Electronic supplementary information

# A self-assembled, multicomponent water oxidation device

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# Synthesis and characterization of [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>

**1** was purchased from Sigma-Aldrich and was used without any further purification.

[**Ru**(1)<sub>3</sub>][**PF**<sub>6</sub>]<sub>2</sub>. Compound 1 (402 mg, 98 mmol) and RuCl<sub>3</sub>.*x*H<sub>2</sub>O (58.3 mg, ≈28 mmol) were added to ethylene glycol (15 mL) and the mixture was heated in a domestic microwave for 1.5 min. The solution turned bright red. NH<sub>4</sub>PF<sub>6</sub> in MeOH was added until the complex precipitated and the solid was removed by filtration. The product was recrystallized from hot methanol yielding red [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (401mg, 0.25 mmol, 88%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) *δ* / ppm 8.11 (s, 6H, H<sup>bpy3</sup>), 7.57 (d, *J* = 4.7 Hz, 6H, H<sup>bpy6</sup>) 7.28 (d, *J* = 4.4 Hz, 6H, H<sup>bpy5</sup>), 2.79 (m, 12H, H<sup>CH2</sup>), 1.68 (m, 12H, H<sup>CH2</sup>), 1.37–1.26 (overlapping m, 66H, H<sup>CH2</sup>), 0.87 (m,18H, H<sup>Me</sup>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) *δ* / ppm 156.4 (C<sup>bpy2</sup>), 154.6 (C<sup>bpy4</sup>), 150.9 (C<sup>bpy6</sup>), 128.3 (C<sup>bpy5</sup>), 123.6 (C<sup>bpy3</sup>), 35.6 (C<sup>CH2</sup>), 32.0 (C<sup>CH2</sup>), 30.2 (C<sup>CH2</sup>), 29.6 (C<sup>CH2</sup>), 29.55 (C<sup>CH2</sup>), 29.5 (C<sup>CH2</sup>), 29.4 (C<sup>CH2</sup>), 22.8 (C<sup>CH2</sup>), 14.3 (C<sup>Me</sup>). UV-Vis (CHCl<sub>3</sub>, 5 x 10<sup>-5</sup> mol dm<sup>-3</sup>) λ<sub>max</sub>/nm (⊡n/ dm mol<sup>-1</sup> cm<sup>-1</sup>) 291 (70255), 330 (14274), sh 364 (8175), sh 432 (14015), 464 (17121). ESI-MS: 663.8 [M-PF<sub>6</sub>]<sup>2+</sup> (calc. 663.5), Found C 62.70, H 8.53, N 5.42; C<sub>84</sub>H<sub>132</sub>F<sub>12</sub>N<sub>6</sub>P<sub>2</sub>Ru requires C 62.39, H 8.23, N 5.20.





Scheme S1. Structures of ligand 1 and [Ru(1)<sub>3</sub>]<sup>2+</sup>.

### **Film preparation**

The FTO-coated glass substrates were cleaned by sonicating in a 2% solution (milli-Q water) of Sonoswiss Cleaner L2 for 20 minutes, rinsing with water and ethanol, drying under N<sub>2</sub>, and finally treated with ozone for 10 minutes. The substrates were used immediately. Langmuir-Blodgett films were prepared according to the procedure outlined in Murray *et al.*<sup>1</sup> Drop-casted films were prepared by dropping 1 mL aliquots of Co<sub>4</sub>POM (8 x 10<sup>-4</sup> M) and [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (7 x 10<sup>-4</sup> M) alternately, drying the sample under N<sub>2</sub> between each addition. Before electrochemical measurements every side of the electrodes were painted with Lacomit varnish leaving only around 1 cm<sup>2</sup> area of the films free. The exact free area was then measured on a scanned image of the electrode using image processing software.

## Scanning electron microscopy (SEM)

SEM measurements including FIB cuts were made using an SEM - FEI Helios Nano Lab 650 instrument at the ZMB, University of Basel, and FESEM (field emission scanning

electron microscopy) was performed at Empa on a Hitachi S-4800 model with an accelerating voltage of 10 KeV and probe current of 10  $\mu$ A. (See Fig. S1–S4, and Fig. S8)

#### **Electrochemical measurement**

A Voltalab 80 PGZ 402 potentiostat was used for the electrochemical experiment using the three electrode configuration where the LB or drop casted  $[Ru(1)_3][PF_6]_2/Co_4POM$  electrode acts as the working electrode in combination with an Ag/AgCl (with sat. KCl) reference electrode and Pt plate as counter electrode. The electrodes were immersed in 30 mM potassium phosphate buffer solution, at pH 7.6 and ambient temperature. No sacrificial oxidant was present, and the samples were not irradiated. (See Fig. 1 and S5).

#### O<sub>2</sub> evolution measurement

O<sub>2</sub> generation with the water oxidation catalyst (WOC) was monitored using a GC-2014 Shimadzu gas chromatograph (GC). The experiment was performed in a custom designed, sealed plastic electrochemical cell (EC) (see Fig. S6a). The headspace of the EC was connected to the GC and the electrodes were attached to the potentiostate. The GC was equipped with a TCD detector and a Hayesep D 10' column and the temperatures of the injector, column and detector were 40, 30 and 140 °C, respectively. The flow rate on the column was 24 mL/min. The buffer in the cell was bubbled with Ar for at least 30 minutes before measurements. The generated O<sub>2</sub> was recirculated between the GC and EC with Ar carrier gas using a pump at 0.2 bar overpressure, enabling the online monitoring of its evolution (Fig. S6b). The gases were injected every 30 minutes in parallel with the chronoamperometry experiment. During the c experiment, a bias of +1.3 V vs Ag / AgCl was applied. The evolved  $O_2$  was quantified based on a calibration with 500 and 1000 ppm O<sub>2</sub> in Ar reference gases. Data analysis was carried out using manual integration of the peaks in the GC software. Retention times were 3.1, 3.9 and 4.2 minutes for H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>, respectively. The air contamination of the headspace was subtracted from the raw data using the  $N_2/O_2$  ratio in air. The thermal conductivity of nitrogen and oxygen approximately the same at 20°C (0.0234 and 0.0238 W/mK respectively), therefore the oxygen and nitrogen data can easily be compared. Since air is made up of mainly 78% nitrogen and 21% oxygen, the oxygen present from the air leakage can be calculated as:  $O_{2air} = N_2/3.7$ . The evolved oxygen was calculated as:  $O_{2total} - O_{2air}$ . We compared the amount of evolved  $O_2$  measured by gas chromatography (GC) with the theoretical number of moles of  $O_2$  obtained by integration of the current density data (shown in Fig. 3) over time and then applying Faraday's Law (integrated current/4F (Faraday constant)).

#### **XRD** measurements

The XRD analyses of all films have been performed on a PANalytical X"Pert PRO, Powder diffractometer (Cu K $\alpha$  radiation).

We compared the XRD of drop cast (DC)  $[Ru(1)_3][PF_6]_2$ , DC Co<sub>4</sub>POM, Langmuir-Blodgett (LB) and DC films of the  $[Ru(1)_3][PF_6]_2/Co_4POM$  mixture before and after electrochemical investigation (Fig. S9). It is evident that the DC  $[Ru(1)_3][PF_6]_2$  film shows the corresponding Bragg reflection peak [-120] of ruthenium metaphosphate, Ru(PO<sub>3</sub>)<sub>3</sub> besides the usual FTO (fluorine doped tin oxide - substrate) Bragg reflection peak intensities. In the case of DC Co<sub>4</sub>POM, we have observed Bragg reflection peaks [13-1] intensities of K<sub>2</sub>CoWO<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> which we believe constituted the structure of Co<sub>4</sub>POM (POM structural formula:  $K_{10}[Co_4(H_2O)_2(\alpha - M_2O)_2(\alpha - M_$ PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]). However, this particular peak disappears for both DC and LB films of the  $[Ru(1)_3][PF_6]_2/Co_4POM$  mixture. The [-120] peak from ruthenium metaphosphate,  $Ru(PO_3)_3$ , is present in DC film before electrochemical treatment, while it is absent in the LB film. However, we have found an interesting signature of a  $CoO_{1.29}$  peak [002] for the DC film and a similar Bragg reflection peak intensity CoO<sub>1.29</sub> was observed [001] also for the LB film. Note that these two films were analysed before electrochemical treatment. After electrochemical treatment, we have not observed any significant Bragg reflection peaks. The presence of stoichiometric cobalt oxide phase before electrochemical operation is corroborated to the synthesis of WOC (water oxidation catalysts).

We have made a detailed analysis of X-ray diffractograms of  $[Ru(1)_3][PF_6]_2$  in powder and thin film form (Fig. S10). From the comparison of both, we see a good match of the Bragg reflection peaks intensity of [-120] and [2-51] from ruthenium metaphosphate. While some other peaks are also perceptible, we could not index them into the right crystallographic

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phases. From this, it is evident that along with  $[Ru(1)_3][PF_6]_2$ , ruthenium metaphosphate is also present. The formation of the latter corroborates with the fact that ruthenium exists in the +3 oxidation state. This is confirmed from its crystallographic structure analysis as described elsewhere<sup>2</sup>. Note that ruthenium metaphosphate exists in a triclinic form with the linkage of Ru<sup>3+</sup> ions and  $[PO_3^-]$  ions in a linear chain.

We have also probed the X-ray diffractograms of cobalt polyoxometallate in detail. We have compared the XRD profiles of Co<sub>4</sub>POM powder, drop cast Co<sub>4</sub>POM, drop-cast films of the [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>/Co<sub>4</sub>POM mixture and drop cast ruthenium complex as shown in Fig. S11. Here, we mostly focus in the Bragg angle position from 30° to 32° with an enlarged section of the X-ray diffractogram. We have observed the presence of peak 1 which corresponds to Bragg reflection peak intensity of [031] from K<sub>2</sub>CoWO<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub> in both Co<sub>4</sub>POM powder and drop casted Co<sub>4</sub>POM. While in case of DC ruthenium complex, Bragg peak [0-31] has shown up which is marked as 2. If we carefully compare the X-ray diffractogram of the mixture, [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>/Co<sub>4</sub>POM, with both of these, we notice a third peak (3) appearing at around 31.15° which is actually a convolution of peak 1 and 2. Therefore, it can be confirmed that due to the preparation of the layers by drop casting process, the Bragg peak was shifted and it contains the signatures of both DC Co<sub>4</sub>POM and DC ruthenium complex.

#### **XPS measurements**

X-ray photoelectron spectroscopy survey spectrum of all films (Fig. S11) were measured on a PHI LS5600 spectrometer equipped with a Mg K $\alpha$  X-ray source and calibrated using C1s = 285.0 eV. From the survey spectrum we have observed that all molecular complex films contain significant amount of carbon and oxygen in their crystal structure. The oxygen atomic concentration varies in each cases related to the amount of ruthenium complex, cobalt POM and the substrate (fluorine-doped tin oxide).

The DC  $[Ru(1)_3][PF_6]_2$  film also shows N1s peak which can be attributed to the bipyridine ligand. The signatures of Si2p and F1s elements originate from the substrate.

The DC Co<sub>4</sub>POM film shows significant amount of W4f and Co2p, as well as Cl2p and K2s signals. The occurrence of Co 2p signature confirms the presence of Co<sub>4</sub>POM on the substrate before electrochemical operation. However, this signal decreases from 4.41 to 1.54 atm% after electrochemical treatment (see Table S1) due to partial desorption of the film.

The Cl2p signal arises from contamination and K1s constitutes the crystal structure of  $K_{10}[Co_4(H_2O)_2(\alpha - PW_9O_{34})]$ .

In the DC films of the mixture of Co<sub>4</sub>POM and [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> before electrochemical operation, Co2p, W4f and K1s signals are detectable but the intensity is lower compared with the Co<sub>4</sub>POM film (Fig. S12) due to lower concentration as a result of alternating layers of Co<sub>4</sub>POM and [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>. Also, the signal could be masked by an over layer effect, i.e. the top [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> layer can mask the cobalt atoms present in the underlying layer. F1s, N1s, and Ru3p signals have also been detected. The N1s and Ru3p signals confirm the presence of [Ru(1)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (where 1 = 4, 4'-bis (<sup>n</sup>nonyl)-2,2'-bipyridine) in the DC mixture film, while F1s comes from the substrate.

After electrochemical operation the Co2p and W4f signals are not present anymore, suggesting that the POM part in the film gets degraded/desorbed after long term operation. However, Co2p and W4f signals for the DC Co<sub>4</sub>POM film do not disappear after electrochemical operation (Table S1). This implies that Co<sub>4</sub>POM on its own can adhere better to the substrate than in the mixed layer-by-layer Co<sub>4</sub>POM/[Ru(**1**)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> films.

Lastly, in the case of LB deposited film, we could not verify the presence of any relevant signals with respect to both  $Co_4POM$  and ruthenium complex  $[Ru(1)_3][PF_6]_2$ . Only signals from the substrate elements can be seen. We believe that the film is too thin.

From the overall investigation of structural and elemental studies of the films, we can conclude that the DC mixture film shows good functionality due to the well orientation of  $Co_4POM$  active site along with the ruthenium complex for water oxidation reaction.



Fig. S1. SEM-FIB image showing the thickness of the LB-Film (image right, black part) before electrocatalysis.



Fig. S2. SEM-FIB image showing the thickness of the LB-Film (image right, black part) after electrocatalysis.



Fig. S3. SEM image showing the surface roughness of FTO (left) and a 60-layer LB-film (right) before electrocatalysis.



Fig. S4. (SEM) image of DC (left) and LB films (right) before electrocatalysis.



Fig. S5. CVs of 50-layer LB and DC films of  $[Ru(1)_3][PF_6]_2/Co_4POM$  on FTO (black and red curves respectively), DC films of  $[Ru(1)_3][PF_6]_2$  (blue) and  $Co_4POM$  (magenta) on FTO, and bare FTO (green). Scan rate: 25 mV s<sup>-1</sup>.







Fig. S6. a) A photograph of the electrochemical reactor and b) scheme of the experimental setup for online, recirculated O<sub>2</sub> measurement, where P: pump pumps the evolved gas and the Ar carrier gas through M: manometer, F: flowmeter, R: electrochemical reactor and GC: gas chromatograph. V: valves close/open the lines to the O<sub>2</sub> reference gases and for Ar carrier gas to flush the system. Pot.: potentiostat is connected to the electrochemical reactor.



Fig. S7. O<sub>2</sub> evolution vs time at 1.0 V applied bias for LB (black) and DC (red) films, dropcasted Co<sub>4</sub>POM (magenta) and  $[Ru(1)_3][PF_6]_2$  (blue) films and an FTO glass (green).



Fig. S8. FESEM-(field emission scanning electron microscopy) images of DC and LB films pre and post electrocatalysis. After electrocatalysis, the bare surface of the FTO substrate is clearly visible.



Fig. S9: Comparison of X-ray diffractograms of drop cast  $[Ru(1)_3][PF_6]_2$ , drop cast Co<sub>4</sub>POM, Langmuir-Blodgett films and drop-cast (DC) films of the  $[Ru(1)_3][PF_6]_2/Co_4POM$  mixture before and after electrochemical activity.



Fig. S10: X – ray diffractograms of powder and drop casted ruthenium complex on FTO.



Fig. S11: Comparison of XRD profile of  $Co_4POM$  powder, drop cast  $Co_4POM$ , drop-cast (DC) films of the  $[Ru(1)_3][PF_6]_2/Co_4POM$  mixture and drop cast ruthenium complex.



Fig. S12: XPS survey spectrum of all films shows the elemental signals from different films.



Fig. S13: Variation of atomic concentration of different chemical species with respect to sample condition.

Table S1: Variation of atomic concentration of DC  $Co_4POM$  only film both before and after electrochemical operation.

Sample	Elements	Atomic concentration
POM	0 1s	
Before		45.5
	C 1s	25.86
	W 4d5	4.94
	Na 1s	12.98
	Co2p3	4.41
	Cl 2p	6.32
POM	0 1s	
After		30.36
	C 1s	57.31
	Sn3d5	5.19
	Na 1s	5.34
	Co2p3	1.54
	W4f7	0.27

<sup>&</sup>lt;sup>1</sup> N. S. Murray, J. A. Rudd, A.-C. Chamayou, E. C. Constable, C. E. Housecroft, M. Neuburger and J. A. Zampese, *RSC Adv.*, 2014, 4, 11766

<sup>&</sup>lt;sup>2</sup> H. Fukuoka, H. Imoto, and T. Saito, *Journal of Solid State Chemistry*, 1995, **119**, 107-114.