# Supporting Information

# Surface Immobilisation of a Tetra-Ruthenium Substituted Polyoxometalate Water Oxidation Catalyst Through the Employment of Conducting Polypyrrole and the Layer by Layer (LBL) Technique.

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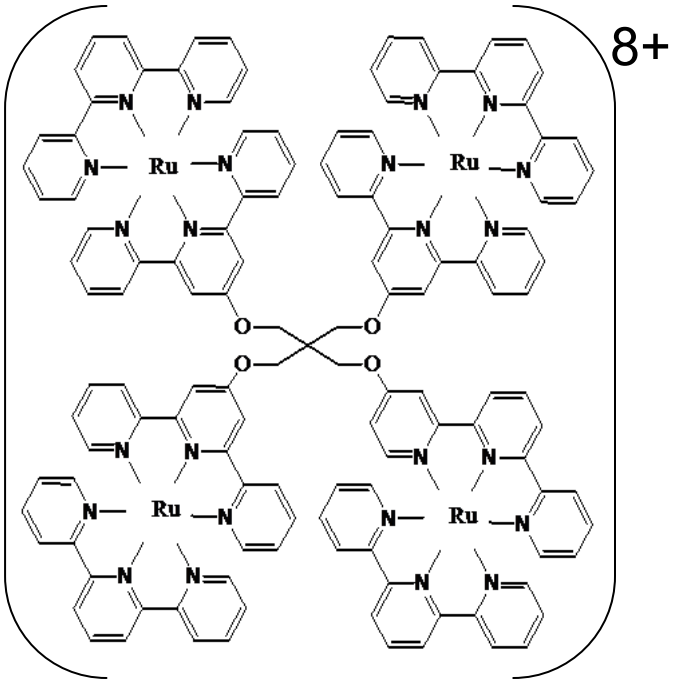



**Figure S1**. Structure of pentaerythritol based Ru-metallodendrimer $[RuDend]^{8+}$

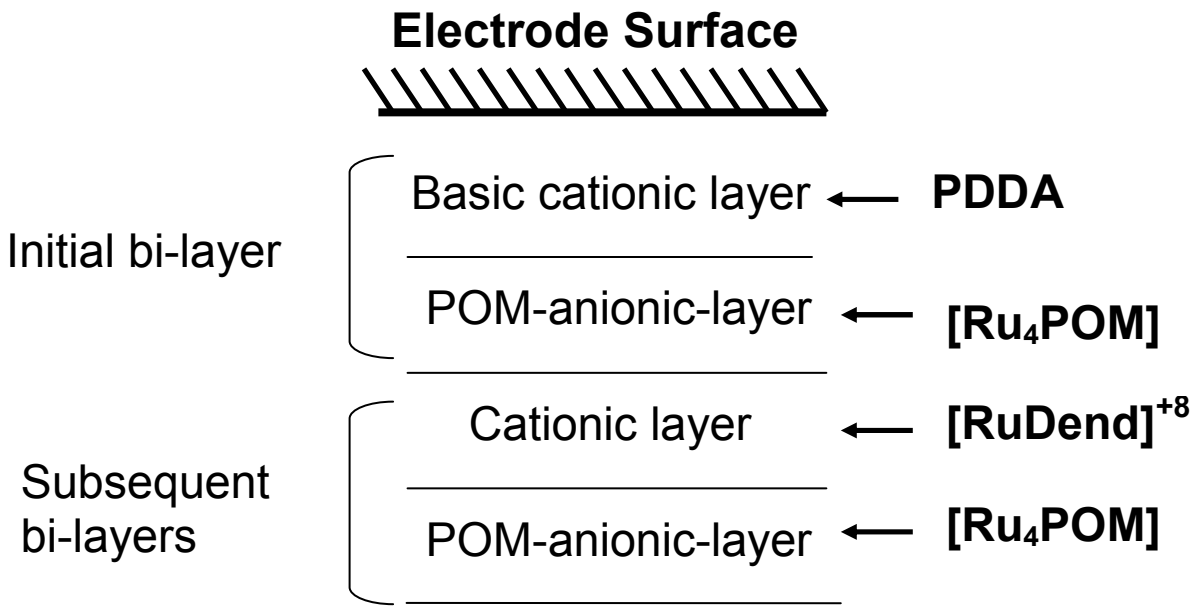



**Figure S2**. Schematic presentation of $Ru_4POM$-$[Ru\text{-}Dend]^{8+}$ based LBL film onto the glassy carbon elctrode surface

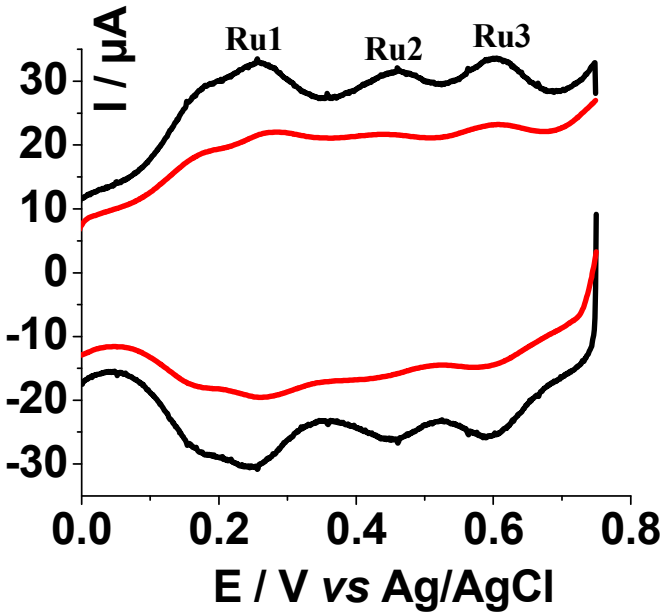



**Figure S3** (A) Cyclic voltammograms of $Ru_4POM$ entrapped into polypyrrole film of surface coverage (**red**)$1.68\times10^{-10}$ mol $cm^{-2}$ grown from acetonitrile and (**black**) $4.36\times10^{-10}$ mol $cm^{-2}$ grown from water in 0.1MHCl at scan rate 50mV/s.

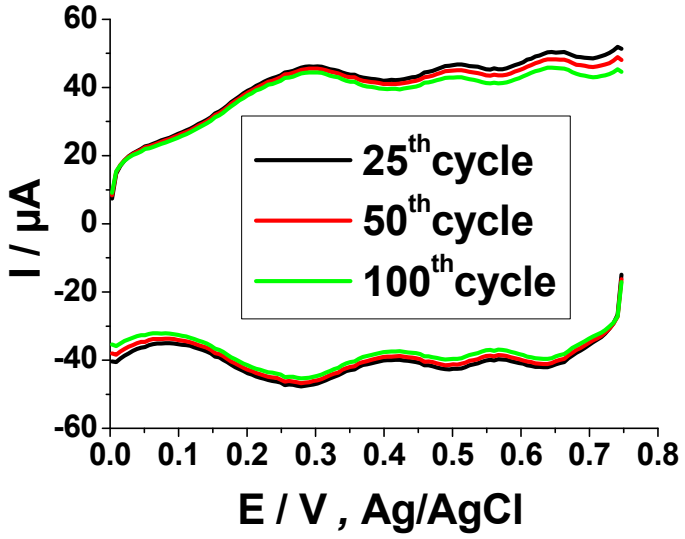



**Figure S4** Cyclic voltammograms of $Ru_4POM$ entrapped into polypyrrole film of surface coverage $6.64\times10^{-10}$ mol $cm^{-2}$ grown from acetonitrile in 0.1MHCl at scan rate 100mV/s.

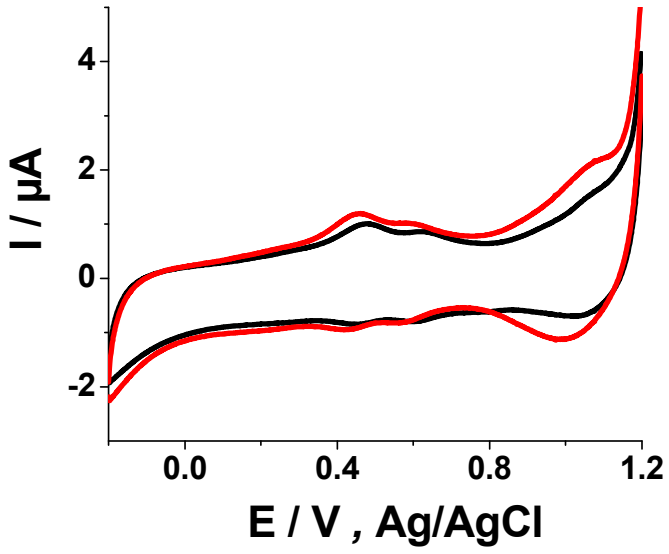



**Figure S5**. (A) Cyclic Voltammograms of 6 bilayers of $Ru_4POM$-$[RuDend]^{8+}$ multilayer assembly (**red**) recorded immediately after formation, (**black**) recorded after 18 hours of formation and stored in 0.1M HCl.

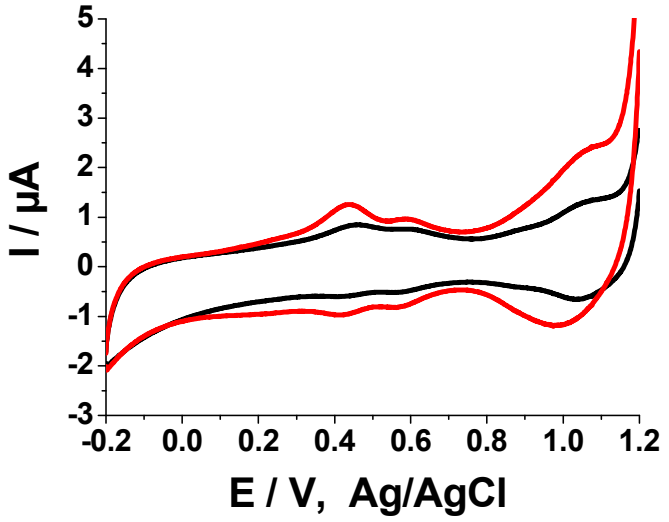



**Figure S6**. (A) Cyclic Voltammograms of 6 bilayers of $Ru_4POM$-$[RuDend]^{8+}$ multilayer assembly (**red**) recorded immediately after formation, (**black**) recorded after catalysis in 0.1M HCl, while catalysis was performed in PBS pH7.

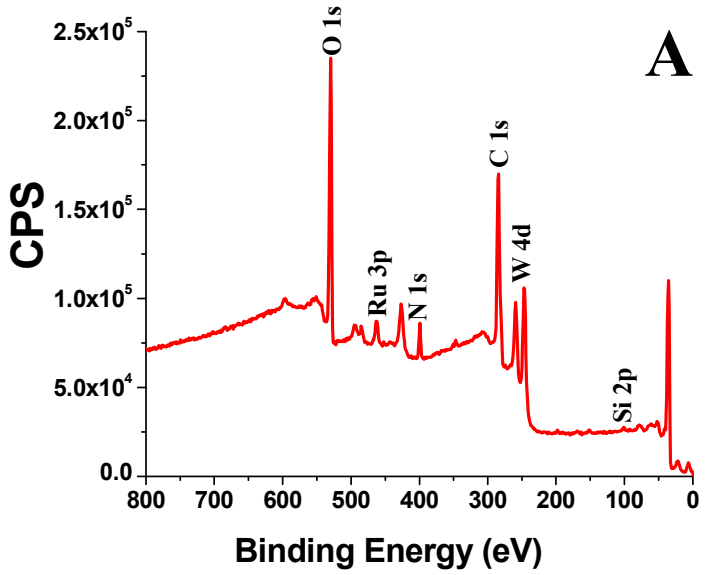
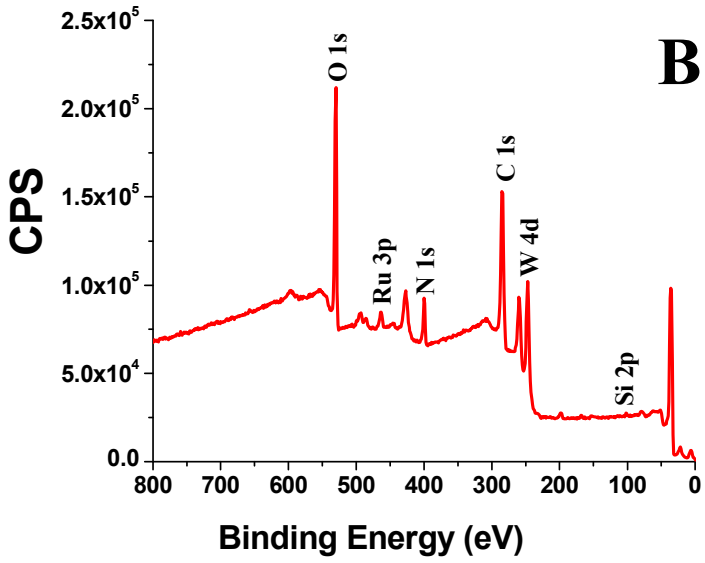



**Figure S7**. (A) XPS spectrum of 11 bilayers of $Ru_4$POM-RuDend multilayer assembly showing full spectrum. (B) XPS spectrum of $Ru_4$POM doped polypyrrole film with deposition charge of 30mC grown from acetonitrile.



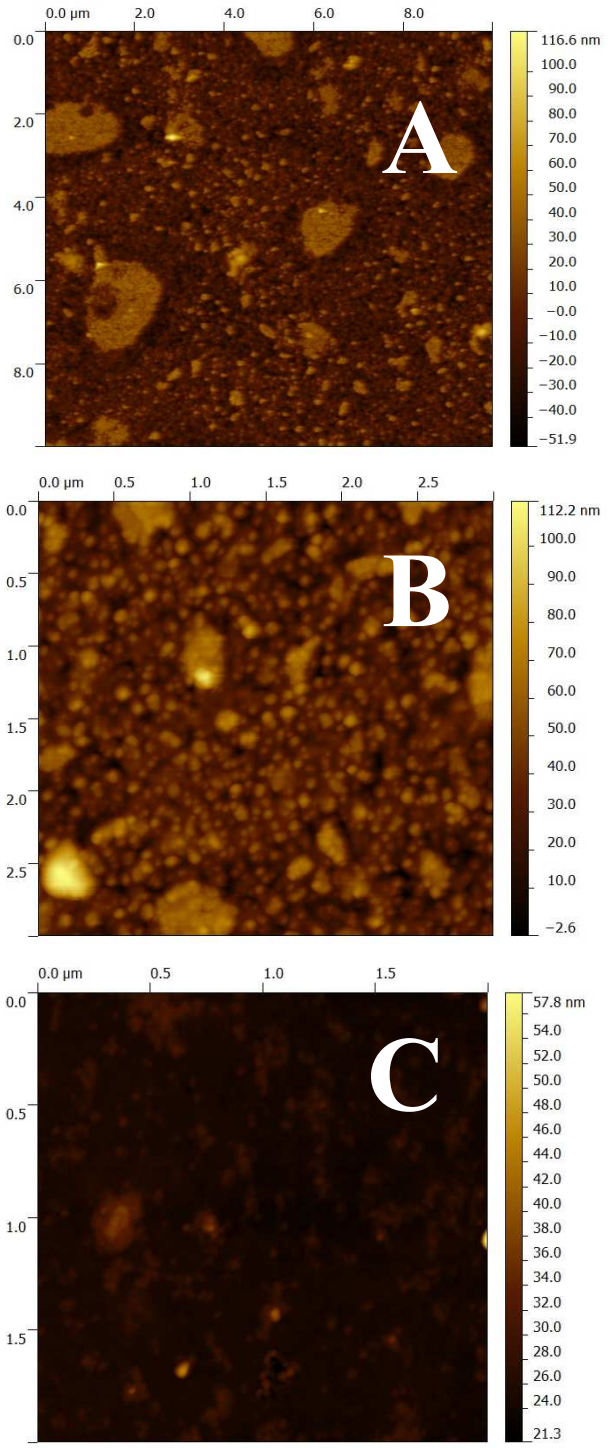



**Figure S8** (A) AFM image of Blank ITO coated glass slide. (B) AFM image of PDDA modified ITO coated glass slide. (C) AFM image of 1st monolayer of $Ru_4POM$ onto PDDA modified ITO coated glass slide.

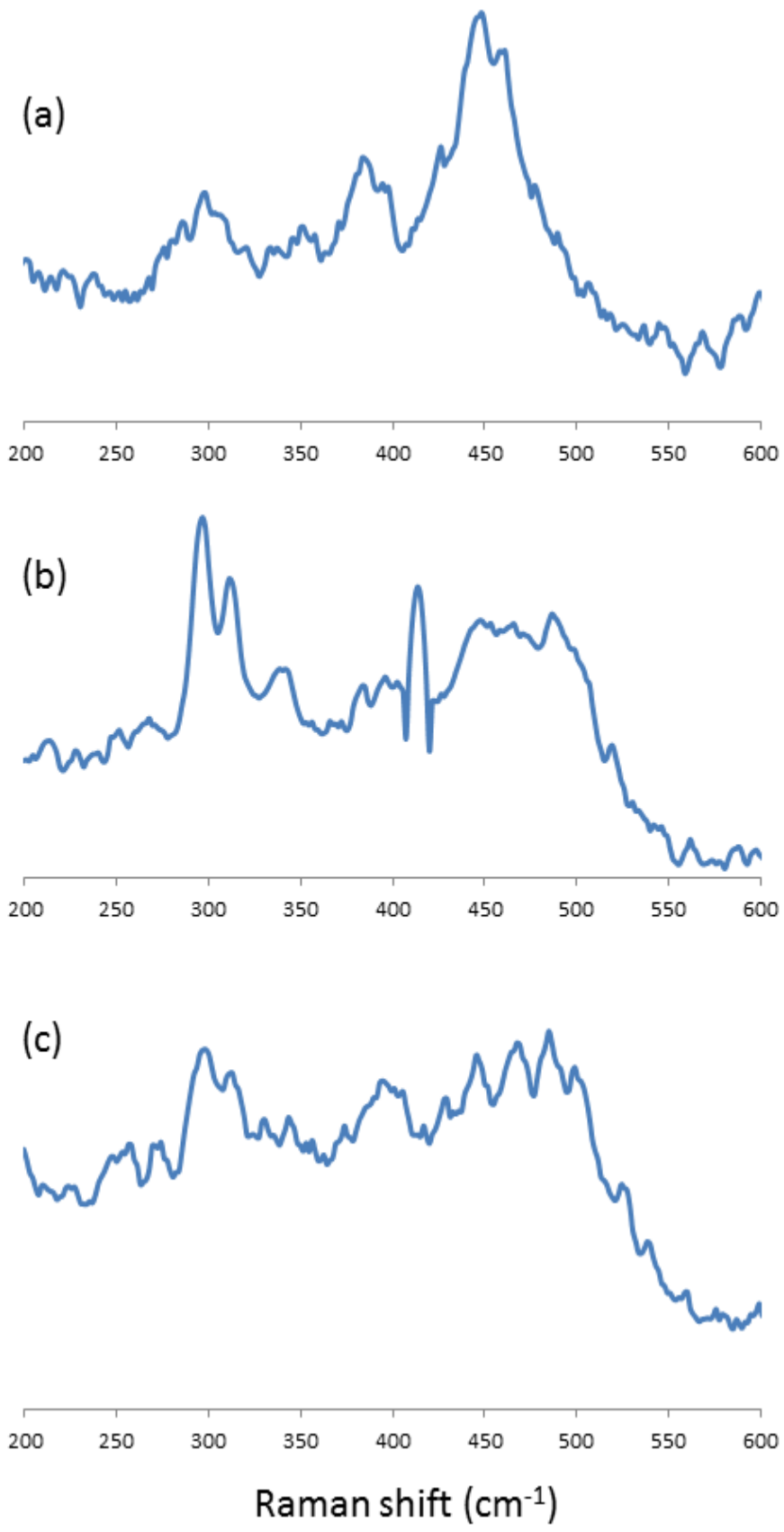



**Figure S9** Resonant raman (exciting line 532 nm) of: (a) $Ru_4POM$ doped polypyrrole film onto ITO electrode; (b) layer-by-layer assembly onto poly(diallyldimethylammonium chloride) (PDDA) modified ITO electrode by alternate depositions of $Ru_4POM$ and of the RuII metallodendrimer 6 monolayers; (c) electrode (b) after cyclic voltammetry towards anodic scan (upto 1.5 V vs Ag/AgCl).

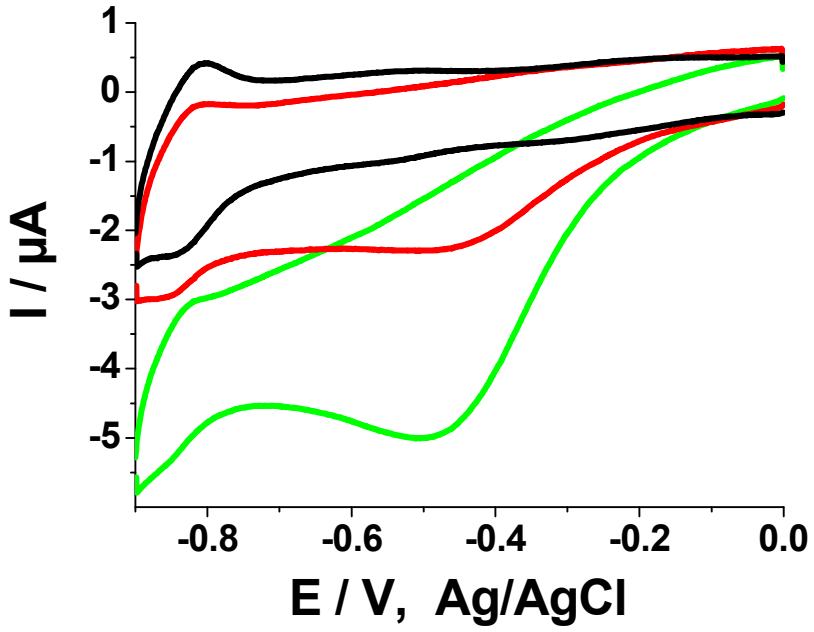



**Figure S10** Cycle voltammogram of 6 bilayers $Ru_4POM$-$[RuDend]^{8+}$ of LBL assembly run in PBS pH7 buffer in the cathodic region before(black) and after(red) catalysis, at scan rate 25mV/s. And after bubbling $O_2$(green) in same solution.