Incorporation of the ruthenium-bis(pyridine)pyrazolate (Ru-bpp) water oxidation catalyst in a hexametallic macrocycle.

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Methods and instrumentation: All electrochemical experiments were performed on a PAR 263A EG&G potentiostat or on an IJ-Cambria HI-660 potentiostat, using a three-electrode cell. Glassy carbon (S = 0.07 cm^2) as working electrode, platinum mesh as counter electrode, and MSE or SSCE as reference electrode unless otherwise indicated. $E_{1/2}$ values reported in this work were estimated from Cyclic Voltammetry (CV) experiments as the average of the oxidative and reductive peak potentials. Differential Pulse Voltammetries (DPV) were performed with pulse amplitudes of 0.05 V, pulse widths of 0.05 s, sampling width of 0.0167 s, and a pulse period of 0.2 s.

Matrix-assisted laser desorption ionization (MALDI) mass spectrometry (MS) experiments were performed on a Bruker Daltonics Autoflex equipped with a nitrogen laser (337 nm).

UV–Vis spectroscopy was performed on a Cary 50 Bio (Varian) UV–Vis spectrophotometer with 1 cm quartz cells.

A 400 MHz Bruker Avance II spectrometer and a Bruker Avance 500 MHz were used to carry out NMR spectroscopy at room temperature unless specified otherwise.

FT-IR measurements carried out on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm⁻¹ resolution.

Elemental analysis was performed by the Elemental Analysis Unit at the University of Santiago de Compostela (Spain) on an EA-1108, CHNS-O elemental analyser from Fisons Instruments.

Manometric measurements were carried out with a Testo 521 differential pressure manometer, with an operating range of 1-100 hPa and an accuracy of within 0.5% of the measurement, coupled to thermostatted reaction vessels for dynamic monitoring of the headspace pressure above each reaction. A 0.1 M triflic acid solution with 25% trifluoroethanol (pH 1.2, 3.85 mL) was added to the sample vessel containing catalyst (2.0 mmol) under stirring and the equivalent volume added to the reference vessel. Once the catalyst was dissolved, the pressures were equalised and a blank solution of triflic acid (150 μ L) was injected into the reference cell and an aqueous triflic acid solution of Ce(NH₄)₂(NO₃)₆ (1.33M, 150 μ L) was then injected into the sample cell with continued stirring and the pressure difference was recorded *vs* time.

Computer modelled structures were optimised using the standard MM2 settings in the software package *Cache WS 6.1.12 for Windows*.



Figure S1. ¹H NMR of **1** in acetone-d6.



Figure S2. ¹H-¹H COSY NMR of **1** in acetone-d6.



Figure S3. HSQC NMR of 1 in acetone-d6.



Figure S4. ¹³C {¹H} PENDANT NMR of 1 in acetone-d6.



Figure S5. ¹H NMR of 2 in acetone-d6.



Figure S6. ¹H-¹H COSY NMR of **2** in acetone-d6.



Figure S7. HSQC NMR of 2 in acetone-d6.



Figure S8. ¹³C {¹H} PENDANT NMR of 2 in acetone-d6.



Figure S9. ¹H NMR of **3** in acetone-d6.



Figure S10. ¹H-¹H COSY NMR of **3** in acetone-d6.



Figure S11. HSQC NMR of 3 in acetone-d6.



Figure S12. ^{13}C { ^{1}H } NMR of 3 in acetone-d6.



Figure S13. ¹H NMR of **3** in acetone-d6 after addition of 1eq of FeCl₂ in MeOD-d4. Downfield shift of signals indicates coordination of Fe. Low filed aromatics suggest benzoate bridge remains intact. Signal broadening indicates polymerization rather than cyclisation.



Figure S14. ¹H NMR of **4** in acetone-d6.



Figure S15. ¹H-¹H COSY NMR of **4** in acetone-d6.



Figure S16. HSQC NMR of 4 in acetone-d6.



Figure S17. ${}^{13}C$ { ${}^{1}H$ } NMR of **4** in acetone-d6.



Figure S18. ¹H NMR of 5 in acetone-d6.



Figure S19. ¹H-¹H COSY of 5 in acetone-d6.



Figure S20. HSQC of 5 in acetone-d6.



Figure S21. HMBC of 5 in acetone-d6.



Figure S22. ¹³C {¹H} PENDANT of 5 in acetone-d6.

Calculations for estimating molecular dimensions from diffusion NMR data

The Stokes-Einstein equation relates the diffusion coefficient, *D*, to the hydrodynamic radius, *r*_s, when a spherical geometry is assumed for the molecule.

$$D = \frac{kT}{6 \pi \eta r_s}$$

The values of *D* for molecules of **1** and **4** are $4.47 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ and $1.05 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$, respectively, and as *rs* is reciprocal to *D*, the ratio of sizes for molecules can therefore be estimated so that $D(5) = 2.3 \times D(2)$.



Figure S23. Electrochemistry (CV, solid black line; DPV, dashed grey line) for **1** (*ca*. 0.9 mM) in DCM, 0.1 M TBA(PF₆). CV scan rate = 50 mV s⁻¹. E *vs* SSCE reference, GC Working, Pt counter). SSCE = +0.240 vs NHE



Figure S24. Electrochemistry (CV, solid black line; DPV, dashed grey line) for **2** (*ca.* 0.9 mM) in DCM, 0.1 M TBA(PF₆). CV scan rate = 50 mV s⁻¹. E *vs* SSCE reference, GC Working, Pt counter). SSCE = +0.240 vs NHE



Figure S25. Electrochemistry (CV, solid black line; DPV, dashed grey line) for **3** (*ca*. 0.7 mM) in DCM, 0.1 M TBA(PF₆). CV scan rate = 20 mV s⁻¹. E *vs* MSE reference, GC Working, Pt counter). MSE = +0.640 *vs* NHE.



Figure S26. Electrochemistry (CV, solid black line; DPV, dashed grey line) for **4** (*ca*. 0.7 mM) in DCM, 0.1 M TBA(PF₆). CV scan rate = 20 mV s⁻¹. E *vs* MSE reference, GC Working, Pt counter). MSE = +0.640 vs NHE.



Figure S27. Electrochemistry (CV, solid black line; DPV, dashed grey line) for **5** (*ca.* 0.3 mM) in DCM, 0.1 M TBA(PF₆). CV scan rate = 20 mV s⁻¹. E *vs* MSE reference, GC Working, Pt counter). MSE = +0.640 vs NHE.

Table S1. Electrochemistry data summary/comparison ^a							
Compound	$E_{1/2} Ru''/Ru'' - Ru''/Ru''' (V)$	<i>E</i> _{1/2} Ru ^{II} /Ru ^{III} – Ru ^{III} /Ru ^{III} (V)	$E_{1/2} \mathrm{Fe}^{II} / \mathrm{Fe}^{III}$ (V)				
1	1.007	1.354					
2	1.018	1.324					
3	1.065	1.357					
4	1,040	1.422					
5	1.039	1.449	1.449				
a) Potentials converted to vs NHE using NHE = SSCE + 240 mV or NHE = MSE + 640 mV							



Figure S28. MS data for 1. Zoom of peak corresponding to $C_{43}H_{29}Cl_3F_6N_{10}PRu_2$ (Bottom left). Simulated pattern for $C_{43}H_{29}Cl_3F_6N_{10}PRu_2$ (Bottom right).



Figure S29. MS data for 2. Zoom of peak corresponding to $C_{50}H_{34}Cl_2F_6N_{10}PRu_2$ (Bottom left). Simulated pattern for $C_{50}H_{34}Cl_2F_6N_{10}PRu_2$ (Bottom right).



Figure S30. MS data for 3. Zoom of peak corresponding to $C_{80}H_{54}F_6N_{10}PRu_2$ (Bottom left). Simulated pattern for $C_{80}H_{54}F_6N_{10}PRu_2$ (Bottom right).



Figure S31. MS data for 4. Zoom of peak corresponding to $C_{73}H_{49}CIF_6N_{16}O_2PRu_2$ (Bottom left). Simulated pattern for $C_{73}H_{49}CIF_6N_{16}O_2PRu_2$ (Bottom right).



Figure S32. MS data for 5. Zoom of peak corresponding to $C_{146}H_{98}Cl_2F_{42}Fe_2N_{32}O_4P_7Ru_4$ (Bottom left). Simulated pattern for $C_{146}H_{98}Cl_2F_{42}Fe_2N_{32}O_4P_7Ru_4$ (Bottom right).



Figure S33. FT-IR comparison of powder samples of compounds **1-5** (1 red; 2 blue; 3 green; 4 orange; 5 black)

Table S2. k_{obs} and TOF values calculated from manometry measurements of precursor 4 and	ł
macrocycle 5	

Entry	WOC	[Catalyst] (µM)	k₀₀₀ (μmol s⁻¹)	TOF (s ⁻¹)	TON ^c
1ª	4	0.5	0.0165	0.0083	3.24
2 ^a	4	0.5	0.0154	0.0077	3.59
3 ^a	5	2.5	0.0128	0.0064	3.73

^aHeadspace = 6.5 mL, Temperature = 25°C, solvent = 25% TFE in 0.1 M triflic acid (4.0 mL), [CAN] = 0.05 M

 $^{\rm c}\text{Calculations}$ based on moles of O_2 divided by moles of Ru_2 catalyst units



Figure S34. MM2 calculated structure of macrocycle still containing benzoate bridging ligands. Colour scheme: C - grey, N - purple, O - red, Ru - teal, H - white.



Figure S35. Solutions of $[Fe(trpy)_2](PF6)_2$ in a 4:1 mixture of 0.1M pH1 HOTf_(aq)– TFE (left vial) and in a 4:1 mixture 0.1M pH7 phosphate buffer–TFE (right vial) immediately after addition of excess NaIO₄ (a) and 1 hr after addition (b).