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

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New terpyridine-functionalised analogues of the *in,in*-[{Ru^{II}(trpy)}$_2$(μ-bpp)$(H_2O)_2$]$^{3+}$ water oxidation catalyst (bpp = bis-(2-pyridyl)pyrazolate) have been synthesised and used to create a hexametallic {Fe_2Ru_4} macrocycle. The macroyclic WOC precursor contains two catalyst units linked by two {Fe(R-trpy)$_2$} bridges and shows similar catalytic activity for water oxygen when compared to the non-cyclic catalyst precursors. The synthesised complexes were fully characterised by standard voltammetric and spectroscopic techniques (CV, DPV, NMR, MS, UV and IR) and the assessment of their performance as WOCs was performed using a Ce^{IV} chemical oxidant in aqueous triflic acid.

Introduction

Molecular water oxidation catalysts (WOCs) based on ruthenium have been an integral part of research into artificial photosynthesis (AP) for a little over three decades now.[1-7] Within the vast number of molecular Ru-based WOCs reported,[8-38] the Ru-bpp catalysts (bpp = 3,5-bis(2-pyridyl)pyrazolato) have been of particular interest because of their distinctive I2M mechanism; only the Ru-bda catalysts (bda = 2,2'-bipyridine-6,6'-dicarboxylato) of Sun *et al* have been reported to follow a similar oxo-coupling mechanism.[39-44] The major drawback with the Ru-bpp catalysts, as with most organic ligand-based WOCs, is consumption of the ligands during operation leading to catalyst degradation and ultimately termination of the catalysis. Largely successful attempts have been made to circumvent this problem by removing the organic ligands altogether and replacing them with inorganic ligands in the form of polyoxometallates (POMs)[45-54] or by encapsulating or heterogenising the molecular catalyst in/on Metal Organic Frameworks (MOFs).[55-57] These strategies, however, have their own limitations such as low catalyst accessibility, MOF degradation, nanoparticle formation and pore clogging.[57-61] The most "stable" homogeneous WOC that contains organic ligands, as judged by turnover number (TON), is the bromophthalazine-Ru-bda complex prepared by Sun *et al* and can achieve >100,000 TON before catalysis ceases.[43] These catalysts are believed to lose their catalytic activity through decoordination of the axial ligands under the harsh catalytic conditions and the high TONs are largely attributed to their extraordinarily fast rates as opposed to any enhanced ligand/complex stability.[41] However, a macrocyclic version of the Ru-bda WOC was very recently reported by Würthner *et al* where catalyst stability was increased through the chelate effect.[62] Although this was the first example of a macrocyclic WOC, macrocycles and supramolecular cages/containers have a long history and have been used to great effect in the catalysis of many organic transformations.[63-73] Embedding the Ru-bpp catalyst in a macrocycle was therefore proposed as a possible approach to increase the catalyst lifetime by inhibiting the intermolecular ligand oxidation pathway, where the activated Ru-oxo site of one catalyst molecule "attacks" the ligand backbone of another catalyst unit.[31]

Herein, we report our attempts to use a *macrocyclic encapsulation strategy* to overcome the degradative intermolecular interactions between Ru-bpp catalysts through

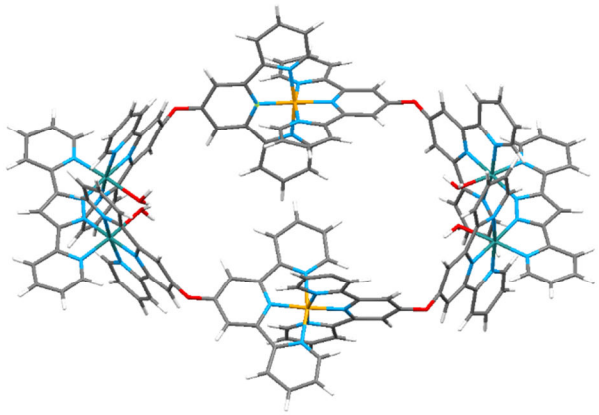

Figure 1. MM2 computer modelled representation of {M_2Ru_4} macrocyclic WOC. Colour scheme: H – white, C – grey, N – blue, O – red, Ru – teal, M – orange.

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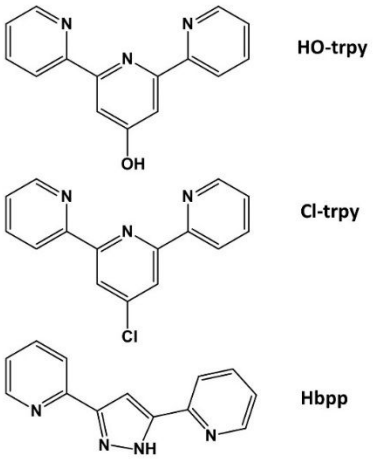
the formation of a hexanuclear $\{Fe_2Ru_4\}$ macrocycle that directs the catalyst active sites away from the sensitive ligand backbone.

Results and discussion

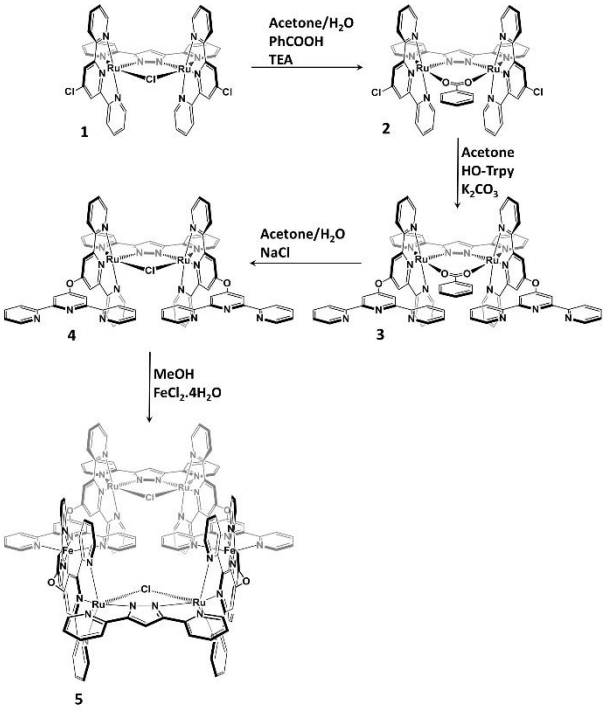
After observing the oxidation products of the bpp ligand backbone after catalysis,[31] our attentions were focused on the design of new catalyst structures that could minimize the interactions between the Ru-oxo active site and the bpp ligand. Consequently the $[(\{Ru^{II}(trpy\text{-}O\text{-}trpy)\}_2(\mu\text{-}bpp)(\mu\text{-}Cl))_2M_2]^{8+}$ structure shown in Figure 1 was designed. The fusion of two catalyst units linked by two $\{M(R\text{-}trpy)_2\}$ bridges generates a macrocyclic structure where the catalyst units are "locked" in an orientation with the active Ru-oxo sites facing into the central cavity and hence cannot interact with the sensitive bpp ligand framework of other catalyst molecules.

Synthesis of the macroyclic WOC began with the modification of the original Ru-bpp catalyst framework and ligands (Schemes 1 and 2). A chlorinated terpyridine ligand (Cl-trpy) was used to create catalyst precursor **1**, $[\{Ru^{II}(Cl\text{-}trpy)\}_2(\mu\text{-}bpp)(\mu\text{-}Cl)](PF_6)_2$, using an adaptation of the original Ru-bpp catalyst preparation.[6] The bridging chloro ligand was then hydrolysed and converted to a bridging benzoate ligand to give compound **2**, $[\{Ru^{II}(Cl\text{-}trpy)\}_2(\mu\text{-}bpp)(\mu\text{-}PhCOO)](PF_6)_2$. The reasoning behind this conversion was in essence a protection strategy, after discovering that only the μ-PhCOO bridge was able to withstand the harsh substitution conditions in the following step. Both the μ-Cl and μ-OAc analogues resulted in complex mixtures upon refluxing in acetone with HO-trpy and K_2CO_3. On the other hand, the conversion of **2** under these conditions was clean and subsequently afforded the pendant terpyridine complex **3**, $[\{Ru^{II}(trpy\text{-}O\text{-}trpy)\}_2(\mu\text{-}bpp)(\mu\text{-}PhCOO)](PF_6)_2$, in high yield. Initial attempts to cyclise derivative **3** directly via reaction with $RuCl_3$ led to precipitation of a solid that was very poorly soluble in most common solvents and difficult to unambiguously identify, although it was suspected to be polymeric in nature. Iron has been proposed as a suitable substitute for ruthenium in the context of water oxidation before[74] so it was thought that a similar substitution to couple the pendant terpyridine groups through the more easily formed $\{Fe(R\text{-}trpy)_2\}$ bridge could also help in this case. This strategy partially worked and a soluble product was obtained. UV-vis and NMR UV-vis and NMR spectroscopy indicated formation of the $\{Fe(R\text{-}trpy)_2\}$, however, the NMR spectra and MS data did not match the cyclic structure but instead suggested a mixture of non-cyclised/oligomeric structures (ESI). At this point a return to the computer generated models highlighted that the bridging benzoate ligands were occupying much of the space within the cavity of the hypothetical macrocyclic products and therefore were most likely preventing cyclisation through steric hindrance (see ESI). To overcome this, a "deprotection" strategy had to be developed in order to replace the μ-PhCOO with a smaller yet still hydrolysable bridging ligand. A procedure for the clean conversion of the μ-PhCOO back to the μ-Cl was established and gave complex **4** $[\{Ru^{II}(trpy\text{-}O\text{-}trpy)\}_2(\mu\text{-}bpp)(\mu\text{-}Cl)](PF_6)$, in high yield. Satisfyingly, the subsequent reaction of **4** with $FeCl_2{\cdot}4H_2O$ then afforded the target macrocycle **5**, $[(\{Ru^{II}(trpy\text{-}O\text{-}trpy)\}_2(\mu\text{-}Cl)(\mu\text{-}bpp))_2Fe^{II}{}_2](PF_6)_8$.

Despite many efforts to crystallise complex **5** for single crystal x-ray diffraction analysis, none of the attempts were successful and so structure confirmation was achieved through voltammetric and spectroscopic techniques. Firstly, the ^1H NMR spectrum of compound **5** was very sharp and clean, indicating formation of a single discrete molecular product. The large downfield shift of the characteristic singlet of the pendant terpyridine and the large up-field shift of the doublet adjacent to the pyridyl nitrogen also strongly indicated coordination to Fe (See Figure 2). Further evidence for the



Scheme 1. Ligands prepared and used in this work.



Scheme 2. Structures and synthetic steps for the preparation of compound **1**-**5**.

formation of macrocycle **5** was obtained through UV-vis spectroscopy and CV (Figure 3): From the overlaid UV-vis spectra of compounds **4** and

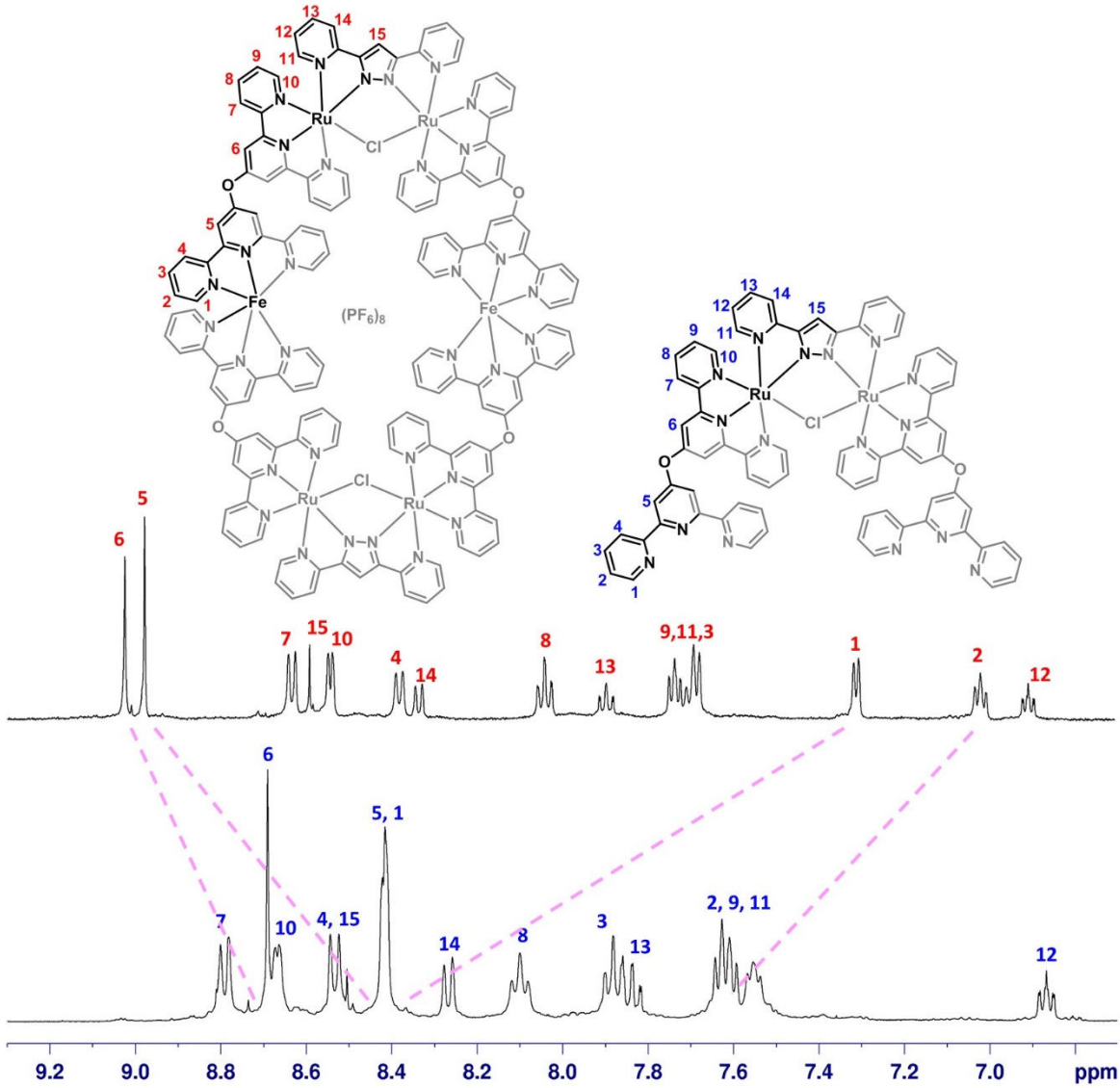


Figure 2. Assigned ^{1}H-NMR spectra of complexes **4** (bottom) and **5** (top) in d6-acetone. The most significant chemical shifts due to coordination of Fe are indicated by the dotted pink lines.

caused by adsorption on the glassy carbon electrode, an effect commonly observed for Ru-bpp-type compounds. Finally, a comparison of DOSY NMR spectra of macrocycle **5** and **5** with a sample of $Fe(trpy)_2(PF6)_2$ it can be seen clearly that the catalyst units and the $Fe(R\text{-}trpy)_2$ units are incorporated within the structure of **5** in a 1:1 ratio. The CV and DPV data for compound **5** also show a marked difference to those of **4** due to the formation of the two new redox active Fe centres. The two redox processes in **4** are assigned to the two reversible 1-electron oxidations for $Ru^{II}/Ru^{II} – Ru^{II}/Ru^{III}$ and for $Ru^{II}/Ru^{III} – Ru^{III}/Ru^{III}$ and give an appropriate 1:1 peak area ratio in the DPV. Two redox processes are also observed in the CV and DPV of **5** instead of the three predicted but this is due to the reversible 1- electron oxidation of the $Fe(R\text{-}trpy)_2$ units overlapping with the $Ru^{II}/Ru^{III} – Ru^{III}/Ru^{III}$ peak. This overlay is evidenced by the relative peak heights in the DPV. Note the ratio is not a perfect 2:1 due to the distorted cathodic waves precursor **2** gave a satisfactory ratio of 2.3:1 for their relative hydrodynamic radii, calculated from the observed diffusion coefficients using the Stokes-Einstein equation (see Figure 3 for spectra and ESI for calculations).[75,76]

Having confirmed the structure of **5**, its water oxidation performance was tested against the non-cyclic precursor **4** in order to investigate the influence the macrocyclic framework had on catalysis. A solution of $Ce^{IV}(NH_4)_2(NO_3)_6$ (CAN) in 0.1 M triflic acid was added to a solution of **5** in 0.1 M triflic acid (with 25% TFE added to help dissolve the complex) and the resulting gas evolution was monitored by manometry. As can be seen in Figure 4, catalysis was observed for macrocycle **5** but the gas evolution profile was very similar to the comparative control experiment, which contained twice the

amount of **4** with respect to **5** but with all other variables the same. The almost identical gas evolution profiles for the two compounds could be explained by examining the strength of the $\{Fe(R\text{-}trpy)_2\}$ link

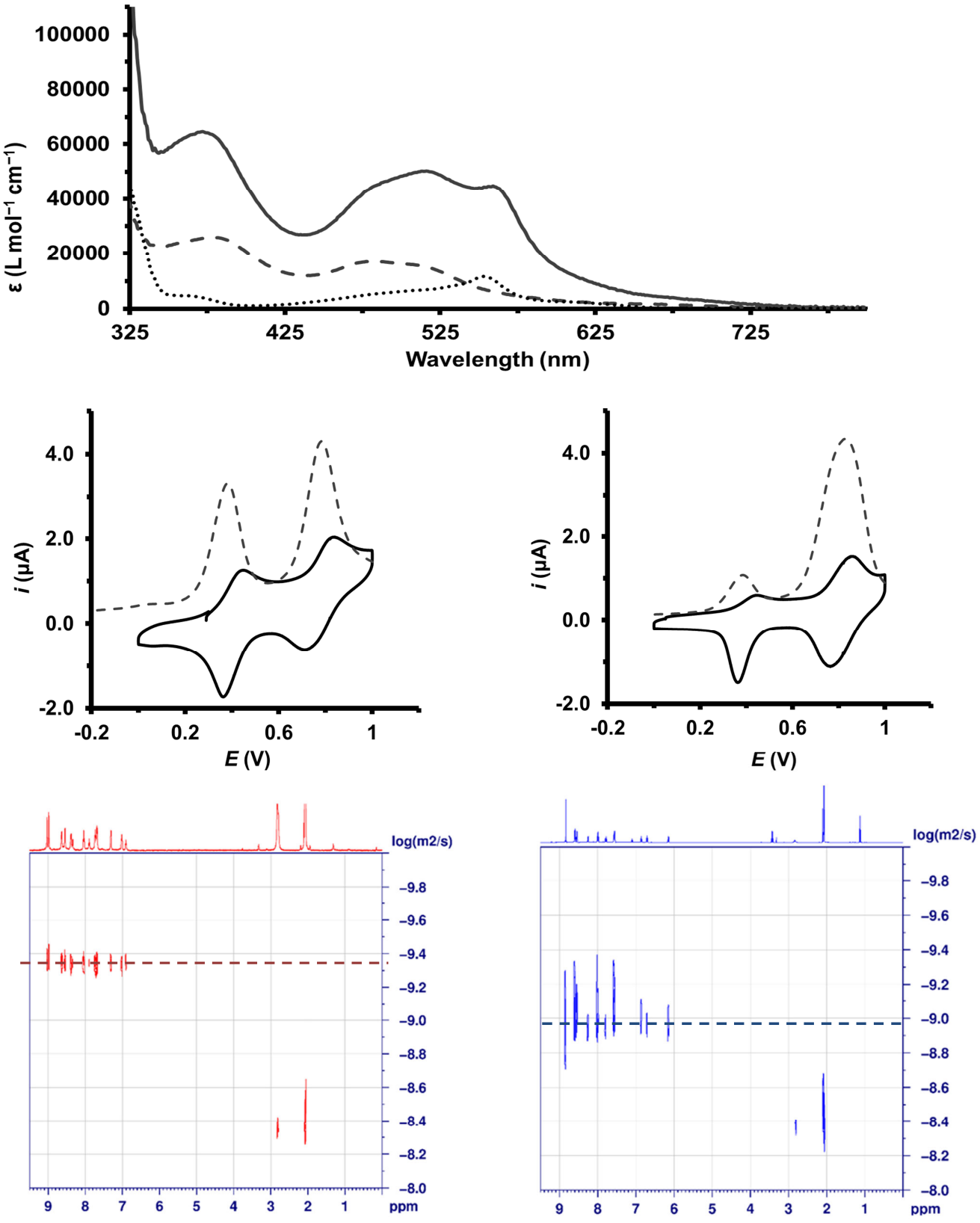


Figure 3. (Top) UV-vis spectra of **4** (1.0×10^{-5} M in propylene carbonate, dashed line), $Fe(trpy)_2(PF_6)_2$ (1.1×10^{-5} M in propylene carbonate, dotted line) and **5** (0.5×10^{-5} M in propylene carbonate, solid line); (Middle) CV and DPV of (left) **4** (*ca.* 0.7 mM in DCM, 0.1 M $TBAPF_6$); (right) **5** (*ca.* 0.3 mM in DCM, 0.1 M $TBAPF_6$). E *vs* MSE reference, GC Working, Pt counter). MSE = +0.640 *vs* NHE; (Bottom) DOSY NMR spectra of **5** (left) and **2** (right) in acetone-d6. Note the X axis values are log(D) so larger molecules have larger values.

within macrocycle **5**: The kinetic stability of Fe(R-trpy)$_2$ clusters is relatively high at neutral pH, however, the ligand exchange coefficient increases significantly at high and low pH.[77,78] Additionally, the oxidation potential for $[Fe^{II}(trpy)_2]^{2+}$ is 1.45 V *vs* NHE, which allows it to be oxidised by the CAN oxidant. Therefore, under the conditions employed for the catalysis experiments, oxidation and hydrolysis of the {Fe(R-trpy)$_2$} link preceded water oxidation, thus producing two equivalents of precursor **4** and an almost identical result to the control experiment. Experiments to test catalyst **5** at neutral pH with other chemical oxidants, where the {Fe(R-trpy)$_2$} link may be more stable, were considered, however, control experiments with $[Fe^{II}(trpy)_2](PF_6)_2$ and sodium periodate demonstrated that hydrolysis still occurred at pH 7 upon oxidation, albeit more slowly than at pH 1 (see ESI). Complete replacement of the weak Fe link would therefore be necessary before the desired "macrocyclic encapsulation effect" on catalysis could be observed and so further efforts have been focused along these lines. Attempts to form the more hydrolytically stable {Ru(R-trpy)$_2$} link as well as covalent links *via* "click chemistry" are still ongoing in our labs.

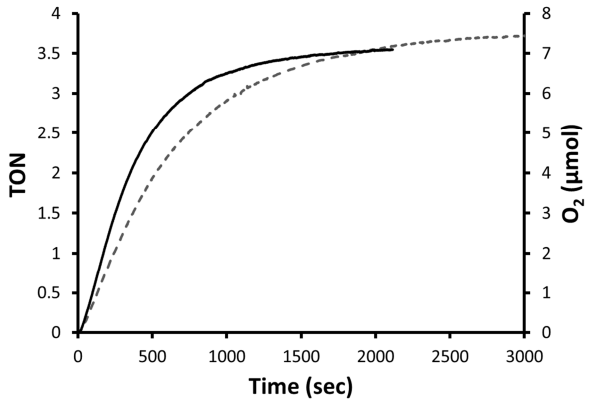


Figure 4. Manometry traces for gas evolution during catalysis for **5** (4.12 mg (0.25 mM), 112 mg CAN (50 mM), 3.0 mL 0.1 M triflic acid + 1.0 mL TFE, grey dashed curve) and; **4** (3.42 mg (0.5 mM), 112 mg CAN (50 mM), 3.0 mL 0.1 M triflic acid + 1.0 mL TFE, solid black curve).

Experimental

Materials: $RuCl_3 \cdot xH_2O$ was supplied by Precious Metals Online PMO Pty Ltd. All other reagents were purchased from Sigma-Aldrich and Alfa Aesar chemical companies. 2,2'-(1H-pyrazole-3,5-diyl)dipyridine (Hbpp),[79-81] HO-trpy[82] and Cl-trpy[82] were prepared according to the their reported procedures. All synthetic manipulations under N_2/Ar were performed using standard Schlenk tubes and vacuum-line techniques.

Synthesis and characterization of 1: In a 100 mL round bottom flask, a suspension of (Cl-trpy)$RuCl_3$ (500 mg, 1.05 mmol, 2.0 eq), LiCl (134 mg, 3.16 µmol, 6.0 eq) and TEA (219 µL, 1.575 mmol, 3.0 eq) in MeOH (40 mL) was degassed by bubbling N_2 for *ca.*10 mins. Meanwhile in a separate vessel, a solution of Hbpp ligand (117 mg, 0.535 mmol, 1.0 eq) and TEA (219 µL, 1.575 mmol, 3.0 eq) in MeOH (10 mL) was prepared and degassed with N_2. The ligand solution was added to the round bottom flask and the blackish brown reaction mixture was then heated to reflux under a N_2 atmosphere for 14 hrs with irradiation (100 W household lamp). The reaction mixture was cooled to room temperature and filtered to remove insoluble by-products. A saturated aqueous solution of NH_4PF_6 (*ca.* 1 mL) was added to the filtrate to produce a brown solid precipitate which was subsequently collected by filtration. The brown solid residue was then triturated with MeOH portions (4×40 mL) and the MeOH triturates were then concentrated to dryness to afford four separate batches of a brown powder of varying purity. The original MeOH reaction filtrate was then diluted with H_2O (*ca.* 40 mL) to precipitate a fifth batch of brown solid, collected by filtration and dried under vacuum. Total yield of product **1** obtained was 394 mg (0.307 mmol, 58% based on Ru). **^{1}H NMR** (acetone-d6, 400 MHz): δ 8.80 (4H, s), 8.62 (4H, d, *J*=6.9 Hz), 8.52 (1H, s), 8.42 (4H, d, *J*=6.9 Hz), 8.27 (2H, d, *J*=7.0 Hz), 7.99 (4H, t, *J*=6.9 Hz), 7.83 (2H, t, *J*=7.0 Hz), 7.66 (4H, t, *J*=6.9 Hz), 7.52 (2H, d, *J*=7.0 Hz), 6.81 (2H, t, *J*=7.0 Hz); **^{13}C NMR** (acetone-d6, 100 MHz): δ 159.7 (C), 158.7 (C), 158.5 (C), 154.0 (CH), 153.6 (CH), 148.6 (C), 140.7 (C), 137.2 (CH), 137.1 (CH), 127.8 (CH), 124.2 (CH), 122.7 (CH), 122.2 (CH), 120.5 (CH), 103.3 (CH); **^{19}F NMR** (acetone-d6, 380 MHz): δ -72.3 (d, *J*=708.0 Hz); **^{31}P NMR** (acetone-d6, 160 MHz): δ -141.1 (sep, *J*=708.0 Hz); **MS** (CH_2Cl_2, acetone, MALDI$^+$): *m/z* 1138.1 ($[M - PF_6^-]^+$); **$E_{1/2}$** (DCM, 0.1 M TBA(PF_6), V vs SSCE): 0.767, 1.114; **IR** (powder, cm^{-1}): 3641w, 3073w, 1603, 1501w, 1448w, 1420m, 1382, 1280w, 1246, 1109, 1041w, 830s, 783s, 752s, 554s; **Anal.** Calc. for $[\{Ru^{II}(Cl\text{-}trpy)\}_2(\mu\text{-}bpp)(\mu\text{-}Cl)](PF_6)_2.H_2O$: C, 39.66; H, 2.40; N, 10.76; Found: C, 39.13; H, 2.73; N, 10.60.

Synthesis and characterization of 2: In a 100 mL round bottom flask, a solution of benzoic acid (66 mg, 0.545 µmol, 2.0 eq) and TEA (152 µL, 1.092 mmol, 4.0 eq) in an acetone-water mixture (1:1, 30 mL) was added to a solution of **1** (350 mg, 0.273 mmol, 1.0 eq) in acetone (30mL). The dark brown solution was then heated to reflux under for 3 hrs. The reaction mixture was cooled to room temperature and a saturated aqueous solution of NH_4PF_6 (*ca.* 1 mL) was added. The solution was concentrated under vacuum to *ca.* $^1/_3$ volume to produce a purplish brown solid precipitate which was subsequently collected by filtration. The solid residue was washed well with water and Et_2O to give a purplish brown powder after drying under vacuum. Total yield of product **2** obtained was 337 mg (0.246 mmol, 90% based on Ru). **^{1}H NMR** (acetone-d6, 500 MHz): δ 8.84 (4H, s), 8.61 (4H, d, *J*=6.9 Hz), 8.60 (1H, s), 8.55 (4H, d, *J*=6.9 Hz), 8.26 (2H, d, *J*=7.0 Hz), 8.00 (4H, t, *J*=6.9 Hz), 7.79 (2H, t, *J*=7.0 Hz), 7.57 (4H, t, *J*=6.9 Hz), 7.56 (2H, d, J=7.0 Hz), 7.10 (1H, t, *J*=7.9 Hz), 6.86 (2H, t, *J*=7.0 Hz), 6.71 (2H, t, *J*=7.9 Hz), 6.15 (2H, d, *J*=7.9 Hz); **^{13}C NMR** (acetone-d6, 100 MHz): δ 185.4 (C), 161.3 (C), 158.8 (C), 156.4 (C), 153.9 (CH), 153.3 (CH), 152.0 (C), 140.8 (C), 137.5 (CH), 136.2 (CH), 134.5 (C), 131.0 (CH), 127.9 (CH), 127.4 (CH), 127.1 (CH), 124.2 (CH), 123.0 (CH), 122.3 (CH), 119.7 (CH), 104.1 (CH); **^{19}F NMR** (acetone-d6, 470 MHz): δ -72.5 (d, *J*=708.2 Hz); **^{31}P NMR** (acetone-d6, 200 MHz): δ -144.2 (sep, *J*=708.2 Hz); **MS** (CH_2Cl_2, acetone, MALDI$^+$): *m/z* 1224.2 ($[M - PF_6^-]^+$); **$E_{1/2}$**

(DCM, 0.1 M TBA(PF_6), V vs SSCE): 0.778, 1.084; **IR** (powder, cm^{-1}): 3645w, 3079w, 1604m, 1526, 1382, 1248w, 1108w, 829s, 783, 752, 729, 555s; **Anal.** Calc. for [{Ru^{II}(Cl-trpy)}$_2$(μ-bpp)(μ-PhCOO)](PF_6)$_2$.2H_2O: C, 42.72; H, 2.72; N, 9.96; Found: C, 40.93; H, 2.72; N, 10.24.

Synthesis and characterization of 3: In a 100 mL round bottom flask, HO-trpy (227 mg, 0.913 µmol, 5.0 eq) and K_2CO_3 (252 mg, 1.826 mmol, 10.0 eq) were added to a solution of **2** (250 mg, 0.183 mmol, 1.0 eq) in acetone (50 mL). The dark brown solution was then heated to reflux for 17 hrs. The reaction mixture was cooled to room temperature and a saturated aqueous solution of NH_4PF_6 (*ca.* 1 mL) was added, followed by dilution with H_2O (20 mL). The solution was concentrated under vacuum to *ca.* $^1/_2$ volume to produce a purplish brown solid precipitate which was subsequently collected by filtration. The solid residue was then washed well with water and Et_2O to give a purplish brown powder after drying under vacuum. Total yield of product **3** obtained was 268 mg (0.149 mmol, 82% based on Ru). **^{1}H NMR** (acetone-d6, 400 MHz): δ 8.81 (4H, d, *J*=8.0 Hz), 8.74 (4H, s), 8.66 (4H, d, *J*=8.0 Hz), 8.55 (9H, m), 8.46 (4H, s), 8.25 (2H, d, *J*=7.1 Hz), 8.07 (4H, t, *J*=8.0 Hz), 7.90 (4H, t, *J*=7.8 Hz), 7.79 (2H, t, *J*=7.1 Hz), 7.69 (2H, d, *J*=7.1 Hz), 7.52 (8H, m), 7.14 (1H, t, *J*=7.6 Hz), 7.07 (2H, t, J=7.6 Hz), 6.91 (2H, t, *J*=7.1 Hz), 6.40 (2H, d, *J*=7.6 Hz); **^{13}C NMR** (acetone-d6, 100 MHz): δ 184.7 (C), 164.4 (C), 162.2 (C), 161.8 (C), 159.4 (C), 158.6 (C), 156.7 (C), 154.8 (C), 154.0 (CH), 153.3 (CH), 152.0 (C), 149.4 (CH), 137.4 (CH), 137.3 (CH), 136.0 (CH), 134.8 (C), 130.9 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 124.8 (CH), 124.2 (CH), 122.3 (CH), 121.2 (CH), 119.6 (CH), 114.0 (CH), 111.2 (CH), 104.0 (CH); **^{19}F NMR** (acetone-d6, 375 MHz): δ -72.5 (d, *J*=707.8 Hz); **^{31}P NMR** (acetone-d6, 160 MHz): δ -141.2 (sep, *J*=707.8 Hz); **MS** (CH_2Cl_2, acetone, MALDI$^+$): *m/z* 1651.4 ([M − PF_6^-]$^+$); **$E_{1/2}$** (DCM, 0.1 M TBA(PF_6), V vs MSE): 0.425, 0.717; **IR** (powder, cm^{-1}): 3643w, 3069w, 1605, 1580, 1562, 1531, 1399, 1352, 1202, 964w, 833s, 788, 753, 556s; **Anal.** Calc. for [{Ru^{II}(trpy-O-trpy)}$_2$(μ-bpp)(μ-PhCOO)](PF_6)$_2$.4H_2O: C, 47.72; H, 3.15; N, 11.13; Found: C, 47.92; H, 3.18; N, 11.63.

Synthesis and characterization of 4: In a 25 mL round bottom flask, a saturated aqueous solution of NaCl (3.0 mL) was added to a solution of **3** (150 mg, 0.084 mmol) in acetone (9.0 mL). The dark purple brown solution was then heated to reflux for 18 hrs. The reaction mixture was cooled to room temperature and a saturated aqueous solution of NH_4PF_6 (*ca.* 1 mL) was added followed by dilution with water (10 mL). The brown solid precipitate was subsequently collected by filtration and washed well with water and Et_2O to give a brown powder after drying under vacuum. Total yield of product **4** obtained was 126 mg (0.074 mmol, 88% based on Ru). **^{1}H NMR** (acetone-d6, 400 MHz): δ 8.79 (4H, d, *J*=6.4 Hz), 8.69 (4H, s), 8.67 (4H, d, *J*=6.4 Hz), 8.53 (4H, d, *J*=8.1 Hz), 8.50 (1H, s), 8.42 (8H, m), 8.27 (2H, d, *J*=7.5 Hz), 8.10 (4H, t, *J*=6.4 Hz), 7.88 (4H, t, *J*=8.1 Hz), 7.84 (2H, t, *J*=7.5 Hz), 7.62 (6H, m), 7.55 (4H, t, *J*=6.4 Hz), 6.87 (2H, t, *J*=7.5 Hz); **^{13}C NMR** (acetone-d6, 125 MHz): δ 164.5 (C), 161.7 (C), 160.4 (C), 159.1 (C), 158.9 (C), 158.4 (C), 154.6 (C), 154.0 (CH), 153.7 (CH), 148.8 (CH), 148.6 (C), 137.6 (CH), 137.0 (CH), 136.8 (CH), 127.6 (CH), 125.1 (CH), 124.2 (CH), 122.2 (CH), 121.5 (CH), 120.4 (CH), 113.7 (CH), 111.6 (CH), 103.3 (CH); **^{19}F NMR** (acetone-d6, 470 MHz): δ -72.4 (d, *J*=708.9 Hz); **^{31}P NMR** (acetone-d6, 200 MHz): δ -144.2 (sep, *J*=708.9 Hz); **MS** (CH_2Cl_2, acetone, MALDI$^+$): *m/z* 1565.3 ([M − PF_6^-]$^+$); **$E_{1/2}$** (DCM, 0.1 M TBA(PF_6), V vs MSE): 0.400, 0.782; **UV–vis** (propylene carbonate): λ_{max}, nm (ε, L mol^{-1} cm^{-1}); 513 (15534), 479 (17047), 379 (26006); **IR** (powder, cm^{-1}): 3647w, 3086w, 1605, 1580, 1563, 1399, 1352w, 1203, 965w, 834s, 787, 753, 553s; **Anal.** Calc. for [{Ru^{II}(trpy-O-trpy)}$_2$(μ-bpp)(μ-Cl)](PF_6).4NaCl.4H_2O: C, 43.50; H, 2.85; N, 11.12; Found: C, 43.19; H, 2.89; N, 11.16.

Synthesis and characterization of 5: In a 25 mL round bottom flask, a solution of KPF_6 (26 mg, 0.142 mmol, 10.0 eq) and $FeCl_2$.4H_2O (4.4 mg, 0.0219 mmol, 1.5 eq) in MeOH (2.5 mL) were added to a solution of precursor **4** (25 mg, 14.6 µmol, 1.0 eq) in acetone (5.0 mL). The resulting deep purple solution was heated to reflux with stirring for 14 hrs. The reaction mixture was cooled to room temperature and filtered to remove insoluble by-products. Dilution of the filtrate with water (5.0 mL) produced a purple precipitate which was subsequently collected by filtration. The purple solid residue was redissolved in acetone (2.0 mL), filtered, and then concentrated to dryness to afford a dark purple powder (12 mg, 2.92 µmol, 20% based on Ru). **^{1}H NMR** (acetone-d6, 500 MHz): δ 9.02 (8H, s), 8.98 (8H, s), 8.63 (8H, d, *J*=7.0 Hz), 8.59 (2H, s), 8.54 (8H, d, *J*=7.0 Hz), 8.38 (8H, d, *J*=6.9 Hz), 8.33 (4H, d, *J*=7.1 Hz), 8.04 (8H, t, *J*=7.0 Hz), 7.90 (4H, t, *J*=7.1 Hz), 7.73 (8H, t, *J*=7.0 Hz), 7.69 (8H, t, *J*=6.9 Hz), 7.68 (4H, d, *J*=7.1 Hz), 7.31 (8H, d, *J*=6.9 Hz), 7.02 (8H, t, *J*=6.9 Hz), 6.90 (4H, t, *J*=7.1 Hz); **^{13}C NMR** (acetone-d6, 125 MHz): δ 165.9 (C), 161.3 (C), 160.8 (C), 159.2 (C), 158.8 (C), 158.4 (C), 157.7 (C), 154.1 (CH), 153.7 (CH), 153.4 (CH), 148.7 (C), 138.4 (CH), 137.3 (CH), 137.0 (CH), 127.8 (CH), 127.5 (CH), 124.5 (CH), 123.8 (CH), 122.3 (CH), 120.5 (CH), 116.5 (CH), 112.5 (CH), 103.3 (CH); **^{19}F NMR** (acetone-d6, 470 MHz): δ -72.0 (d, *J*=709.2 Hz); **^{31}P NMR** (acetone-d6, 200 MHz): δ -144.3 (sep, *J*=709.2 Hz); **MS** (CH_2Cl_2, acetone, MALDI$^+$): *m/z* 3967.2 ([M − PF_6^-]$^+$); **$E_{1/2}$** (DCM, 0.1 M TBA(PF_6), V vs MSE): 0.399, 0.809; **UV–vis** (propylene carbonate): λ_{max}, nm (ε, L mol^{-1} cm^{-1}); 559 (44835), 516 (50268), 476 (42741), 371 (64599); **IR** (powder, cm^{-1}): 3644w, 3083w, 1600, 1396, 1206, 964w, 829s, 786s, 753, 555s; **Anal.** Calc. for [({Ru^{II}(trpy-O-trpy)}$_2$(μ-Cl)(μ-bpp))$_2$$Fe^{II}_2$]($PF_6$)$_8$.10H2O: C, 40.86; H, 2.77; N, 10.44; Found: C, 40.41; H, 2.47; N, 10.11.

Conclusions

In summary, this work successfully functionalised the Ru-bpp catalyst, post-synthesis, with free pendent trpy-O-trpy "arms" following a protection-substitution-deprotection strategy. The pendent trpy-O-trpy arms were subsequently exploited to couple two catalyst units together *via* two {Fe(R-trpy)$_2$} bridges to form a novel macrocyclic WOC precursor. The catalytic activity of the macrocyclic complex was assessed under comparable conditions (CAN, pH 1) with the parent Ru-bpp catalyst but the macrocycle was unfortunately not stable enough to withstand the oxidative acidic environment and no enhanced activity or stability was observed. Current efforts are

focussed on replacing the {Fe(R-trpy)$_2$} with a more robust linker group and applying the macrocyclic encapsulation strategy to other WOC systems that are also plagued by intermolecular ligand oxidation.

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