-*poly***RuOH$_2^{2+}$** following 450 reductive cycles at various depths that are indicated by the pink rectangle (right).

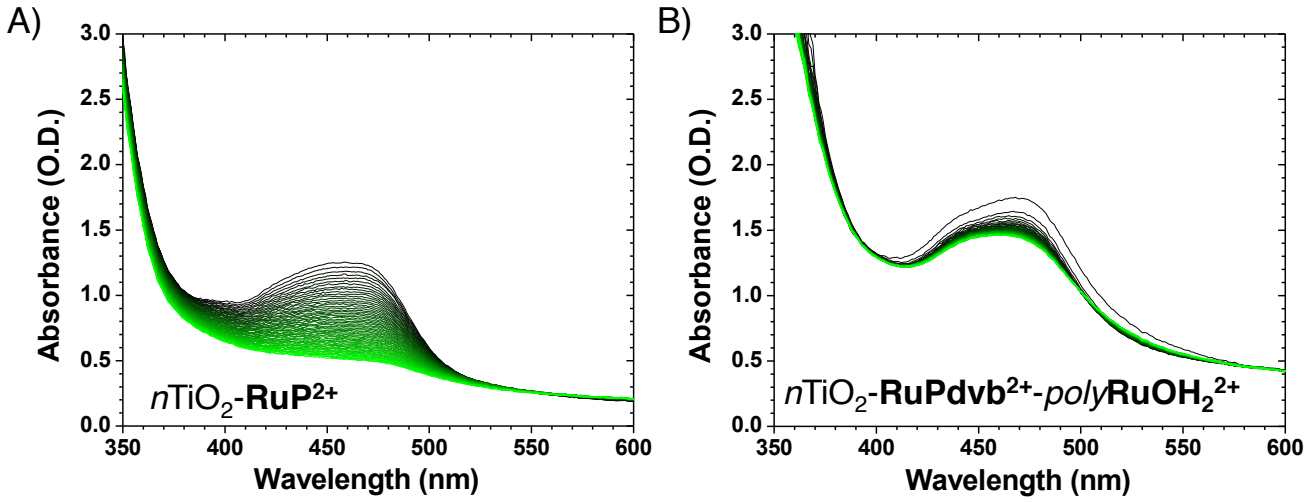



**Figure S10**. Changes in the absorption spectrum of *n*$TiO_2$-**RuP** (A) and *n*$TiO_2$-**RuPdvb$^{2+}$**-*poly***RuOH$_2^{2+}$** following 70 reductive cycles (B, 1:1 chromophore:catalyst) in aqueous 0.1 M $HClO_4$ under constant 455 nm irradiation (475 mW/cm$^2$) from 0 h (green) to 16 h (black) recorded every 15 min.

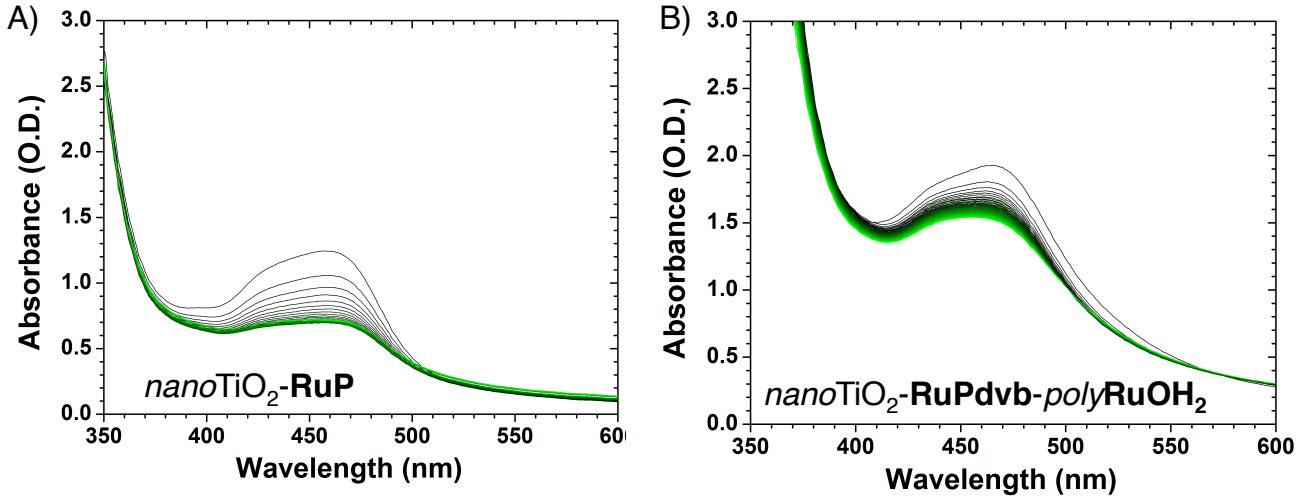



**Figure S11**. Changes in the absorption spectrum of *n*$TiO_2$-**RuP** (A) and *n*$TiO_2$-**RuPdvb**$^{2+}$-*poly***RuOH**$_2^{2+}$ following 70 reductive cycles (B, 1:1 chromophore:catalyst) in pH 4.7 aqueous solution (0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$) under constant 455 nm irradiation (475 mW/cm$^2$) from 0 h (green) to 16 h (black) recorded every 15 min.

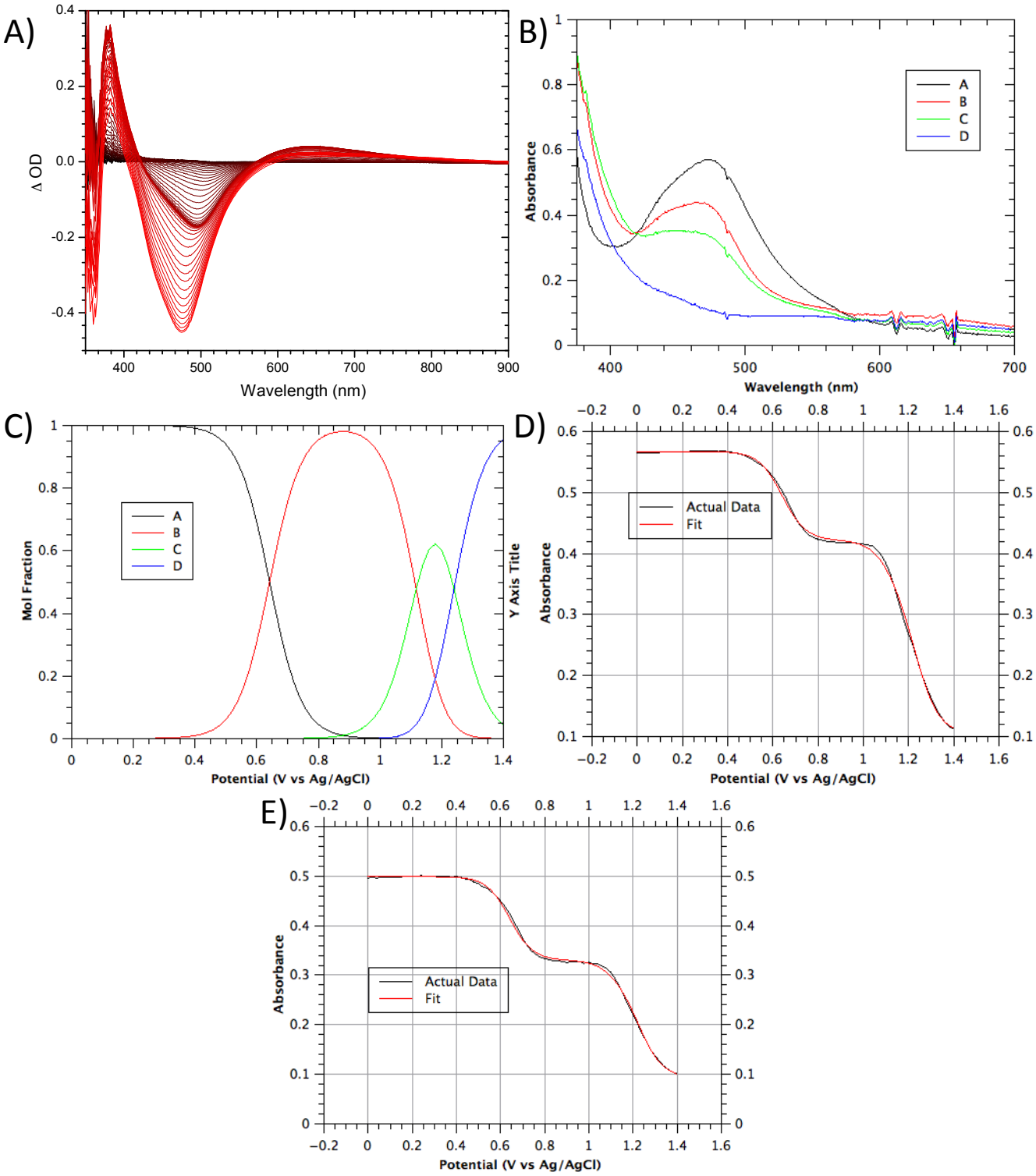



**Figure S12**. (A) Spectroelectrochemistry of *n*ITO-**RuPdvb**$^{2+}$-*poly***RuOH$_2$**$^{2+}$ in 0.1 M $HClO_4$ with a Pt-mesh counter electrode and Ag/AgCl reference electrode. The *n*ITO-**RuPdvb**$^{2+}$-*poly***RuOH$_2$**$^{2+}$ slide was stepped 0.02 V and held there for 300 s. Following each potential step, a UV/Visible spectrum of the slide was obtained. (B) Calculated spectra for the multiwavelength fit to the kinetic model A ⇄ B ⇄ C ⇄ D with A = $[Ru^{II}\text{-}Ru^{II}\text{-}OH_2]^{4+}$, B = $[Ru^{II}\text{-}Ru^{III}\text{-}OH_2]^{5+}$, C = $[Ru^{II}\text{-}Ru^{IV}\text{=}O]^{5+}$, and D = $[Ru^{III}\text{-}Ru^{IV}\text{=}O]^{6+}$. (C) Calculated concentration profiles versus the applied potential (V vs Ag/AgCl) for the model A ⇄ B ⇄ C ⇄ D. (D) Changes in absorption versus potential at 476 nm ($\lambda_{max,\,MLCT}$ for **RuPdvb**$^{2+}$) in black and calculated fit (red) using the model A ⇄ B ⇄ C ⇄ D. (E) Changes in absorption versus potential at 491

nm ($\lambda_{max,\,MLCT}$ for **RuOH$_2^{2+}$**) in black and calculated fit (red) using the model A ⇄ B ⇄ C ⇄ D. The data was fit using SPECFIT/32 by a series of three sequential Nernstian steps (A ⇄ B ⇄ C ⇄ D).

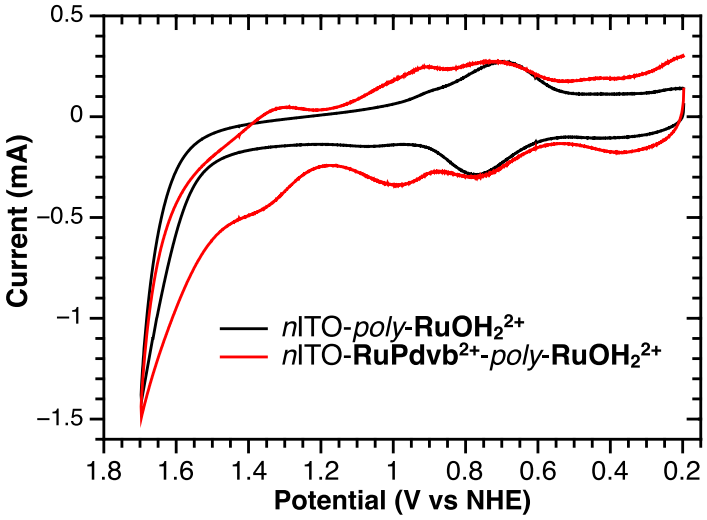



**Figure S13**. Cyclic voltammograms at 10 mV/s of *n*ITO-**RuPdvb$^{2+}$**-*poly***RuOH$_2^{2+}$** (red) and *n*ITO-*poly***RuOH$_2^{2+}$** (black) in pH 4.7 aqueous solution (0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$); Pt-mesh counter electrode and Ag/AgCl reference electrode. The voltammograms are normalized to the $Ru^{III}$-OH/$Ru^{II}$-$OH_2$ redox couple for comparison purposes.

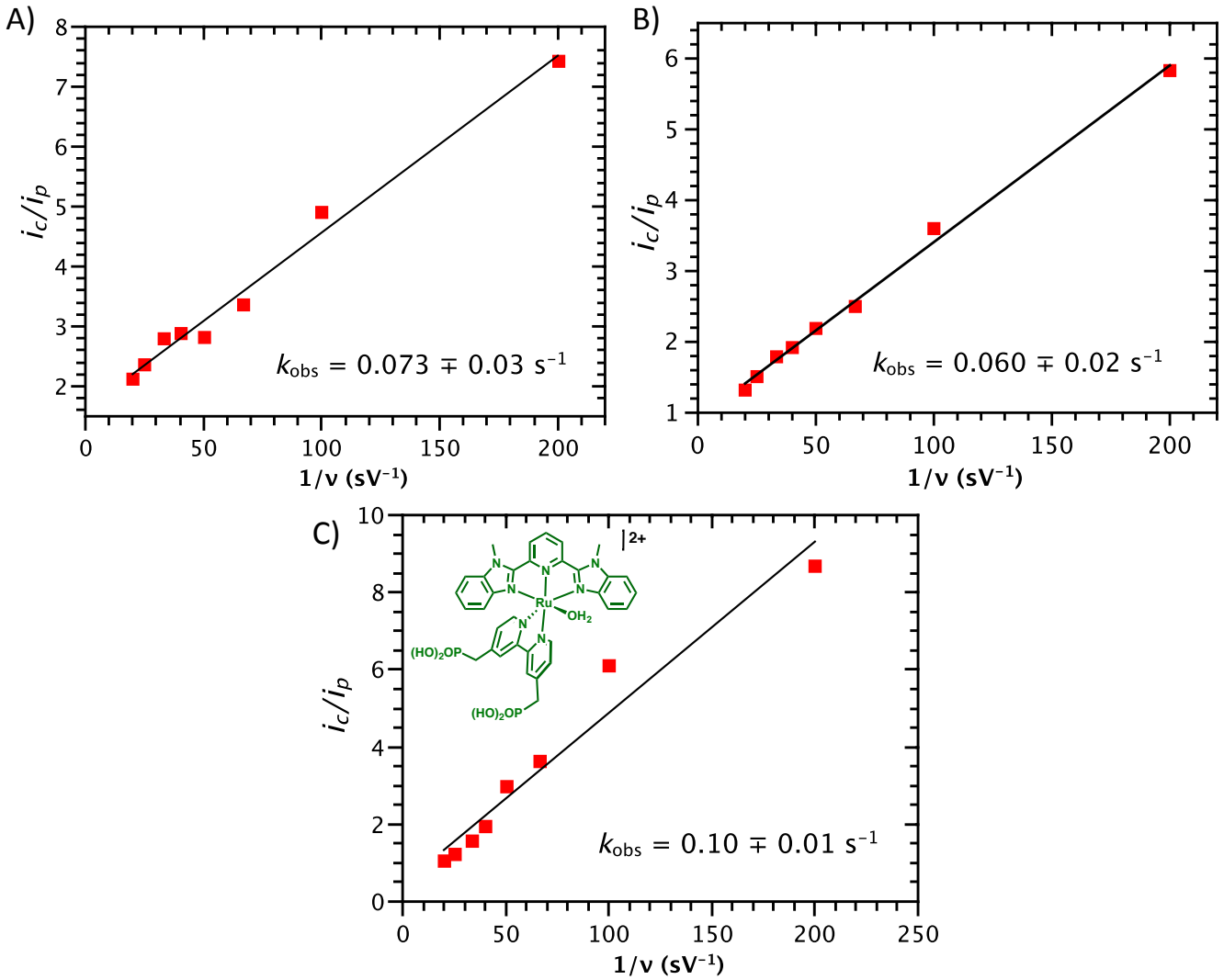



**Figure S14**. Plots of $i_c/i_p$ ($i_c$ is the current at 1.7 V vs NHE, $i_p$ is the peak current for the $Ru^{III}$-$OH_2$/$Ru^{II}$-$OH_2$ redox couple) versus $1/\nu$ for (A) *n*ITO-**RuPdvb$^{2+}$**-*poly***RuOH$_2^{2+}$**, (B) *n*ITO-*poly***RuOH$_2^{2+}$** and (C) *n*ITO-[Ru(Mebimpy)(4,4'-$(PO_3H_2\text{-}CH_2)_2$-bpy)$(OH_2)]^{2+}$ (**RuPOH$_2^{2+}$**) in pH 4.7 aqueous solution (0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$); Pt-mesh counter electrode and Ag/AgCl reference electrode. Surface coverages for each complex were ~ 1.1 × 10$^{-8}$ mol cm$^{-2}$ at 23 °C. The catalytic rate constant, $k_{obs}$, for water oxidation was evaluated from the slope of the each plot.

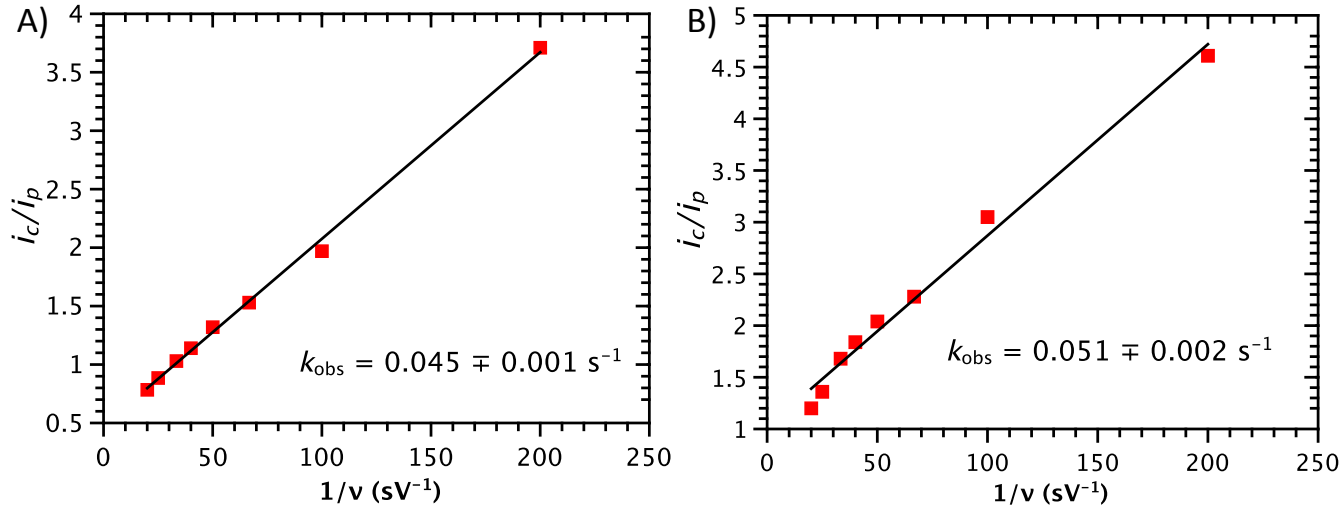



**Figure S15**. Plots of $i_c/i_p$ ($i_c$ is the current at 1.7 V vs NHE, $i_p$ is the peak current for the $Ru^{III}$-$OH_2$/$Ru^{II}$-$OH_2$ redox couple) versus $1/\nu$ for (A) *p*FTO-*poly***RuOH$_2^{2+}$**, and (B) *p*FTO-**RuPdvb$^{2+}$**-*poly***RuOH$_2^{2+}$** in pH 4.7 aqueous solution (0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$); Pt-mesh counter electrode and Ag/AgCl reference electrode. Surface coverages for each complex were ~ $1 \times 10^{-10}$ mol cm$^{-2}$ at 23 °C. The catalytic rate constant, $k_{obs}$, for water oxidation was evaluated from the slope of the each plot.

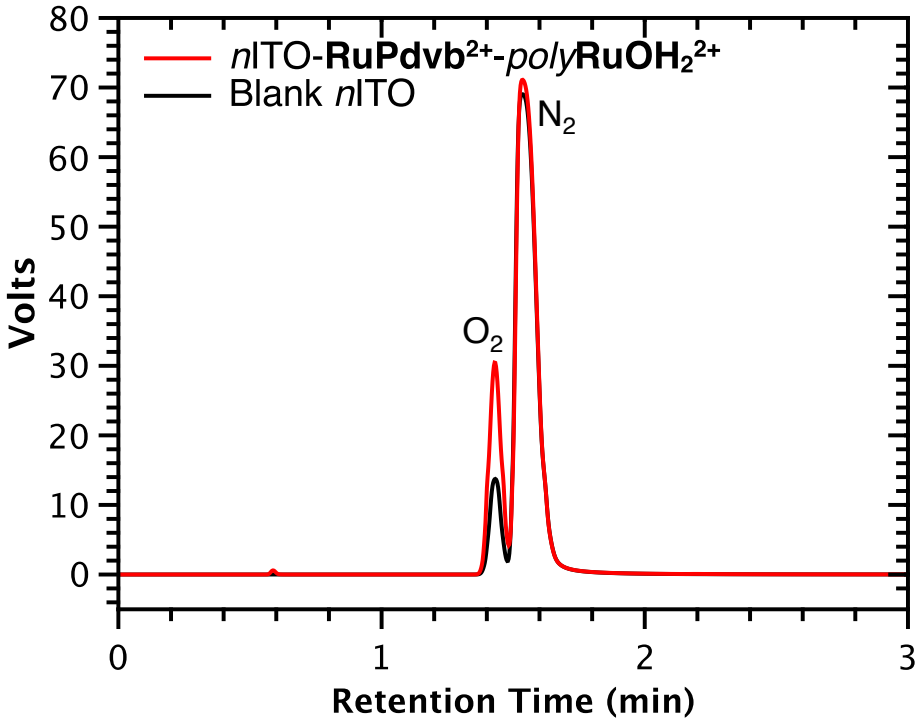



**Figure S16**. Gas chromatographs of headspace following electrolysis of blank *n*ITO (black) and *n*ITO-**RuPdvb$^{2+}$**-*poly***RuOH$_2^{2+}$** (red) at 1.7 V (vs NHE) in pH 4.7 ((0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$); Pt-mesh counter electrode and Ag/AgCl reference electrode. Surface coverages for both **RuPdvb$^{2+}$** and *poly***RuOH$_2^{2+}$** were ~ $1.1 \times 10^{-8}$ mol cm$^{-2}$.

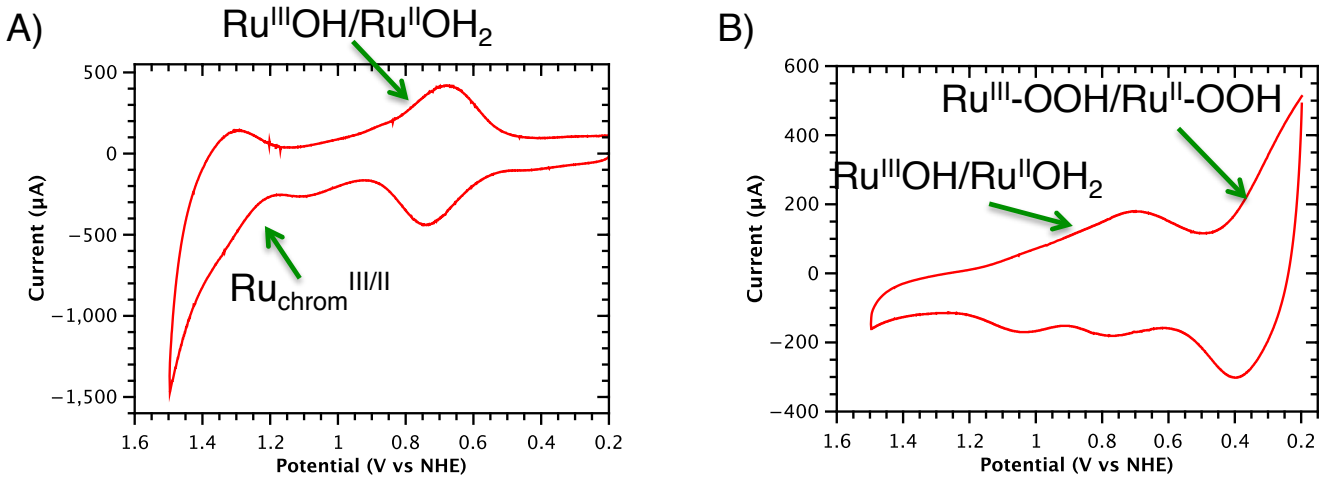



**Figure S17**. Cyclic voltammograms of *n*ITO-**RuPdvb**$^{2+}$-*poly***RuOH$_2$**$^{2+}$ pre (A) and post 2 hr (B) electrolysis at 1.7 V (vs NHE) in pH 4.7 ((0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$); Pt-mesh counter electrode and Ag/AgCl reference electrode. Surface coverages for both **RuPdvb**$^{2+}$ and *poly***RuOH$_2$**$^{2+}$ were ~ 1.1 × $10^{-8}$ mol cm$^{-2}$ pre electrolysis. As noted in the figure, the new waves below 0.4 V are due to a peroxide intermediate in the overall water oxidation cycle. The surface coverage post electrolysis (Figure S17(B)) for *poly***RuOH$_2$**$^{2+}$ was calculated as the sum of the integrated charge under the Ru$^{III}$-OH/Ru$^{II}$-OH$_2$ and Ru$^{III}$-OOH/Ru$^{II}$-OOH waves. The latter is known as a surface-bound intermediate in the water oxidation cycle for the **RuPOH$_2$**$^{2+}$ catalyst.[11-14]

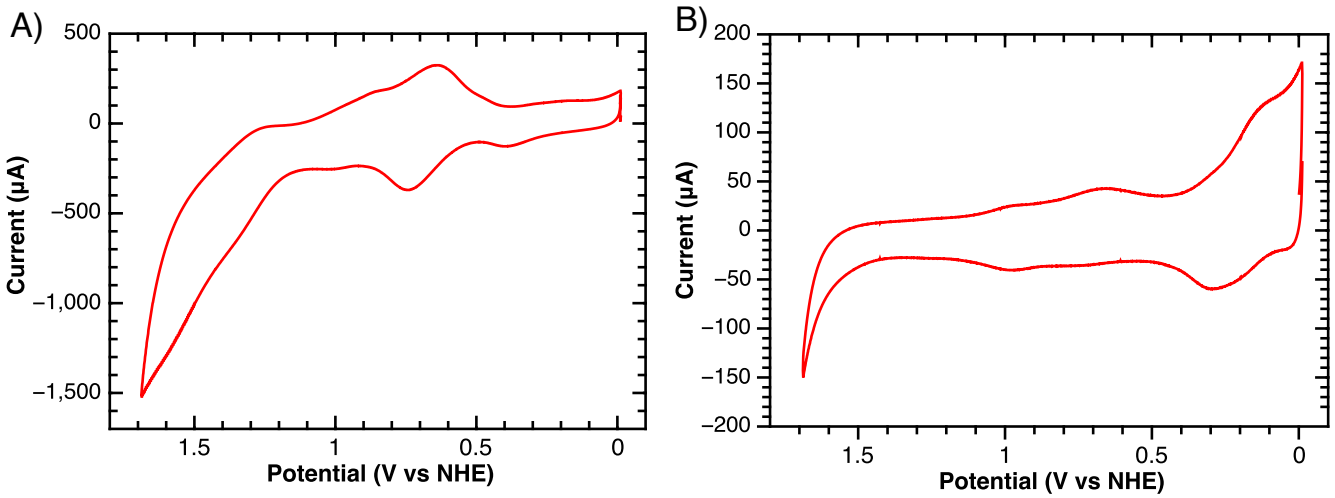
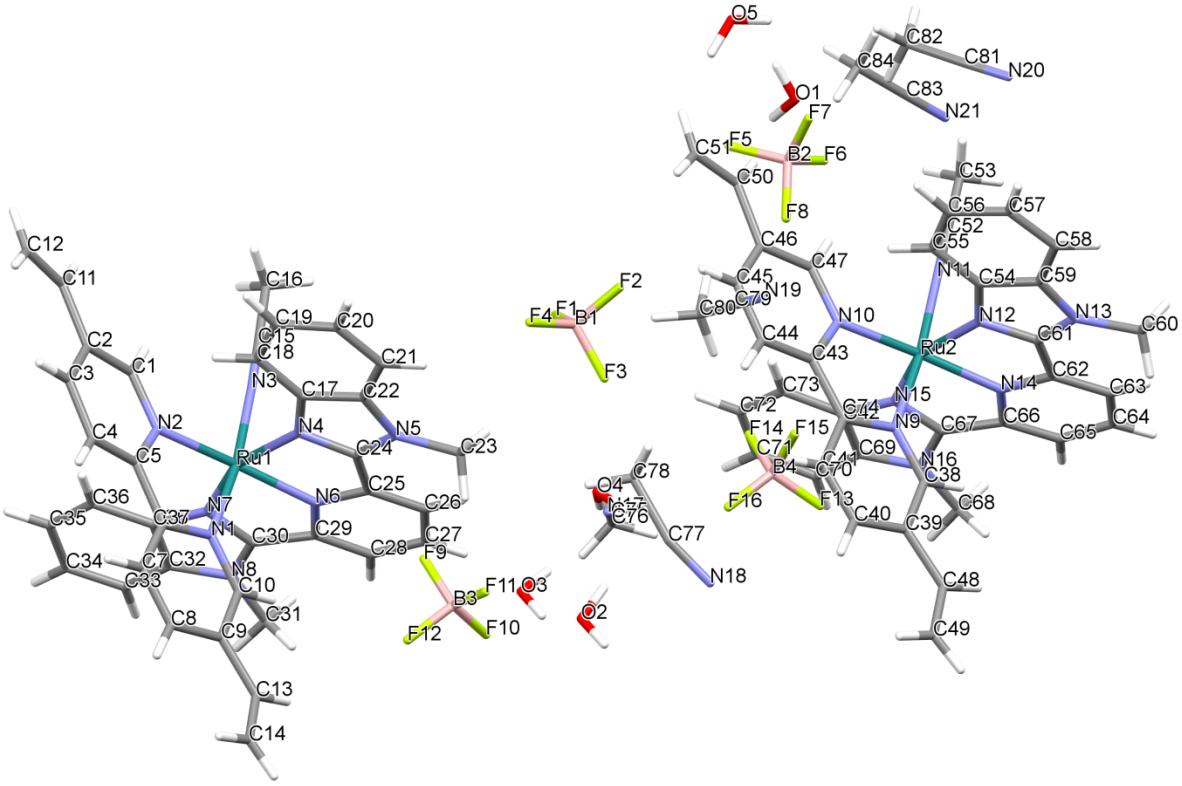



**Figure S18**. Cyclic voltammograms of *n*ITO-**RuPdvb**$^{2+}$-*poly***RuOH$_2$**$^{2+}$ pre (A) and post 14 hr (B) electrolysis at 1.7 V (vs NHE) in pH 4.7 ((0.1 M HOAc/$^-$OAc, 0.5 M $NaClO_4$); Pt-mesh counter electrode and Ag/AgCl reference electrode. Surface coverages for both **RuPdvb**$^{2+}$ and *poly***RuOH$_2$**$^{2+}$ were ~ 1.1 × $10^{-8}$ mol cm$^{-2}$ pre electrolysis. Following the 14 hr electrolysis, only ~ 16% of *poly***RuOH$_2$**$^{2+}$ remained mainly as the peroxide intermediate.




## Table S1 Crystal data and structure refinement for DLA-3-216

| | |
|---|---|
| Identification code | DLA-3-216 |
| Empirical formula | $C_{84}H_{89}B_4F_{16}N_{21}O_5Ru_2$ |
| Formula weight | 2022.14 |
| Temperature/K | 100.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 19.0462(4) |
| b/Å | 25.0845(6) |
| c/Å | 19.0686(4) |
| α/° | 90 |
| β/° | 92.458(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 9101.9(3) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.476 |
| m/mm$^{-1}$ | 3.511 |
| F(000) | 4128.0 |
| Crystal size/mm$^3$ | 0.461 × 0.13 × 0.042 |
| 2Θ range for data collection | 4.644 to 140.488° |
| Index ranges | $-19 \le h \le 23$, $-29 \le k \le 30$, $-20 \le l \le 22$ |
| Reflections collected | 66621 |
| Independent reflections | 16885[R(int) = 0.0785] |
| Data/restraints/parameters | 16885/18/1197 |
| Goodness-of-fit on F$^2$ | 1.014 |

| | |
|---|---|
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0687, $wR_2$ = 0.1660 |
| Final R indexes [all data] | $R_1$ = 0.1148, $wR_2$ = 0.1920 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.03/-0.69 |

**Table S2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for DLA-3-216. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Ru1 | 9389.8(2) | 2275.1(2) | 4468.3(2) | 30.23(13) |
| N1 | 10388(3) | 2239(2) | 4892(2) | 32.1(11) |
| N2 | 9470(3) | 1473(2) | 4712(3) | 33.5(11) |
| N3 | 8384(3) | 2203(2) | 4075(3) | 32.2(11) |
| N4 | 9013(3) | 2529(2) | 5417(2) | 31.6(11) |
| N5 | 8751(3) | 3226(2) | 6092(3) | 37.0(12) |
| N6 | 9367(2) | 3065(2) | 4330(3) | 30.1(10) |
| N7 | 9746(2) | 2350(2) | 3460(2) | 32.0(11) |
| N8 | 10076(3) | 2896(2) | 2611(3) | 38.3(12) |
| C1 | 8969(3) | 1091(3) | 4602(3) | 38.1(14) |
| C2 | 8997(4) | 592(3) | 4921(4) | 40.9(15) |
| C3 | 9574(4) | 484(3) | 5369(3) | 44.2(16) |
| C4 | 10102(4) | 857(3) | 5462(3) | 40.8(15) |
| C5 | 10049(3) | 1346(3) | 5121(3) | 35.3(13) |
| C6 | 10586(3) | 1764(3) | 5181(3) | 35.2(13) |
| C7 | 11244(3) | 1690(3) | 5502(3) | 40.7(15) |
| C8 | 11716(3) | 2111(3) | 5540(3) | 42.5(16) |
| C9 | 11526(3) | 2609(3) | 5255(3) | 37.4(14) |
| C10 | 10857(3) | 2647(3) | 4924(3) | 35.7(13) |
| C11 | 8422(4) | 208(3) | 4766(4) | 51.1(18) |
| C12 | 8327(4) | -245(3) | 5092(5) | 59(2) |
| C13 | 11981(3) | 3081(3) | 5292(4) | 47.7(17) |
| C14 | 12581(4) | 3118(4) | 5636(5) | 67(2) |
| C15 | 7823(3) | 2139(3) | 3876(3) | 36.6(14) |
| C16 | 7105(3) | 2054(3) | 3609(4) | 50.2(18) |
| C17 | 8783(3) | 2334(3) | 6047(3) | 37.0(14) |
| C18 | 8673(3) | 1812(3) | 6275(3) | 39.2(14) |
| C19 | 8396(4) | 1745(3) | 6927(3) | 43.7(16) |
| C20 | 8253(4) | 2189(3) | 7357(3) | 42.9(16) |
| C21 | 8356(3) | 2706(3) | 7147(3) | 37.4(14) |
| C22 | 8618(3) | 2772(3) | 6481(3) | 34.4(13) |
| C23 | 8692(4) | 3773(3) | 6353(4) | 49.5(17) |
| C24 | 8975(3) | 3065(3) | 5460(3) | 34.9(13) |
| C25 | 9117(3) | 3383(3) | 4835(3) | 35.1(14) |
| C26 | 9008(4) | 3919(3) | 4727(4) | 43.7(16) |
| C27 | 9160(4) | 4136(3) | 4072(4) | 47.5(17) |
| C28 | 9430(4) | 3811(3) | 3567(4) | 45.3(16) |
| C29 | 9535(3) | 3275(3) | 3704(3) | 36.0(14) |
| C30 | 9796(3) | 2855(3) | 3242(3) | 36.0(14) |
| C31 | 10282(4) | 3383(3) | 2246(4) | 48.5(18) |

| | | | | |
|---|---|---|---|---|
| C32 | 10210(3) | 2389(3) | 2386(3) | 36.6(14) |
| C33 | 10482(4) | 2193(3) | 1769(4) | 45.2(16) |
| C34 | 10546(4) | 1660(3) | 1704(4) | 50.3(18) |
| C35 | 10329(4) | 1297(3) | 2239(4) | 46.9(17) |
| C36 | 10059(3) | 1482(3) | 2851(3) | 40.1(15) |
| C37 | 9999(3) | 2037(3) | 2913(3) | 36.3(14) |
| Ru2 | 5109.5(2) | 7343.9(2) | 5400.8(2) | 29.41(12) |
| N9 | 6128(3) | 7325(2) | 5793(2) | 32.3(11) |
| N10 | 5228(3) | 6536(2) | 5600(3) | 31.6(11) |
| N11 | 4094(3) | 7282.4(19) | 5029(2) | 29.8(10) |
| N12 | 4743(3) | 7567(2) | 6363(3) | 33.7(11) |
| N13 | 4433(3) | 8232(2) | 7066(3) | 40.0(13) |
| N14 | 5056(3) | 8136(2) | 5291(3) | 33.1(11) |
| N15 | 5447(3) | 7450(2) | 4391(3) | 31.3(11) |
| N16 | 5775(3) | 8011(2) | 3557(3) | 36.5(12) |
| C38 | 6565(3) | 7737(3) | 5840(3) | 37.5(14) |
| C39 | 7247(3) | 7701(3) | 6125(3) | 39.6(14) |
| C40 | 7474(4) | 7212(3) | 6373(4) | 49.0(18) |
| C41 | 7037(4) | 6779(3) | 6323(4) | 47.1(17) |
| C42 | 6350(3) | 6838(3) | 6019(3) | 38.2(14) |
| C43 | 5855(3) | 6396(3) | 5942(3) | 37.3(14) |
| C44 | 5957(4) | 5885(3) | 6180(4) | 45.8(17) |
| C45 | 5452(4) | 5504(3) | 6073(4) | 50.6(18) |
| C46 | 4829(4) | 5634(3) | 5702(4) | 45.3(16) |
| C47 | 4748(3) | 6155(3) | 5477(3) | 36.4(14) |
| C48 | 7679(3) | 8190(3) | 6167(4) | 45.8(17) |
| C49 | 8321(4) | 8232(4) | 6439(5) | 73(3) |
| C50 | 4246(4) | 5254(3) | 5559(4) | 52.3(18) |
| C51 | 4212(5) | 4774(3) | 5819(5) | 63(2) |
| C52 | 3525(3) | 7246(3) | 4840(3) | 35.5(14) |
| C53 | 2804(3) | 7206(3) | 4576(4) | 46.1(17) |
| C54 | 4509(3) | 7344(3) | 6974(3) | 36.4(14) |
| C55 | 4420(3) | 6816(3) | 7172(3) | 37.5(14) |
| C56 | 4141(4) | 6723(3) | 7825(4) | 45.2(16) |
| C57 | 3966(3) | 7146(3) | 8270(3) | 48.5(18) |
| C58 | 4047(3) | 7671(3) | 8077(4) | 44.2(16) |
| C59 | 4320(3) | 7762(3) | 7421(3) | 38.9(15) |
| C60 | 4317(4) | 8771(3) | 7346(4) | 47.8(17) |
| C61 | 4673(3) | 8096(3) | 6430(3) | 36.8(14) |
| C62 | 4806(3) | 8434(3) | 5821(4) | 39.0(15) |
| C63 | 4678(4) | 8974(3) | 5720(4) | 47.6(17) |
| C64 | 4805(4) | 9204(3) | 5080(4) | 49.4(17) |
| C65 | 5081(4) | 8902(3) | 4549(4) | 44.8(16) |
| C66 | 5215(3) | 8365(3) | 4674(3) | 35.6(14) |
| C67 | 5481(3) | 7958(3) | 4198(3) | 34.1(13) |
| C68 | 5949(4) | 8519(3) | 3204(4) | 49.1(18) |

| | | | | |
|---|---|---|---|---|
| C69 | 5884(3) | 7505(3) | 3312(3) | 35.4(13) |
| C70 | 6159(3) | 7321(3) | 2689(3) | 38.6(14) |
| C71 | 6187(3) | 6779(3) | 2600(3) | 41.7(15) |
| C72 | 5962(3) | 6421(3) | 3118(3) | 38.0(14) |
| C73 | 5711(3) | 6606(3) | 3741(3) | 34.7(13) |
| C74 | 5680(3) | 7152(2) | 3836(3) | 31.1(13) |
| F1 | 5366(5) | 4858(3) | 1401(4) | 145(3) |
| F2 | 5060(4) | 5121(4) | 2481(4) | 148(3) |
| F3 | 5983(6) | 5364(4) | 2068(5) | 190(5) |
| F4 | 5832(7) | 4528(4) | 2325(5) | 219(6) |
| B1 | 5556(6) | 4944(4) | 2061(6) | 66(3) |
| F5 | 3297(4) | 5388(2) | 3471(4) | 116(3) |
| F6 | 2949(3) | 6231(2) | 3350(3) | 70.0(14) |
| F7 | 2873(3) | 5803(3) | 4389(3) | 110(3) |
| F8 | 3931(3) | 6014(3) | 3992(3) | 97(2) |
| B2 | 3260(5) | 5862(4) | 3816(6) | 59(2) |
| F9 | 8750(8) | 4519(4) | 1913(5) | 226(7) |
| F10 | 9202(4) | 5303(2) | 1749(3) | 111(3) |
| F11 | 9056(5) | 4987(2) | 2827(3) | 119(3) |
| F12 | 9764(5) | 4617(5) | 2170(7) | 232(7) |
| B3 | 9166(6) | 4875(4) | 2159(5) | 58(2) |
| F13 | 7913(4) | 6646(2) | 7888(3) | 94(2) |
| F14 | 7400(3) | 5890(2) | 7503(3) | 77.9(15) |
| F15 | 7496(3) | 6080(3) | 8664(3) | 103(2) |
| F16 | 8454(3) | 5862(2) | 8149(3) | 79.6(15) |
| B4 | 7837(6) | 6131(5) | 8005(6) | 67(3) |
| O1 | 2055(4) | 6007(3) | 1981(3) | 91(2) |
| O2 | 9418(8) | 5558(8) | 4784(8) | 294(10) |
| O3 | 9770(4) | 4787(3) | 6002(5) | 247(8) |
| O4 | 8870(4) | 4778(3) | 7896(5) | 192(6) |
| O5 | 3548(4) | 4102(3) | 9153(5) | 109(3) |
| N17 | 7953(10) | 5525(5) | 4077(8) | 176(7) |
| C75 | 7819(8) | 5663(5) | 3483(10) | 114(6) |
| C76 | 7677(7) | 5804(6) | 2763(9) | 145(7) |
| N18 | 8802(5) | 6266(4) | 6208(5) | 99(3) |
| C77 | 8551(7) | 5790(6) | 6190(7) | 107(4) |
| C78 | 8032(12) | 5308(8) | 6086(12) | 246(11) |
| N19 | 6443(6) | 5234(4) | 9575(6) | 104(3) |
| C79 | 6518(6) | 5107(4) | 9003(8) | 91(4) |
| C80 | 6576(7) | 4968(5) | 8239(7) | 126(5) |
| N20 | 2979(5) | 6447(4) | 9831(5) | 89(3) |
| C81 | 2948(5) | 6103(4) | 9472(5) | 66(2) |
| C82 | 2888(6) | 5636(4) | 8989(6) | 88(3) |
| N21 | 2687(4) | 6640(3) | 6156(4) | 72(2) |
| C83 | 2703(4) | 6221(4) | 6364(5) | 59(2) |
| C84 | 2718(6) | 5683(4) | 6633(8) | 122(5) |

**Table S3 Anisotropic Displacement Parameters (Å$^2$×10$^3$) for DLA-3-216. The Anisotropic displacement factor exponent takes the form: -2π$^2$[h$^2$a*$^2$U$_{11}$+...+2hka×b×U$_{12}$]**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ru1 | 26.2(2) | 40.2(3) | 24.1(2) | 3.47(17) | -0.49(16) | -0.24(19) |
| N1 | 31(3) | 43(3) | 22(3) | 0.0(19) | 1.4(19) | 3(2) |
| N2 | 34(3) | 38(3) | 29(3) | 6(2) | 6(2) | 3(2) |
| N3 | 32(3) | 37(3) | 27(3) | 2.8(19) | 0(2) | 4(2) |
| N4 | 32(3) | 40(3) | 23(3) | -2.4(19) | -2.7(19) | -1(2) |
| N5 | 35(3) | 43(3) | 33(3) | -1(2) | 5(2) | 2(2) |
| N6 | 21(2) | 36(3) | 32(3) | 7(2) | -2.4(19) | -2(2) |
| N7 | 24(2) | 51(3) | 21(3) | 1(2) | -0.6(18) | 0(2) |
| N8 | 33(3) | 51(3) | 31(3) | 7(2) | 0(2) | -8(2) |
| C1 | 40(4) | 44(4) | 29(3) | 2(2) | -5(3) | -3(3) |
| C2 | 48(4) | 35(3) | 41(4) | 2(3) | 7(3) | 0(3) |
| C3 | 60(4) | 41(4) | 32(4) | 4(3) | 7(3) | 7(3) |
| C4 | 43(4) | 47(4) | 33(4) | 4(3) | 3(3) | 4(3) |
| C5 | 33(3) | 46(4) | 27(3) | 1(2) | 2(2) | 7(3) |
| C6 | 33(3) | 48(4) | 25(3) | -2(2) | 0(2) | 4(3) |
| C7 | 40(4) | 47(4) | 35(4) | 3(3) | 3(3) | 7(3) |
| C8 | 33(3) | 65(5) | 29(4) | 2(3) | -8(3) | 6(3) |
| C9 | 31(3) | 59(4) | 22(3) | 1(3) | 0(2) | -2(3) |
| C10 | 26(3) | 50(4) | 31(3) | 1(3) | 1(2) | -6(3) |
| C11 | 51(4) | 48(4) | 54(5) | 0(3) | 3(3) | -2(3) |
| C12 | 64(5) | 45(4) | 70(6) | -5(4) | 11(4) | -9(4) |
| C13 | 33(3) | 70(5) | 40(4) | -3(3) | -2(3) | -3(3) |
| C14 | 48(5) | 67(6) | 83(7) | -8(4) | -22(4) | -4(4) |
| C15 | 31(3) | 46(4) | 33(3) | 1(2) | 3(3) | 3(3) |
| C16 | 31(3) | 70(5) | 49(5) | 0(3) | -3(3) | -2(3) |
| C17 | 28(3) | 55(4) | 28(3) | -2(3) | 3(2) | -1(3) |
| C18 | 41(4) | 46(4) | 30(4) | 4(3) | 1(3) | -2(3) |
| C19 | 52(4) | 52(4) | 28(4) | 0(3) | 9(3) | -3(3) |
| C20 | 50(4) | 51(4) | 27(3) | 2(3) | 8(3) | 6(3) |
| C21 | 38(3) | 47(4) | 27(3) | -3(3) | -1(2) | 2(3) |
| C22 | 30(3) | 45(4) | 28(3) | 1(2) | -2(2) | -2(3) |
| C23 | 63(5) | 49(4) | 37(4) | -4(3) | 7(3) | 2(4) |
| C24 | 28(3) | 46(4) | 31(3) | -1(2) | -1(2) | -2(3) |
| C25 | 30(3) | 51(4) | 24(3) | 2(2) | 0(2) | 2(3) |
| C26 | 45(4) | 41(4) | 46(4) | 4(3) | 8(3) | -2(3) |
| C27 | 60(5) | 40(4) | 42(4) | 9(3) | 2(3) | -3(3) |
| C28 | 50(4) | 47(4) | 39(4) | 11(3) | 2(3) | -9(3) |
| C29 | 29(3) | 50(4) | 29(3) | 5(3) | -5(2) | 0(3) |
| C30 | 33(3) | 46(4) | 29(3) | 9(2) | 1(2) | -2(3) |
| C31 | 59(5) | 49(4) | 38(4) | 5(3) | 12(3) | -12(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C32 | 30(3) | 50(4) | 30(3) | 1(3) | 0(2) | -1(3) |
| C33 | 43(4) | 61(5) | 32(4) | 5(3) | 2(3) | -4(3) |
| C34 | 54(4) | 66(5) | 30(4) | -8(3) | 4(3) | 1(4) |
| C35 | 49(4) | 48(4) | 43(4) | -4(3) | 0(3) | 0(3) |
| C36 | 37(3) | 50(4) | 33(4) | 3(3) | 0(3) | -1(3) |
| C37 | 29(3) | 49(4) | 32(4) | 3(3) | 0(2) | 3(3) |
| Ru2 | 29.1(2) | 36.0(2) | 23.0(2) | 1.35(17) | -0.37(16) | -0.63(19) |
| N9 | 32(3) | 39(3) | 25(3) | 1.2(19) | 0.6(19) | 2(2) |
| N10 | 34(3) | 33(3) | 27(3) | 2.7(18) | 3(2) | 1(2) |
| N11 | 30(3) | 32(3) | 27(3) | 1.1(18) | 3.2(19) | 0(2) |
| N12 | 29(3) | 43(3) | 28(3) | -3(2) | -5(2) | -4(2) |
| N13 | 40(3) | 47(3) | 33(3) | -11(2) | -3(2) | 2(3) |
| N14 | 28(3) | 41(3) | 31(3) | -5(2) | -1(2) | -3(2) |
| N15 | 30(3) | 38(3) | 26(3) | 3.8(19) | 0.5(19) | -3(2) |
| N16 | 36(3) | 41(3) | 33(3) | 6(2) | 1(2) | -8(2) |
| C38 | 33(3) | 49(4) | 31(3) | -3(3) | 1(2) | 3(3) |
| C39 | 39(3) | 54(4) | 25(3) | -4(3) | 1(2) | -1(3) |
| C40 | 34(4) | 73(5) | 40(4) | 2(3) | -2(3) | 3(3) |
| C41 | 44(4) | 60(5) | 37(4) | 5(3) | 0(3) | 13(3) |
| C42 | 37(3) | 51(4) | 26(3) | 4(2) | 0(3) | 2(3) |
| C43 | 41(4) | 42(4) | 29(3) | 3(2) | 5(3) | 8(3) |
| C44 | 40(4) | 55(4) | 43(4) | 13(3) | 5(3) | 9(3) |
| C45 | 57(5) | 42(4) | 54(5) | 9(3) | 9(4) | 3(3) |
| C46 | 54(4) | 42(4) | 41(4) | 4(3) | 12(3) | 0(3) |
| C47 | 40(3) | 39(3) | 31(3) | 0(2) | 9(3) | 4(3) |
| C48 | 35(4) | 67(5) | 35(4) | -6(3) | -2(3) | -4(3) |
| C49 | 53(5) | 82(7) | 84(7) | -1(5) | -9(5) | -9(5) |
| C50 | 60(5) | 45(4) | 52(5) | -3(3) | 8(4) | -3(4) |
| C51 | 78(6) | 44(5) | 66(6) | 3(4) | -2(4) | -14(4) |
| C52 | 39(4) | 44(4) | 24(3) | 2(2) | 3(2) | 4(3) |
| C53 | 28(3) | 69(5) | 41(4) | 1(3) | -1(3) | -3(3) |
| C54 | 27(3) | 57(4) | 25(3) | -3(3) | -4(2) | 4(3) |
| C55 | 34(3) | 55(4) | 24(3) | -5(2) | -3(2) | 3(3) |
| C56 | 41(4) | 61(5) | 33(4) | 0(3) | 1(3) | -3(3) |
| C57 | 32(3) | 90(6) | 24(4) | -3(3) | 4(3) | -4(3) |
| C58 | 29(3) | 67(5) | 36(4) | -9(3) | -5(3) | 3(3) |
| C59 | 32(3) | 52(4) | 33(4) | -7(3) | -6(2) | -1(3) |
| C60 | 48(4) | 47(4) | 48(4) | -14(3) | -2(3) | 3(3) |
| C61 | 31(3) | 43(4) | 36(4) | -5(3) | 0(3) | -5(3) |
| C62 | 30(3) | 43(4) | 44(4) | -6(3) | 2(3) | -5(3) |
| C63 | 48(4) | 44(4) | 51(5) | -4(3) | 8(3) | -2(3) |
| C64 | 55(4) | 37(4) | 57(5) | 1(3) | 5(3) | -1(3) |
| C65 | 48(4) | 40(4) | 46(4) | 1(3) | -5(3) | -8(3) |
| C66 | 33(3) | 39(3) | 35(4) | 5(2) | 0(3) | -7(3) |
| C67 | 27(3) | 47(4) | 28(3) | 8(2) | -7(2) | -1(3) |
| C68 | 57(4) | 47(4) | 44(4) | 16(3) | 3(3) | -11(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C69 | 34(3) | 44(4) | 28(3) | 5(2) | −1(2) | −2(3) |
| C70 | 33(3) | 58(4) | 25(3) | 6(3) | 4(2) | −2(3) |
| C71 | 40(4) | 59(4) | 27(3) | 3(3) | 4(3) | 5(3) |
| C72 | 36(3) | 46(4) | 32(4) | −4(3) | 1(3) | 2(3) |
| C73 | 30(3) | 47(4) | 27(3) | 5(2) | 2(2) | 4(3) |
| C74 | 27(3) | 42(3) | 24(3) | 4(2) | −1(2) | 0(2) |
| F1 | 234(10) | 129(7) | 68(5) | −27(4) | −28(5) | −55(6) |
| F2 | 131(7) | 195(9) | 122(7) | 32(6) | 55(5) | 53(6) |
| F3 | 247(11) | 203(10) | 124(7) | −90(7) | 61(7) | −134(9) |
| F4 | 365(16) | 134(8) | 156(9) | 11(6) | 1(9) | 169(10) |
| B1 | 87(8) | 52(6) | 59(6) | −13(4) | −4(5) | 23(5) |
| F5 | 121(5) | 67(4) | 157(7) | −26(4) | −42(5) | 12(4) |
| F6 | 73(3) | 69(3) | 69(3) | 16(2) | 19(3) | 7(3) |
| F7 | 93(4) | 133(6) | 106(5) | 67(4) | 52(4) | 37(4) |
| F8 | 80(4) | 165(6) | 45(3) | 20(3) | −12(3) | −58(4) |
| B2 | 55(5) | 47(5) | 75(7) | 9(4) | 21(5) | 3(4) |
| F9 | 376(17) | 190(10) | 108(7) | 20(6) | −34(9) | −186(11) |
| F10 | 248(8) | 44(3) | 41(3) | 4(2) | 4(4) | −19(4) |
| F11 | 242(9) | 66(4) | 51(4) | 15(3) | 35(4) | 31(5) |
| F12 | 155(9) | 297(14) | 253(13) | 153(11) | 105(9) | 130(9) |
| B3 | 73(7) | 47(5) | 56(6) | −10(4) | 10(5) | 6(5) |
| F13 | 155(6) | 66(4) | 59(4) | 10(3) | −42(4) | −9(4) |
| F14 | 105(4) | 74(4) | 52(3) | −6(2) | −22(3) | −9(3) |
| F15 | 82(4) | 155(7) | 72(4) | −8(4) | −2(3) | −23(4) |
| F16 | 76(4) | 77(4) | 85(4) | 10(3) | −13(3) | −1(3) |
| B4 | 53(5) | 82(8) | 66(7) | −17(5) | −7(5) | −4(5) |
| O1 | 120(6) | 86(5) | 67(5) | −4(4) | 13(4) | 24(4) |
| O2 | 188(14) | 510(30) | 186(16) | 16(17) | 6(12) | −103(16) |
| O3 | 265(16) | 206(14) | 262(17) | 72(12) | −78(14) | −176(13) |
| O4 | 206(12) | 88(7) | 291(16) | −36(9) | 120(11) | −12(8) |
| O5 | 62(4) | 75(5) | 189(9) | −7(5) | −12(5) | −6(4) |
| N17 | 300(20) | 79(9) | 157(14) | −7(8) | 84(15) | 4(11) |
| C75 | 127(11) | 56(7) | 166(16) | 7(8) | 73(12) | 8(7) |
| C76 | 116(11) | 134(14) | 192(18) | 58(12) | 67(11) | 56(10) |
| N18 | 96(6) | 92(6) | 106(6) | 12(5) | −15(5) | 9(5) |
| C77 | 113(6) | 107(6) | 102(6) | 0(4) | 7(4) | −14(4) |
| C78 | 249(14) | 229(14) | 262(14) | −10(9) | 51(9) | −23(9) |
| N19 | 100(8) | 102(8) | 110(9) | 22(6) | 14(7) | 31(6) |
| C79 | 69(7) | 62(7) | 144(12) | 11(7) | 33(8) | 2(5) |
| C80 | 153(13) | 81(9) | 148(13) | −36(8) | 57(10) | −40(9) |
| N20 | 99(7) | 83(7) | 84(7) | −16(5) | −12(5) | 8(5) |
| C81 | 64(6) | 67(6) | 68(6) | 1(4) | 15(4) | 8(5) |
| C82 | 119(9) | 61(6) | 88(8) | −7(5) | 45(7) | −5(6) |
| N21 | 79(5) | 76(6) | 62(5) | 0(4) | 3(4) | 7(4) |
| C83 | 56(5) | 56(5) | 67(6) | −2(4) | 13(4) | −2(4) |
| C84 | 105(9) | 57(7) | 208(16) | 37(8) | 53(10) | 21(6) |

**Table S4 Bond Lengths for DLA-3-216.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Ru1 | N1 | 2.035(5) | N13 | C59 | 1.382(9) |
| Ru1 | N2 | 2.069(5) | N13 | C60 | 1.472(8) |
| Ru1 | N3 | 2.036(5) | N13 | C61 | 1.358(8) |
| Ru1 | N4 | 2.075(5) | N14 | C62 | 1.358(8) |
| Ru1 | N6 | 1.998(5) | N14 | C66 | 1.356(8) |
| Ru1 | N7 | 2.076(5) | N15 | C67 | 1.329(8) |
| N1 | C6 | 1.359(8) | N15 | C74 | 1.383(7) |
| N1 | C10 | 1.358(8) | N16 | C67 | 1.374(8) |
| N2 | C1 | 1.362(8) | N16 | C68 | 1.486(8) |
| N2 | C5 | 1.360(8) | N16 | C69 | 1.371(8) |
| N3 | C15 | 1.129(8) | C38 | C39 | 1.389(9) |
| N4 | C17 | 1.384(7) | C39 | C40 | 1.379(10) |
| N4 | C24 | 1.350(8) | C39 | C48 | 1.475(10) |
| N5 | C22 | 1.388(8) | C40 | C41 | 1.369(10) |
| N5 | C23 | 1.466(8) | C41 | C42 | 1.415(9) |
| N5 | C24 | 1.357(8) | C42 | C43 | 1.459(9) |
| N6 | C25 | 1.353(8) | C43 | C44 | 1.371(9) |
| N6 | C29 | 1.357(8) | C44 | C45 | 1.366(10) |
| N7 | C30 | 1.338(8) | C45 | C46 | 1.394(10) |
| N7 | C37 | 1.406(8) | C46 | C47 | 1.382(9) |
| N8 | C30 | 1.341(8) | C46 | C50 | 1.480(10) |
| N8 | C31 | 1.468(8) | C48 | C49 | 1.312(10) |
| N8 | C32 | 1.370(9) | C50 | C51 | 1.305(10) |
| C1 | C2 | 1.392(9) | C52 | C53 | 1.446(9) |
| C2 | C3 | 1.390(10) | C54 | C55 | 1.389(9) |
| C2 | C11 | 1.477(10) | C54 | C59 | 1.407(9) |
| C3 | C4 | 1.379(10) | C55 | C56 | 1.394(9) |
| C4 | C5 | 1.391(9) | C56 | C57 | 1.409(10) |
| C5 | C6 | 1.465(9) | C57 | C58 | 1.378(10) |
| C6 | C7 | 1.385(9) | C58 | C59 | 1.394(9) |
| C7 | C8 | 1.386(10) | C61 | C62 | 1.468(9) |
| C8 | C9 | 1.403(9) | C62 | C63 | 1.390(9) |
| C9 | C10 | 1.401(8) | C63 | C64 | 1.380(10) |
| C9 | C13 | 1.467(10) | C64 | C65 | 1.387(10) |
| C11 | C12 | 1.312(10) | C65 | C66 | 1.390(9) |
| C13 | C14 | 1.297(10) | C66 | C67 | 1.469(9) |
| C15 | C16 | 1.456(9) | C69 | C70 | 1.397(8) |
| C17 | C18 | 1.399(9) | C69 | C74 | 1.402(8) |
| C17 | C22 | 1.419(9) | C70 | C71 | 1.371(9) |
| C18 | C19 | 1.381(8) | C71 | C72 | 1.414(9) |
| C19 | C20 | 1.417(9) | C72 | C73 | 1.381(8) |

| | | | | | |
|---|---|---|---|---|---|
| C20 | C21 | 1.372(9) | C73 | C74 | 1.384(9) |
| C21 | C22 | 1.394(8) | F1 | B1 | 1.312(12) |
| C24 | C25 | 1.468(8) | F2 | B1 | 1.339(12) |
| C25 | C26 | 1.375(9) | F3 | B1 | 1.331(14) |
| C26 | C27 | 1.405(9) | F4 | B1 | 1.263(12) |
| C27 | C28 | 1.377(10) | F5 | B2 | 1.362(11) |
| C28 | C29 | 1.382(9) | F6 | B2 | 1.398(11) |
| C29 | C30 | 1.472(9) | F7 | B2 | 1.352(10) |
| C32 | C33 | 1.395(9) | F8 | B2 | 1.362(11) |
| C32 | C37 | 1.409(9) | F9 | B3 | 1.270(13) |
| C33 | C34 | 1.349(10) | F10 | B3 | 1.331(11) |
| C34 | C35 | 1.439(10) | F11 | B3 | 1.330(11) |
| C35 | C36 | 1.375(9) | F12 | B3 | 1.310(12) |
| C36 | C37 | 1.402(9) | F13 | B4 | 1.319(13) |
| Ru2 | N9 | 2.049(5) | F14 | B4 | 1.381(11) |
| Ru2 | N10 | 2.073(5) | F15 | B4 | 1.446(12) |
| Ru2 | N11 | 2.038(5) | F16 | B4 | 1.372(12) |
| Ru2 | N12 | 2.069(5) | N17 | C75 | 1.20(2) |
| Ru2 | N14 | 2.000(5) | C75 | C76 | 1.43(2) |
| Ru2 | N15 | 2.074(5) | N18 | C77 | 1.287(15) |
| N9 | C38 | 1.329(8) | C77 | C78 | 1.57(2) |
| N9 | C42 | 1.356(8) | N19 | C79 | 1.150(16) |
| N10 | C43 | 1.381(8) | C79 | C80 | 1.507(17) |
| N10 | C47 | 1.336(8) | N20 | C81 | 1.100(12) |
| N11 | C52 | 1.130(8) | C81 | C82 | 1.491(12) |
| N12 | C54 | 1.383(8) | N21 | C83 | 1.125(11) |
| N12 | C61 | 1.340(8) | C83 | C84 | 1.443(12) |

**Table S5 Bond Angles for DLA-3-216.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N1 | Ru1 | N2 | 79.0(2) | C38 | N9 | Ru2 | 126.0(4) |
| N1 | Ru1 | N3 | 172.1(2) | C38 | N9 | C42 | 119.5(6) |
| N1 | Ru1 | N4 | 91.16(19) | C42 | N9 | Ru2 | 114.5(4) |
| N1 | Ru1 | N7 | 91.99(18) | C43 | N10 | Ru2 | 114.8(4) |
| N2 | Ru1 | N4 | 97.3(2) | C47 | N10 | Ru2 | 126.7(4) |
| N2 | Ru1 | N7 | 105.8(2) | C47 | N10 | C43 | 118.3(5) |
| N3 | Ru1 | N2 | 93.2(2) | C52 | N11 | Ru2 | 178.2(5) |
| N3 | Ru1 | N4 | 89.61(19) | C54 | N12 | Ru2 | 140.4(5) |
| N3 | Ru1 | N7 | 90.36(19) | C61 | N12 | Ru2 | 113.0(4) |
| N4 | Ru1 | N7 | 156.9(2) | C61 | N12 | C54 | 106.5(5) |
| N6 | Ru1 | N1 | 96.4(2) | C59 | N13 | C60 | 125.2(6) |
| N6 | Ru1 | N2 | 173.9(2) | C61 | N13 | C59 | 106.8(6) |
| N6 | Ru1 | N3 | 91.43(19) | C61 | N13 | C60 | 128.0(6) |
| N6 | Ru1 | N4 | 78.8(2) | C62 | N14 | Ru2 | 119.1(4) |
| N6 | Ru1 | N7 | 78.1(2) | C66 | N14 | Ru2 | 119.9(4) |
| C6 | N1 | Ru1 | 116.0(4) | C66 | N14 | C62 | 120.8(6) |
| C10 | N1 | Ru1 | 125.9(4) | C67 | N15 | Ru2 | 113.6(4) |
| C10 | N1 | C6 | 118.1(5) | C67 | N15 | C74 | 106.6(5) |
| C1 | N2 | Ru1 | 127.2(4) | C74 | N15 | Ru2 | 139.7(4) |
| C5 | N2 | Ru1 | 114.0(4) | C67 | N16 | C68 | 126.4(6) |
| C5 | N2 | C1 | 118.0(5) | C69 | N16 | C67 | 106.7(5) |
| C15 | N3 | Ru1 | 176.4(5) | C69 | N16 | C68 | 126.9(6) |
| C17 | N4 | Ru1 | 141.5(4) | N9 | C38 | C39 | 123.3(6) |
| C24 | N4 | Ru1 | 112.3(4) | C38 | C39 | C48 | 118.5(6) |
| C24 | N4 | C17 | 106.3(5) | C40 | C39 | C38 | 117.7(7) |
| C22 | N5 | C23 | 124.6(6) | C40 | C39 | C48 | 123.7(6) |
| C24 | N5 | C22 | 107.6(5) | C41 | C40 | C39 | 120.0(7) |
| C24 | N5 | C23 | 127.7(6) | C40 | C41 | C42 | 119.7(7) |
| C25 | N6 | Ru1 | 119.8(4) | N9 | C42 | C41 | 119.6(6) |
| C25 | N6 | C29 | 120.0(6) | N9 | C42 | C43 | 117.4(6) |
| C29 | N6 | Ru1 | 119.8(4) | C41 | C42 | C43 | 123.0(6) |
| C30 | N7 | Ru1 | 113.8(4) | N10 | C43 | C42 | 113.4(6) |
| C30 | N7 | C37 | 105.6(5) | C44 | C43 | N10 | 120.1(6) |
| C37 | N7 | Ru1 | 140.6(5) | C44 | C43 | C42 | 126.5(6) |
| C30 | N8 | C31 | 127.9(6) | C45 | C44 | C43 | 121.0(7) |
| C30 | N8 | C32 | 107.3(5) | C44 | C45 | C46 | 119.4(7) |
| C32 | N8 | C31 | 124.5(6) | C45 | C46 | C50 | 123.9(7) |
| N2 | C1 | C2 | 123.5(6) | C47 | C46 | C45 | 117.4(7) |
| C1 | C2 | C11 | 119.0(7) | C47 | C46 | C50 | 118.7(7) |
| C3 | C2 | C1 | 117.3(6) | N10 | C47 | C46 | 123.7(7) |
| C3 | C2 | C11 | 123.7(6) | C49 | C48 | C39 | 126.6(8) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4 | C3 | C2 | 119.9(6) | C51 | C50 | C46 | 125.1(8) |
| C3 | C4 | C5 | 120.1(6) | N11 | C52 | C53 | 178.1(7) |
| N2 | C5 | C4 | 121.0(6) | N12 | C54 | C55 | 131.4(6) |
| N2 | C5 | C6 | 115.0(6) | N12 | C54 | C59 | 108.0(6) |
| C4 | C5 | C6 | 124.0(6) | C55 | C54 | C59 | 120.5(6) |
| N1 | C6 | C5 | 114.5(5) | C54 | C55 | C56 | 117.3(6) |
| N1 | C6 | C7 | 121.8(6) | C55 | C56 | C57 | 121.4(7) |
| C7 | C6 | C5 | 123.7(6) | C58 | C57 | C56 | 121.9(6) |
| C6 | C7 | C8 | 119.6(6) | C57 | C58 | C59 | 116.4(6) |
| C7 | C8 | C9 | 120.1(6) | N13 | C59 | C54 | 106.8(6) |
| C8 | C9 | C13 | 123.9(6) | N13 | C59 | C58 | 130.6(7) |
| C10 | C9 | C8 | 116.7(6) | C58 | C59 | C54 | 122.5(7) |
| C10 | C9 | C13 | 119.4(6) | N12 | C61 | N13 | 111.9(6) |
| N1 | C10 | C9 | 123.6(6) | N12 | C61 | C62 | 118.4(6) |
| C12 | C11 | C2 | 126.0(8) | N13 | C61 | C62 | 129.6(6) |
| C14 | C13 | C9 | 126.0(8) | N14 | C62 | C61 | 110.4(6) |
| N3 | C15 | C16 | 179.1(7) | N14 | C62 | C63 | 119.9(6) |
| N4 | C17 | C18 | 131.1(6) | C63 | C62 | C61 | 129.6(6) |
| N4 | C17 | C22 | 108.6(6) | C64 | C63 | C62 | 119.5(7) |
| C18 | C17 | C22 | 120.2(6) | C63 | C64 | C65 | 120.3(7) |
| C19 | C18 | C17 | 117.5(6) | C64 | C65 | C66 | 118.4(7) |
| C18 | C19 | C20 | 121.1(7) | N14 | C66 | C65 | 120.9(6) |
| C21 | C20 | C19 | 122.7(6) | N14 | C66 | C67 | 109.8(5) |
| C20 | C21 | C22 | 116.1(6) | C65 | C66 | C67 | 129.2(6) |
| N5 | C22 | C17 | 105.8(5) | N15 | C67 | N16 | 111.4(6) |
| N5 | C22 | C21 | 131.8(6) | N15 | C67 | C66 | 118.3(5) |
| C21 | C22 | C17 | 122.4(6) | N16 | C67 | C66 | 130.4(6) |
| N4 | C24 | N5 | 111.7(6) | N16 | C69 | C70 | 131.5(6) |
| N4 | C24 | C25 | 118.7(6) | N16 | C69 | C74 | 107.0(5) |
| N5 | C24 | C25 | 129.4(6) | C70 | C69 | C74 | 121.6(6) |
| N6 | C25 | C24 | 109.9(6) | C71 | C70 | C69 | 116.8(6) |
| N6 | C25 | C26 | 121.7(6) | C70 | C71 | C72 | 121.9(6) |
| C26 | C25 | C24 | 128.4(6) | C73 | C72 | C71 | 120.9(6) |
| C25 | C26 | C27 | 118.4(6) | C72 | C73 | C74 | 117.6(6) |
| C28 | C27 | C26 | 119.4(7) | N15 | C74 | C69 | 108.2(6) |
| C27 | C28 | C29 | 120.0(6) | N15 | C74 | C73 | 130.7(5) |
| N6 | C29 | C28 | 120.4(6) | C73 | C74 | C69 | 121.1(6) |
| N6 | C29 | C30 | 110.2(6) | F1 | B1 | F2 | 117.1(11) |
| C28 | C29 | C30 | 129.3(6) | F1 | B1 | F3 | 106.3(10) |
| N7 | C30 | N8 | 112.7(6) | F3 | B1 | F2 | 100.3(9) |
| N7 | C30 | C29 | 117.5(5) | F4 | B1 | F1 | 109.8(10) |
| N8 | C30 | C29 | 129.7(6) | F4 | B1 | F2 | 109.1(11) |
| N8 | C32 | C33 | 132.3(6) | F4 | B1 | F3 | 114.0(13) |
| N8 | C32 | C37 | 107.2(6) | F5 | B2 | F6 | 107.5(9) |
| C33 | C32 | C37 | 120.5(7) | F7 | B2 | F5 | 109.6(8) |
| C34 | C33 | C32 | 117.7(6) | F7 | B2 | F6 | 110.8(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C33 | C34 | C35 | 122.1(7) | F7 | B2 | F8 | 111.7(9) |
| C36 | C35 | C34 | 121.1(7) | F8 | B2 | F5 | 107.3(8) |
| C35 | C36 | C37 | 116.2(6) | F8 | B2 | F6 | 109.8(7) |
| N7 | C37 | C32 | 107.2(6) | F9 | B3 | F10 | 113.5(10) |
| C36 | C37 | N7 | 130.5(6) | F9 | B3 | F11 | 112.3(10) |
| C36 | C37 | C32 | 122.3(6) | F9 | B3 | F12 | 100.7(11) |
| N9 | Ru2 | N10 | 79.4(2) | F11 | B3 | F10 | 114.0(8) |
| N9 | Ru2 | N12 | 91.89(19) | F12 | B3 | F10 | 109.9(10) |
| N9 | Ru2 | N15 | 90.87(19) | F12 | B3 | F11 | 105.2(10) |
| N10 | Ru2 | N15 | 105.06(19) | F13 | B4 | F14 | 112.3(10) |
| N11 | Ru2 | N9 | 174.2(2) | F13 | B4 | F15 | 106.8(9) |
| N11 | Ru2 | N10 | 94.82(19) | F13 | B4 | F16 | 114.6(9) |
| N11 | Ru2 | N12 | 88.75(19) | F14 | B4 | F15 | 106.5(8) |
| N11 | Ru2 | N15 | 90.79(18) | F16 | B4 | F14 | 114.1(9) |
| N12 | Ru2 | N10 | 98.1(2) | F16 | B4 | F15 | 101.3(9) |
| N12 | Ru2 | N15 | 156.8(2) | N17 | C75 | C76 | 177.1(16) |
| N14 | Ru2 | N9 | 96.0(2) | N18 | C77 | C78 | 162.0(16) |
| N14 | Ru2 | N10 | 174.5(2) | N19 | C79 | C80 | 176.0(14) |
| N14 | Ru2 | N11 | 89.7(2) | N20 | C81 | C82 | 178.6(12) |
| N14 | Ru2 | N12 | 78.8(2) | N21 | C83 | C84 | 179.5(11) |
| N14 | Ru2 | N15 | 78.0(2) | | | | |

**Table S6 Torsion Angles for DLA-3-216.**

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| Ru1 | N1 | C6 | C5 | 1.8(7) | Ru2 | N9 | C38 | C39 | 178.6(4) |
| Ru1 | N1 | C6 | C7 | -178.4(5) | Ru2 | N9 | C42 | C41 | -177.8(5) |
| Ru1 | N1 | C10 | C9 | 176.4(4) | Ru2 | N9 | C42 | C43 | 1.5(7) |
| Ru1 | N2 | C1 | C2 | -164.6(5) | Ru2 | N10 | C43 | C42 | -7.2(6) |
| Ru1 | N2 | C5 | C4 | 165.2(5) | Ru2 | N10 | C43 | C44 | 171.8(5) |
| Ru1 | N2 | C5 | C6 | -13.5(6) | Ru2 | N10 | C47 | C46 | -171.6(5) |
| Ru1 | N4 | C17 | C18 | -5.1(12) | Ru2 | N12 | C54 | C55 | -1.1(11) |
| Ru1 | N4 | C17 | C22 | 178.1(5) | Ru2 | N12 | C54 | C59 | -178.4(5) |
| Ru1 | N4 | C24 | N5 | -177.9(4) | Ru2 | N12 | C61 | N13 | -180.0(4) |
| Ru1 | N4 | C24 | C25 | 6.9(7) | Ru2 | N12 | C61 | C62 | 4.5(7) |
| Ru1 | N6 | C25 | C24 | 6.7(7) | Ru2 | N14 | C62 | C61 | 5.2(7) |
| Ru1 | N6 | C25 | C26 | -171.6(5) | Ru2 | N14 | C62 | C63 | -171.5(5) |
| Ru1 | N6 | C29 | C28 | 171.1(5) | Ru2 | N14 | C66 | C65 | 170.2(5) |
| Ru1 | N6 | C29 | C30 | -6.8(7) | Ru2 | N14 | C66 | C67 | -5.9(7) |
| Ru1 | N7 | C30 | N8 | 175.3(4) | Ru2 | N15 | C67 | N16 | 173.7(4) |
| Ru1 | N7 | C30 | C29 | -5.6(7) | Ru2 | N15 | C67 | C66 | -6.1(7) |
| Ru1 | N7 | C37 | C32 | -174.2(5) | Ru2 | N15 | C74 | C69 | -174.8(5) |
| Ru1 | N7 | C37 | C36 | 5.4(11) | Ru2 | N15 | C74 | C73 | 7.3(11) |
| N1 | C6 | C7 | C8 | 0.8(10) | N9 | C38 | C39 | C40 | -0.4(9) |
| N2 | C1 | C2 | C3 | -0.5(10) | N9 | C38 | C39 | C48 | -178.3(6) |
| N2 | C1 | C2 | C11 | 179.8(6) | N9 | C42 | C43 | N10 | 3.8(8) |
| N2 | C5 | C6 | N1 | 7.9(8) | N9 | C42 | C43 | C44 | -175.1(6) |
| N2 | C5 | C6 | C7 | -172.0(6) | N10 | C43 | C44 | C45 | 1.3(10) |
| N4 | C17 | C18 | C19 | -176.0(6) | N12 | C54 | C55 | C56 | -177.3(6) |
| N4 | C17 | C22 | N5 | 0.3(7) | N12 | C54 | C59 | N13 | 1.0(7) |
| N4 | C17 | C22 | C21 | 178.5(5) | N12 | C54 | C59 | C58 | 178.6(6) |
| N4 | C24 | C25 | N6 | -8.9(8) | N12 | C61 | C62 | N14 | -6.3(8) |
| N4 | C24 | C25 | C26 | 169.3(6) | N12 | C61 | C62 | C63 | 170.0(7) |
| N5 | C24 | C25 | N6 | 176.8(6) | N13 | C61 | C62 | N14 | 179.1(6) |
| N5 | C24 | C25 | C26 | -5.0(11) | N13 | C61 | C62 | C63 | -4.5(12) |
| N6 | C25 | C26 | C27 | 0.2(10) | N14 | C62 | C63 | C64 | 0.1(11) |
| N6 | C29 | C30 | N7 | 8.0(8) | N14 | C66 | C67 | N15 | 7.8(8) |
| N6 | C29 | C30 | N8 | -173.2(6) | N14 | C66 | C67 | N16 | -172.0(6) |
| N8 | C32 | C33 | C34 | -179.6(7) | N16 | C69 | C70 | C71 | -179.0(6) |
| N8 | C32 | C37 | N7 | -0.8(7) | N16 | C69 | C74 | N15 | 0.3(7) |
| N8 | C32 | C37 | C36 | 179.6(6) | N16 | C69 | C74 | C73 | 178.5(5) |
| C1 | N2 | C5 | C4 | -4.9(9) | C38 | N9 | C42 | C41 | 2.0(9) |
| C1 | N2 | C5 | C6 | 176.4(5) | C38 | N9 | C42 | C43 | -178.7(5) |
| C1 | C2 | C3 | C4 | -2.3(10) | C38 | C39 | C40 | C41 | 1.2(10) |
| C1 | C2 | C11 | C12 | -170.4(8) | C38 | C39 | C48 | C49 | 177.7(8) |
| C2 | C3 | C4 | C5 | 1.5(10) | C39 | C40 | C41 | C42 | -0.4(10) |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C3 | C2 | C11 | C12 | 9.8(12) | | C40 | C39 | C48 | C49 | −0.1(12) | | | | | |
| C3 | C4 | C5 | N2 | 2.3(10) | | C40 | C41 | C42 | N9 | −1.2(10) | | | | | |
| C3 | C4 | C5 | C6 | −179.2(6) | | C40 | C41 | C42 | C43 | 179.5(6) | | | | | |
| C4 | C5 | C6 | N1 | −170.7(6) | | C41 | C42 | C43 | N10 | −176.9(6) | | | | | |
| C4 | C5 | C6 | C7 | 9.4(10) | | C41 | C42 | C43 | C44 | 4.2(10) | | | | | |
| C5 | N2 | C1 | C2 | 4.1(9) | | C42 | N9 | C38 | C39 | −1.2(9) | | | | | |
| C5 | C6 | C7 | C8 | −179.3(6) | | C42 | C43 | C44 | C45 | −179.8(6) | | | | | |
| C6 | N1 | C10 | C9 | −1.8(9) | | C43 | N10 | C47 | C46 | 3.2(9) | | | | | |
| C6 | C7 | C8 | C9 | 0.0(10) | | C43 | C44 | C45 | C46 | 1.5(11) | | | | | |
| C7 | C8 | C9 | C10 | −1.6(9) | | C44 | C45 | C46 | C47 | −1.9(10) | | | | | |
| C7 | C8 | C9 | C13 | 177.9(6) | | C44 | C45 | C46 | C50 | −179.7(7) | | | | | |
| C8 | C9 | C10 | N1 | 2.6(9) | | C45 | C46 | C47 | N10 | −0.5(10) | | | | | |
| C8 | C9 | C13 | C14 | −6.4(12) | | C45 | C46 | C50 | C51 | 7.4(12) | | | | | |
| C10 | N1 | C6 | C5 | −179.8(5) | | C47 | N10 | C43 | C42 | 177.4(5) | | | | | |
| C10 | N1 | C6 | C7 | 0.0(9) | | C47 | N10 | C43 | C44 | −3.6(9) | | | | | |
| C10 | C9 | C13 | C14 | 173.1(8) | | C47 | C46 | C50 | C51 | −170.4(8) | | | | | |
| C11 | C2 | C3 | C4 | 177.5(6) | | C48 | C39 | C40 | C41 | 179.0(6) | | | | | |
| C13 | C9 | C10 | N1 | −177.0(5) | | C50 | C46 | C47 | N10 | 177.5(6) | | | | | |
| C17 | N4 | C24 | N5 | 1.6(7) | | C54 | N12 | C61 | N13 | 2.6(7) | | | | | |
| C17 | N4 | C24 | C25 | −173.7(5) | | C54 | N12 | C61 | C62 | −172.9(5) | | | | | |
| C17 | C18 | C19 | C20 | −2.1(10) | | C54 | C55 | C56 | C57 | −0.9(10) | | | | | |
| C18 | C17 | C22 | N5 | −176.9(6) | | C55 | C54 | C59 | N13 | −176.7(5) | | | | | |
| C18 | C17 | C22 | C21 | 1.2(9) | | C55 | C54 | C59 | C58 | 0.9(9) | | | | | |
| C18 | C19 | C20 | C21 | 2.2(11) | | C55 | C56 | C57 | C58 | 1.5(11) | | | | | |
| C19 | C20 | C21 | C22 | −0.5(10) | | C56 | C57 | C58 | C59 | −0.9(10) | | | | | |
| C20 | C21 | C22 | N5 | 176.4(7) | | C57 | C58 | C59 | N13 | 176.7(6) | | | | | |
| C20 | C21 | C22 | C17 | −1.2(9) | | C57 | C58 | C59 | C54 | −0.3(9) | | | | | |
| C22 | N5 | C24 | N4 | −1.4(7) | | C59 | N13 | C61 | N12 | −2.0(7) | | | | | |
| C22 | N5 | C24 | C25 | 173.2(6) | | C59 | N13 | C61 | C62 | 172.9(6) | | | | | |
| C22 | C17 | C18 | C19 | 0.5(9) | | C59 | C54 | C55 | C56 | −0.2(9) | | | | | |
| C23 | N5 | C22 | C17 | −176.2(6) | | C60 | N13 | C59 | C54 | −178.7(6) | | | | | |
| C23 | N5 | C22 | C21 | 5.9(11) | | C60 | N13 | C59 | C58 | 4.0(11) | | | | | |
| C23 | N5 | C24 | N4 | 175.3(6) | | C60 | N13 | C61 | N12 | 177.2(6) | | | | | |
| C23 | N5 | C24 | C25 | −10.1(11) | | C60 | N13 | C61 | C62 | −7.9(11) | | | | | |
| C24 | N4 | C17 | C18 | 175.7(7) | | C61 | N12 | C54 | C55 | 175.3(6) | | | | | |
| C24 | N4 | C17 | C22 | −1.1(7) | | C61 | N12 | C54 | C59 | −2.1(7) | | | | | |
| C24 | N5 | C22 | C17 | 0.6(7) | | C61 | N13 | C59 | C54 | 0.5(7) | | | | | |
| C24 | N5 | C22 | C21 | −177.3(6) | | C61 | N13 | C59 | C58 | −176.8(6) | | | | | |
| C24 | C25 | C26 | C27 | −177.7(6) | | C61 | C62 | C63 | C64 | −175.9(7) | | | | | |
| C25 | N6 | C29 | C28 | −2.2(9) | | C62 | N14 | C66 | C65 | −4.5(9) | | | | | |
| C25 | N6 | C29 | C30 | 179.9(5) | | C62 | N14 | C66 | C67 | 179.4(5) | | | | | |
| C25 | C26 | C27 | C28 | −1.7(11) | | C62 | C63 | C64 | C65 | −2.1(11) | | | | | |
| C26 | C27 | C28 | C29 | 1.3(11) | | C63 | C64 | C65 | C66 | 0.8(11) | | | | | |
| C27 | C28 | C29 | N6 | 0.7(10) | | C64 | C65 | C66 | N14 | 2.5(10) | | | | | |
| C27 | C28 | C29 | C30 | 178.1(7) | | C64 | C65 | C66 | C67 | 177.7(6) | | | | | |
| C28 | C29 | C30 | N7 | −169.7(6) | | C65 | C66 | C67 | N15 | −167.9(6) | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C28 | C29 | C30 | N8 | 9.2(12) | C65 | C66 | C67 | N16 | 12.4(11) |
| C29 | N6 | C25 | C24 | -179.9(5) | C66 | N14 | C62 | C61 | 179.9(5) |
| C29 | N6 | C25 | C26 | 1.8(9) | C66 | N14 | C62 | C63 | 3.2(9) |
| C30 | N7 | C37 | C32 | 1.4(7) | C67 | N15 | C74 | C69 | 2.4(7) |
| C30 | N7 | C37 | C36 | -179.0(7) | C67 | N15 | C74 | C73 | -175.5(6) |
| C30 | N8 | C32 | C33 | 178.3(7) | C67 | N16 | C69 | C70 | 179.1(7) |
| C30 | N8 | C32 | C37 | -0.2(7) | C67 | N16 | C69 | C74 | -2.8(7) |
| C31 | N8 | C30 | N7 | -172.6(6) | C68 | N16 | C67 | N15 | -174.7(6) |
| C31 | N8 | C30 | C29 | 8.5(11) | C68 | N16 | C67 | C66 | 5.1(10) |
| C31 | N8 | C32 | C33 | -7.6(11) | C68 | N16 | C69 | C70 | -1.6(11) |
| C31 | N8 | C32 | C37 | 173.9(6) | C68 | N16 | C69 | C74 | 176.5(6) |
| C32 | N8 | C30 | N7 | 1.2(7) | C69 | N16 | C67 | N15 | 4.6(7) |
| C32 | N8 | C30 | C29 | -177.7(6) | C69 | N16 | C67 | C66 | -175.6(6) |
| C32 | C33 | C34 | C35 | 1.5(11) | C69 | C70 | C71 | C72 | -1.3(10) |
| C33 | C32 | C37 | N7 | -179.5(6) | C70 | C69 | C74 | N15 | 178.6(6) |
| C33 | C32 | C37 | C36 | 0.8(10) | C70 | C69 | C74 | C73 | -3.2(9) |
| C33 | C34 | C35 | C36 | -1.5(12) | C70 | C71 | C72 | C73 | -0.7(10) |
| C34 | C35 | C36 | C37 | 1.0(10) | C71 | C72 | C73 | C74 | 0.7(9) |
| C35 | C36 | C37 | N7 | 179.7(6) | C72 | C73 | C74 | N15 | 178.9(6) |
| C35 | C36 | C37 | C32 | -0.7(10) | C72 | C73 | C74 | C69 | 1.2(9) |
| C37 | N7 | C30 | N8 | -1.7(7) | C74 | N15 | C67 | N16 | -4.4(7) |
| C37 | N7 | C30 | C29 | 177.4(5) | C74 | N15 | C67 | C66 | 175.8(5) |
| C37 | C32 | C33 | C34 | -1.2(10) | C74 | C69 | C70 | C71 | 3.2(9) |

**Table S7 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for DLA-3-216.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H1 | 8579 | 1170 | 4292 | 46 |
| H3 | 9605 | 153 | 5610 | 53 |
| H4 | 10501 | 780 | 5760 | 49 |
| H7 | 11372 | 1353 | 5695 | 49 |
| H8 | 12169 | 2062 | 5760 | 51 |
| H10 | 10725 | 2976 | 4710 | 43 |
| H11 | 8092 | 298 | 4398 | 61 |
| H12A | 8644 | -352 | 5464 | 71 |
| H12B | 7940 | -467 | 4955 | 71 |
| H13 | 11822 | 3387 | 5040 | 57 |
| H14A | 12762 | 2821 | 5896 | 80 |
| H14B | 12840 | 3441 | 5629 | 80 |
| H16A | 7109 | 1918 | 3127 | 75 |
| H16B | 6847 | 2392 | 3613 | 75 |
| H16C | 6873 | 1794 | 3906 | 75 |
| H18 | 8784 | 1514 | 5993 | 47 |
| H19 | 8300 | 1396 | 7090 | 52 |
| H20 | 8078 | 2127 | 7809 | 51 |
| H21 | 8255 | 3001 | 7438 | 45 |
| H23A | 8285 | 3947 | 6119 | 74 |
| H23B | 9120 | 3971 | 6254 | 74 |
| H23C | 8631 | 3766 | 6861 | 74 |
| H26 | 8833 | 4137 | 5087 | 52 |
| H27 | 9078 | 4503 | 3978 | 57 |
| H28 | 9544 | 3955 | 3126 | 54 |
| H31A | 10604 | 3291 | 1877 | 73 |
| H31B | 10517 | 3627 | 2581 | 73 |
| H31C | 9862 | 3556 | 2035 | 73 |
| H33 | 10617 | 2426 | 1407 | 54 |
| H34 | 10741 | 1519 | 1293 | 60 |
| H35 | 10372 | 924 | 2168 | 56 |
| H36 | 9921 | 1247 | 3210 | 48 |
| H38 | 6403 | 8073 | 5670 | 45 |
| H40 | 7935 | 7175 | 6580 | 59 |
| H41 | 7193 | 6441 | 6492 | 57 |
| H44 | 6387 | 5795 | 6423 | 55 |
| H45 | 5524 | 5153 | 6249 | 61 |
| H47 | 4327 | 6248 | 5220 | 44 |
| H48 | 7470 | 8506 | 5979 | 55 |
| H49A | 8553 | 7928 | 6635 | 88 |

| | | | | |
|---|---|---|---|---|
| H49B | 8553 | 8567 | 6441 | 88 |
| H50 | 3868 | 5368 | 5254 | 63 |
| H51A | 4579 | 4645 | 6126 | 75 |
| H51B | 3819 | 4554 | 5701 | 75 |
| H53A | 2779 | 6979 | 4158 | 69 |
| H53B | 2626 | 7563 | 4454 | 69 |
| H53C | 2516 | 7051 | 4938 | 69 |
| H55 | 4544 | 6531 | 6875 | 45 |
| H56 | 4067 | 6366 | 7972 | 54 |
| H57 | 3788 | 7068 | 8716 | 58 |
| H58 | 3923 | 7956 | 8376 | 53 |
| H60A | 3871 | 8912 | 7149 | 72 |
| H60B | 4703 | 9005 | 7217 | 72 |
| H60C | 4300 | 8753 | 7858 | 72 |
| H63 | 4503 | 9184 | 6089 | 57 |
| H64 | 4704 | 9571 | 5004 | 59 |
| H65 | 5176 | 9058 | 4109 | 54 |
| H68A | 5518 | 8681 | 3002 | 74 |
| H68B | 6273 | 8448 | 2829 | 74 |
| H68C | 6171 | 8764 | 3547 | 74 |
| H70 | 6319 | 7560 | 2344 | 46 |
| H71 | 6362 | 6640 | 2178 | 50 |
| H72 | 5985 | 6048 | 3035 | 46 |
| H73 | 5565 | 6367 | 4093 | 42 |
| H1A | 2243 | 5949 | 1581 | 136 |
| H1B | 1832 | 5723 | 2110 | 136 |
| H2A | 9648 | 5789 | 5046 | 441 |
| H2B | 8975 | 5643 | 4756 | 441 |
| H3A | 9391 | 4954 | 5854 | 371 |
| H4A | 9001 | 5017 | 8206 | 288 |
| H4B | 8883 | 4915 | 7477 | 288 |
| H3B | 10004 | 4987 | 6304 | 288 |
| H5A | 3999 | 4053 | 9143 | 164 |
| H5B | 3461 | 4352 | 9453 | 164 |
| H76A | 8084 | 5714 | 2489 | 218 |
| H76B | 7585 | 6187 | 2728 | 218 |
| H76C | 7265 | 5606 | 2580 | 218 |
| H78A | 7711 | 5377 | 5681 | 369 |
| H78B | 7762 | 5264 | 6508 | 369 |
| H78C | 8301 | 4982 | 6004 | 369 |
| H80A | 6105 | 4944 | 8014 | 189 |
| H80B | 6816 | 4625 | 8199 | 189 |
| H80C | 6845 | 5246 | 8008 | 189 |
| H82A | 3250 | 5660 | 8641 | 132 |
| H82B | 2422 | 5636 | 8750 | 132 |
| H82C | 2952 | 5307 | 9260 | 132 |

| | | | | |
|---|---|---|---|---|
| H84A | 2572 | 5435 | 6257 | 183 |
| H84B | 2395 | 5654 | 7018 | 183 |
| H84C | 3196 | 5595 | 6806 | 183 |

## Experimental

Single crystals of $C_{84}H_{89}B_4F_{16}N_{21}O_5Ru_2$ [DLA-3-216] were grown by solution diffusion of diethyl ether into a **$RuOH_2$** solution in $CH_3CN$ resulting in $CH_3CN$ coordination. A suitable crystal was selected and placed on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

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Crystal structure determination of [DLA-3-216]

Crystal Data for $C_{84}H_{89}B_4F_{16}N_{21}O_5Ru_2$ ($M$ =2022.14): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 19.0462(4) Å, $b$ = 25.0845(6) Å, $c$ = 19.0686(4) Å, $\beta$ = 92.458(2)°, $V$ = 9101.9(3) Å$^3$, $Z$ = 4, $T$ = 100.15 K, μ(CuKα) = 3.511 mm$^{-1}$, $Dcalc$ = 1.476 g/mm$^3$, 66621 reflections measured ($4.644 \leq 2\Theta \leq 140.488$), 16885 unique ($R_{int}$ = 0.0785) which were used in all calculations. The final $R_1$ was 0.0687 ($I > 2\sigma(I)$) and $wR_2$ was 0.1920 (all data).

This report has been created with Olex2, compiled on Apr 9 2013 14:10:59. Please let us know if there are any errors or if you would like to have additional features.

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