

Stabilized Photoanodes for Water Oxidation by Integrating Organic Dyes, Water Oxidation Catalysts, and Electron Transfer Mediators

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Supplementary Information

Experimental section:

Uv-Vis spectroscopy

Samples for optical measurements were fabricated in the same way as the devices described as above.

Incident photon to current efficiency (IPCE) measurements

IPCE measurements were performed with a 75 W xenon lamp (Oriel) and Oriel

Cornerstone 260

monochromator. Photocurrent data was taken at 10 nm increments and the light intensity at each wavelength was recorded using a UDT S370 optometer coupled to a UDT 260 detector. A CH Instruments 660D potentiostat was used to record the photocurrent transients and a bias of 0.4V vs. Ag/AgCl was used to collect the IPCE data.

Generator/collector O₂ detection

The generator/collector experiments for O₂ detection used a four electrode setup along with a bipotentiostat. Two FTO working electrodes in conjunction with a Pt counter and Ag/AgCl reference electrode were used. One FTO (generator) electrode was prepared as described for the core/shell photoanodes used in this study; the other FTO (collector) electrode was unmodified. Assembly of the generator/collector setup involved placing the two FTO electrodes with the conductive sides facing with narrow 1 mm thick glass spacers between the lateral edges and sealing the sides with epoxy (Hysol).

To measure the faradaic efficiency for O₂ production, the charge passed at the generator electrode during the illumination phase of the experiment was compared to the total charge passed at the collector electrode (poised at -0.85 V vs. Ag/AgCl) during the entire experiment. The faradaic efficiency was corrected for the collection efficiency of the generator/collector setup (70%) that was determined experimentally.

Transient Absorption.

When TA was carried out, the slides were inserted at a 45° angle into a standard 1 cm² Pyrex cuvette. The top of the cuvette was fit with an O-ring seal with a Kontes valve inlet to allow the contents to be purged with Argon (Airgas, UHP). Measurements were performed by using 425nm nanosecond laser pulses produced by a Nd:YAG laser combined with a VersaScan OPO (5–7 ns, operated at 1 Hz, beam diameter 0.5 cm) integrated into a commercially available Edinburgh LP920 laser flash photolysis spectrometer system. A white light probe pulse was generated by a pulsed 450 W Xe lamp. The probe light was passed through a 400 nm long pass filter before reaching the sample to avoid direct band gap excitation of TiO₂, then detected by a photomultiplier tube (Hamamatsu R928).

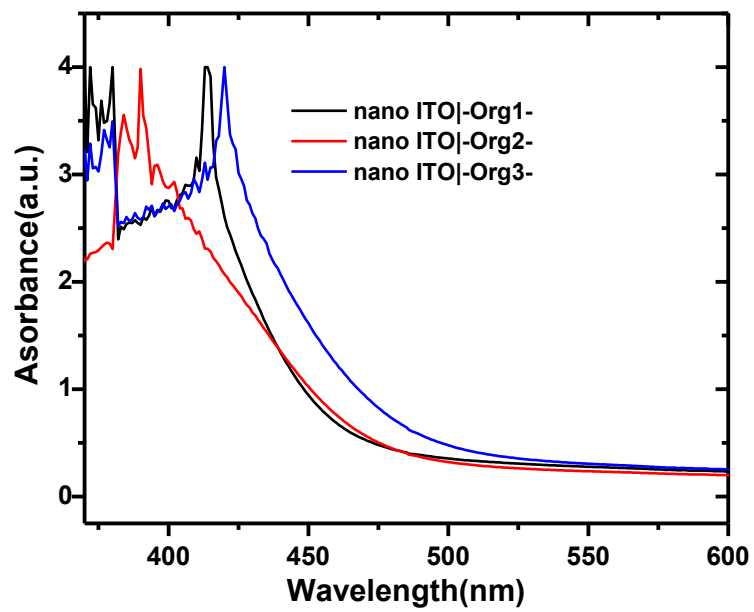


Fig. S1. The UV-Visible spectroscopy of the Organic dye on *nano* ITO.

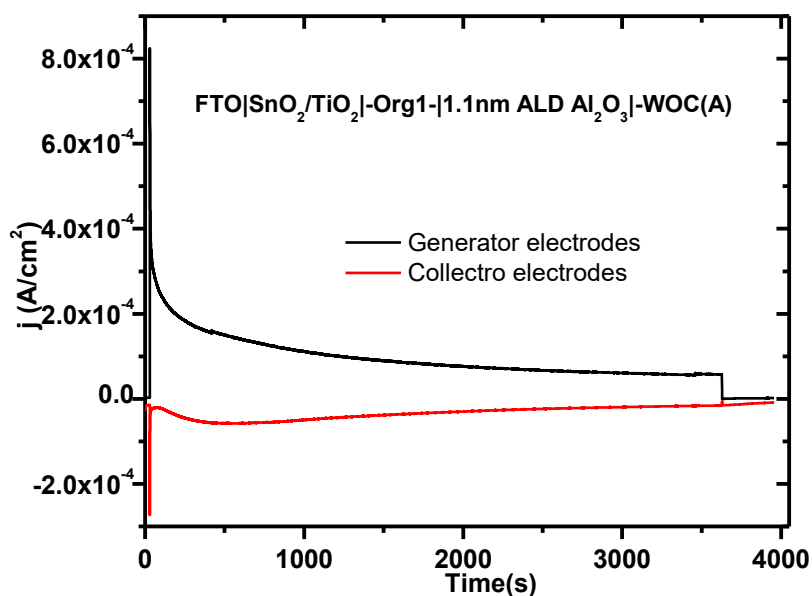


Fig. S2. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org1-|1.1nm Al₂O₃|-RuP²⁺-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 49%.

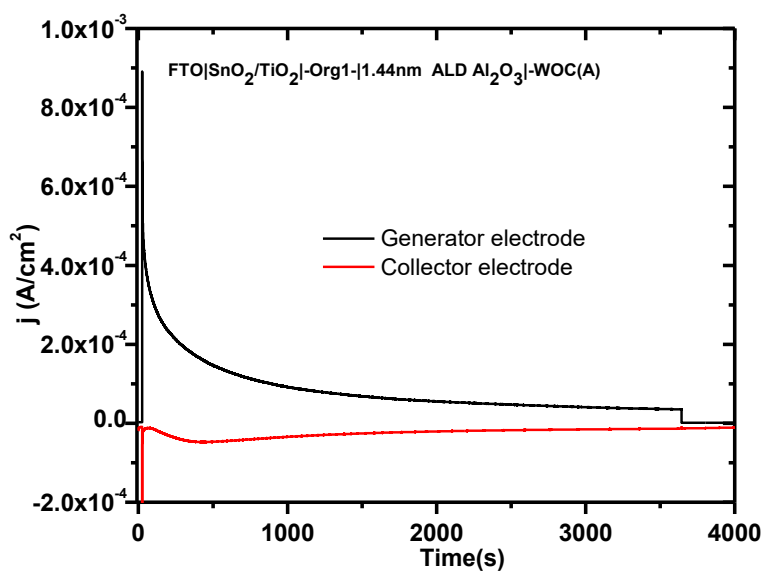


Fig. S3. O₂ measurements for water oxidation from (black), FTO|SnO₂/TiO₂|-Org1-|1.44nm Al₂O₃|- WOC, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 43%.

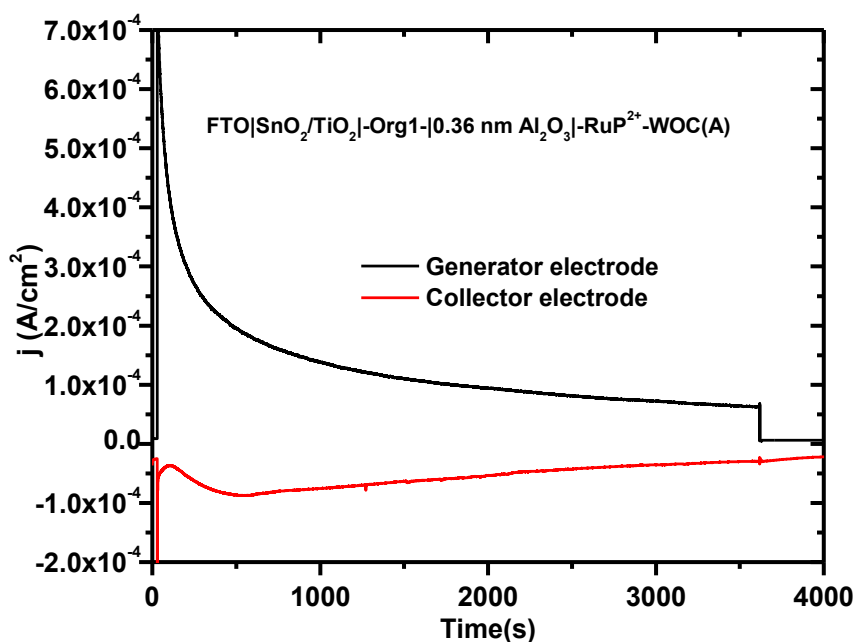


Fig. S4. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org1-[0.36nm Al₂O₃]-RuP²⁺-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.2 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 55%.

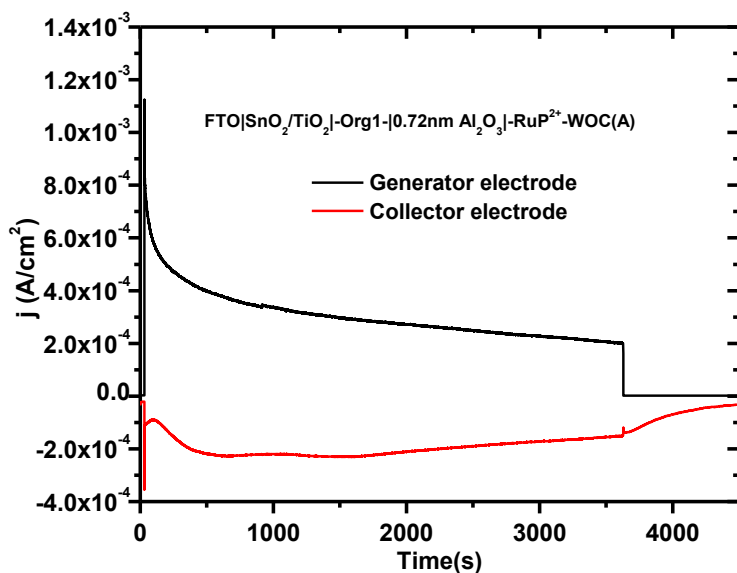


Fig. S5. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org1-|0.72nm ALD Al₂O₃|-RuP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 93%.

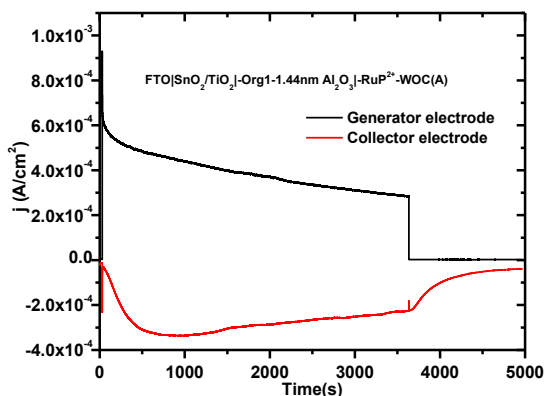


Fig. S6. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|Org1-1.44nm Al₂O₃|RuP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 97%.

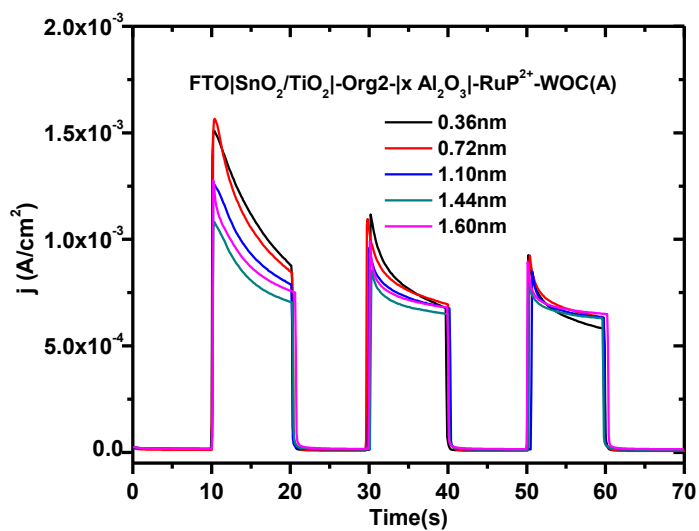


Fig. S7. Current–time (I-t) traces over 10 s dark–light cycles for water oxidation by the electrodes, **FTO|SnO₂/TiO₂|-Org2-|x Al₂O₃|-RuP²⁺-WOC(A)**, at an applied bias of 0.4 V versus Ag/AgCl; pH = 4.65, 0.1 M acetate, 0.4 M NaClO₄. **WOC(A)** is the catalyst, [Ru(bda)(4-O(CH₂)₃P(O₃H₂)₂-pyr)₂].

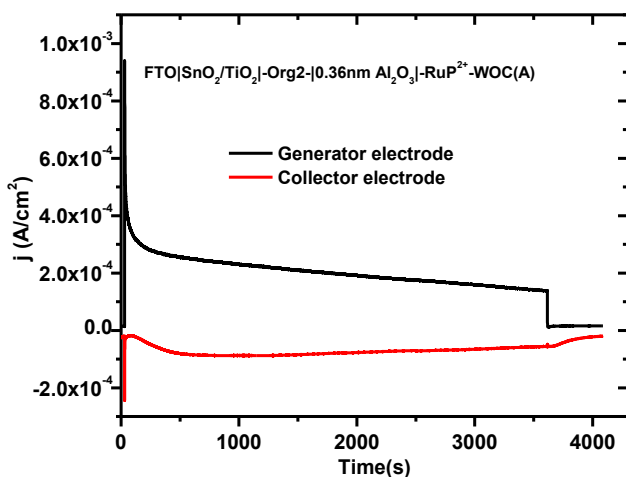


Fig. S8. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org2-|0.36nm Al₂O₃|-RuP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 55%.

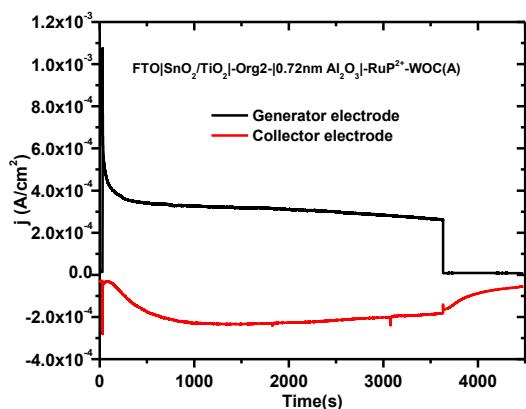


Fig. S9. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org2-**
|0.72nm Al₂O₃|-RuP²⁺-WOC, on 1 cm² slides illuminated with 100 mW cm⁻² white light
 with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The
 current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode
 biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4
 M NaClO₄. FE of O₂ production is around 96%.

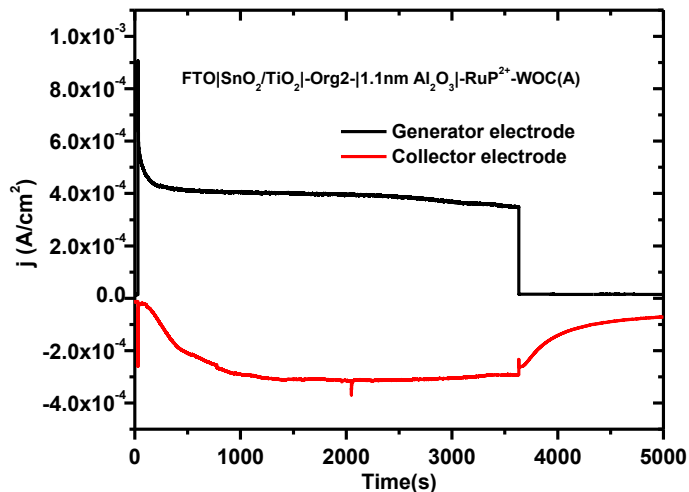


Fig. S10. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org2-|1.1nm Al₂O₃|-RuP²⁺-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 100%.

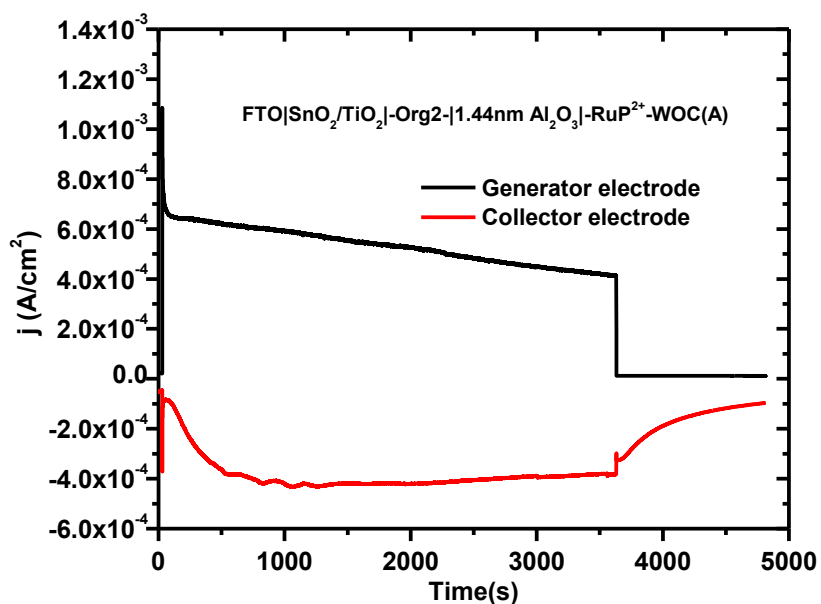


Fig. S11. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org2-|1.44nm Al₂O₃|-RuP²⁺-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 100%.

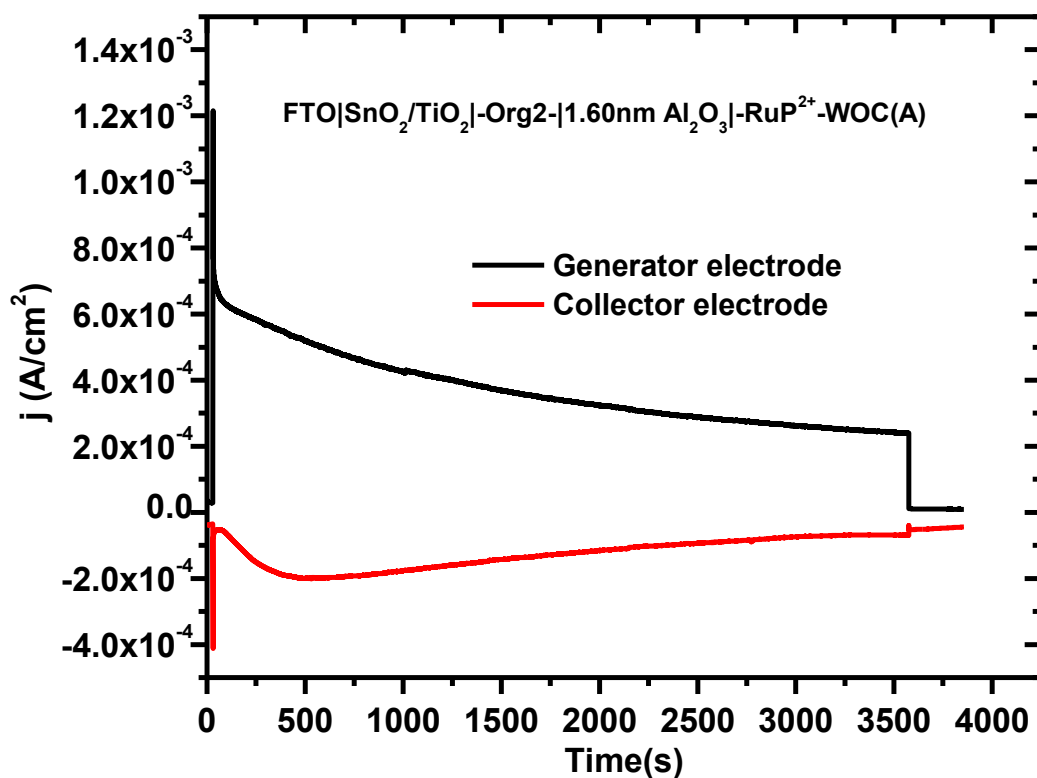


Fig. S12. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org2-|15cycles ALD Al₂O₃|-RuP²⁺-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 49%.

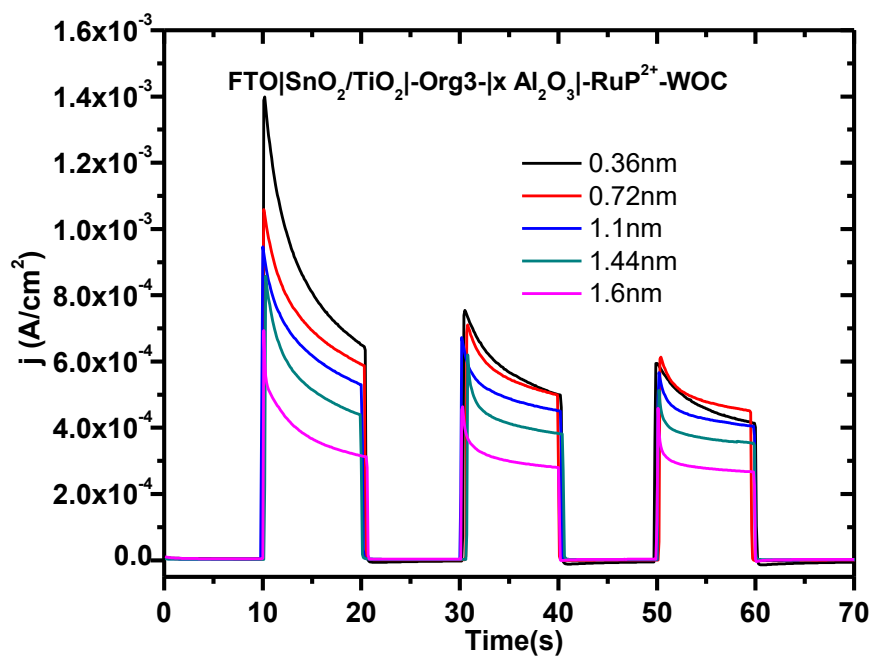


Fig. S13. Current–time (I-t) traces over 10 s dark–light cycles for water oxidation by the electrodes, **FTO|SnO₂/TiO₂|-Org3-|x Al₂O₃|-RuP²⁺-WOC(A)**, at an applied bias of 0.4 V versus Ag/AgCl; pH = 4.65, 0.1 M acetate, 0.4 M NaClO₄. **WOC(A)** is the catalyst, [Ru(bda)(4-O(CH₂)₃P(O₃H₂)₂-pyr)₂].

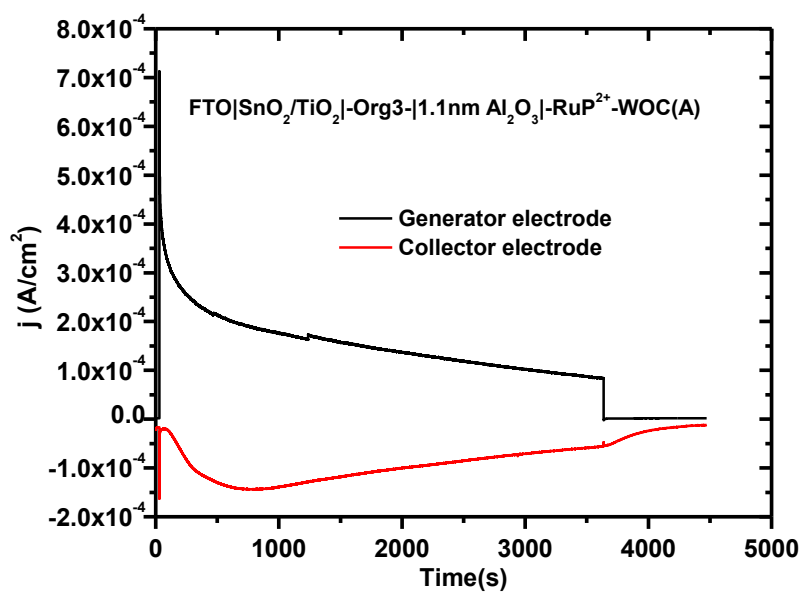


Fig. S14. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org3-|1.1nm Al₂O₃|-RuP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 100%.

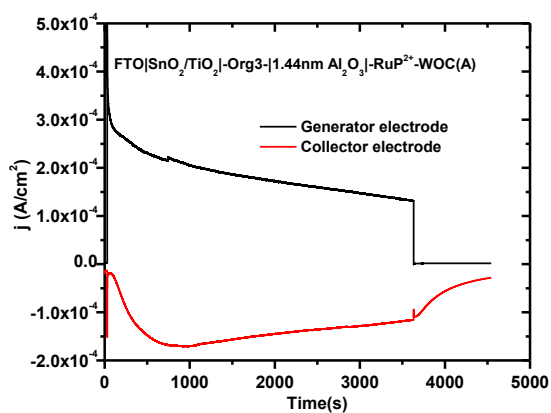


Fig. S15. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|Org3-[1.44nm Al₂O₃]-RuP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 100%.

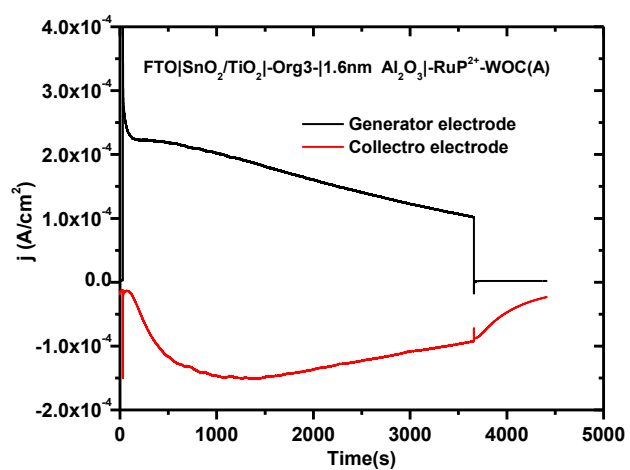
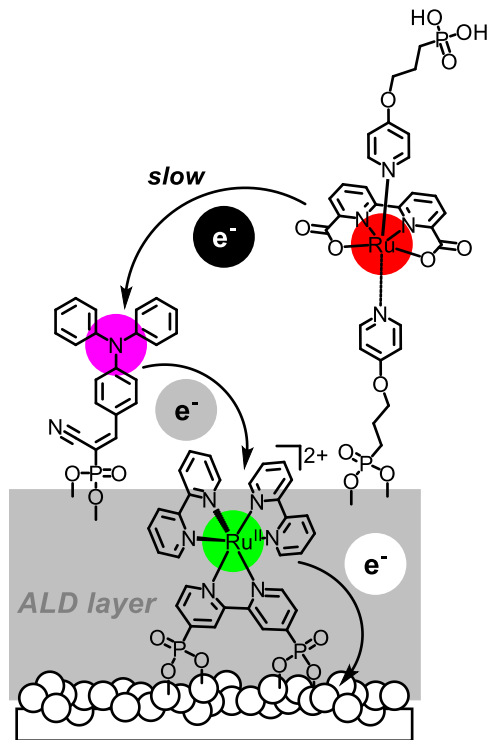


Fig. S16. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|Org3-[9cycles ALD Al₂O₃]-RuP²⁺-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 95%.



Scheme S1: One series of experiments, electrodes were prepared with the position of the dyes reversed. In this assembly, with **RuP²⁺** as the light absorber, followed by ALD deposition of an Al₂O₃ overlayer of **Org1** by adsorption, gave the electrode, - **FTO|SnO₂/TiO₂|-RuP²⁺|1.1nmAl₂O₃|-Org1-WOC(A).**

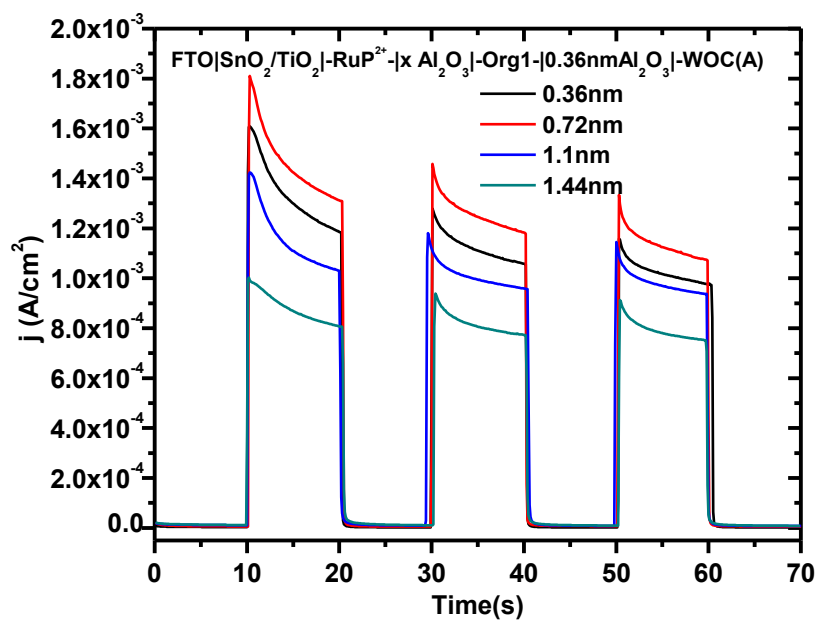


Fig. S17. Current–time (I-t) traces over 10 s dark–light cycles for water oxidation by the electrodes, FTO|SnO₂/TiO₂|-RuP²⁺-|Al₂O₃|-Org1-|0.36nm Al₂O₃|-WOC(A), at an applied bias of 0.4 V versus Ag/AgCl; pH = 4.65, 0.1 M acetate, 0.4 M NaClO₄

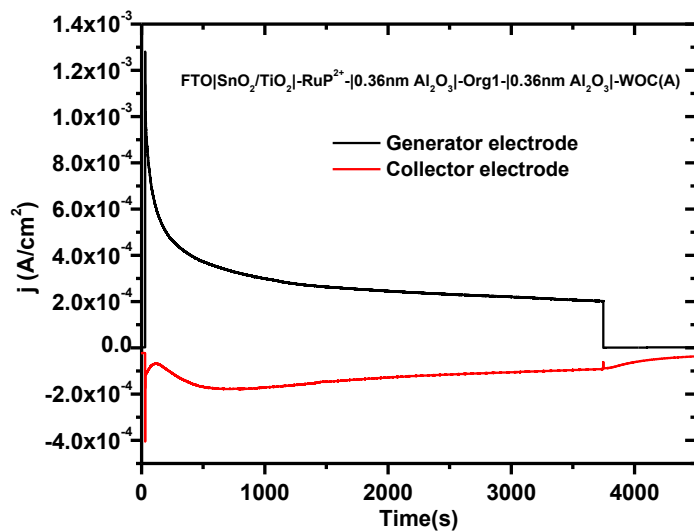


Fig. S18. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-RuP²⁺-|0.36nm Al₂O₃|-Org1-|0.36nm Al₂O₃|-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 67%.

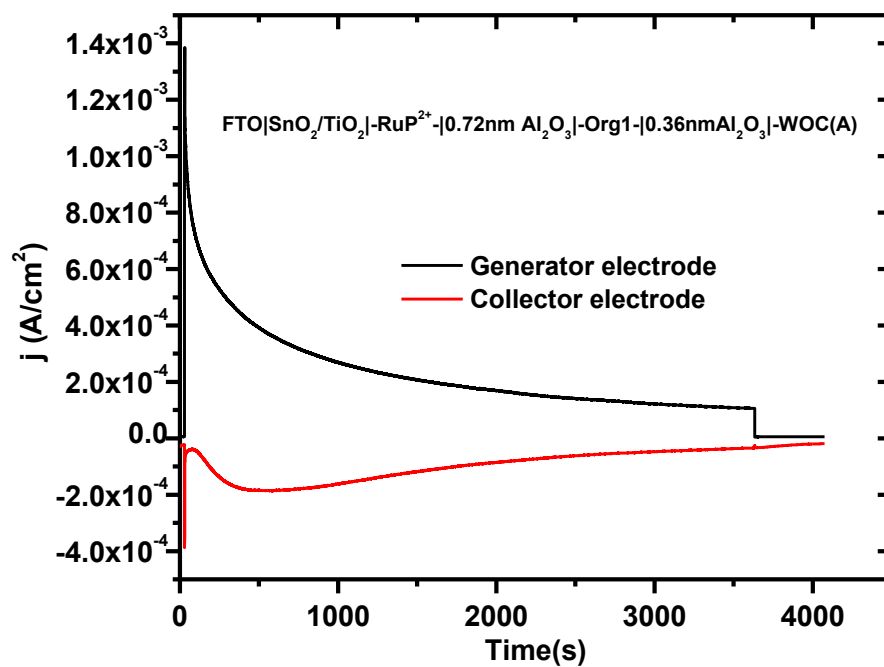


Fig. S19. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-RuP²⁺-|0.72nm Al₂O₃|-Org1-|0.36nm Al₂O₃|-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 61%.

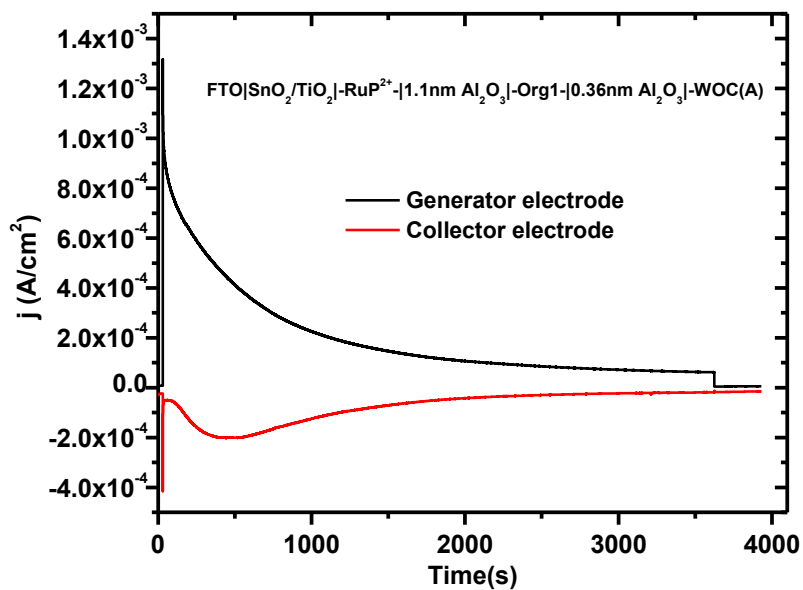
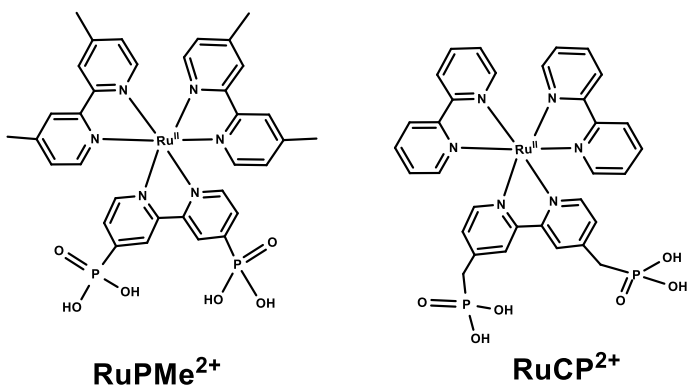


Fig. S20. O_2 measurements for water oxidation from (black), $\text{FTO}|\text{SnO}_2/\text{TiO}_2|-\text{RuP}^{2+}-$
 $|\text{1.1nm Al}_2\text{O}_3|-\text{Org1}-|\text{0.36nm Al}_2\text{O}_3|-\text{WOC(A)}$, on 1 cm^2 slides illuminated with 100 mW cm^{-2} white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O_2 sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO_4 . FE of O_2 production is around 58%.



Scheme S2. The structures of the other electron transfer mediators RuPMe²⁺ and RuCP²⁺

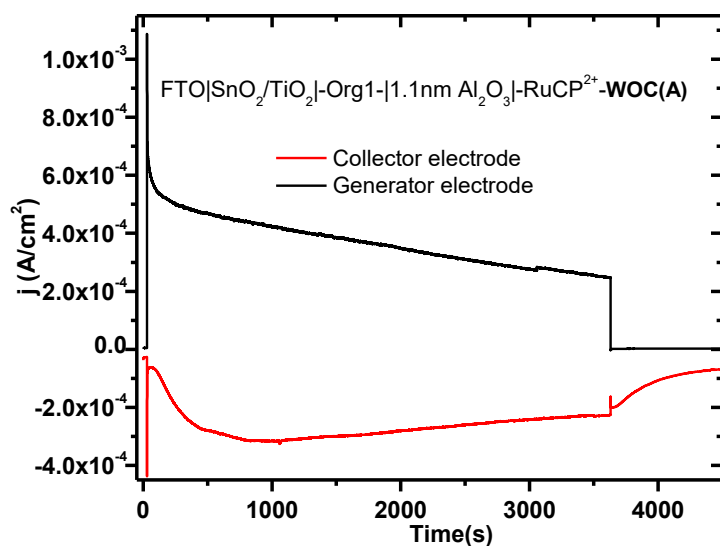


Fig. S21. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org1-|1.1nm Al₂O₃|-RuCP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 95%.

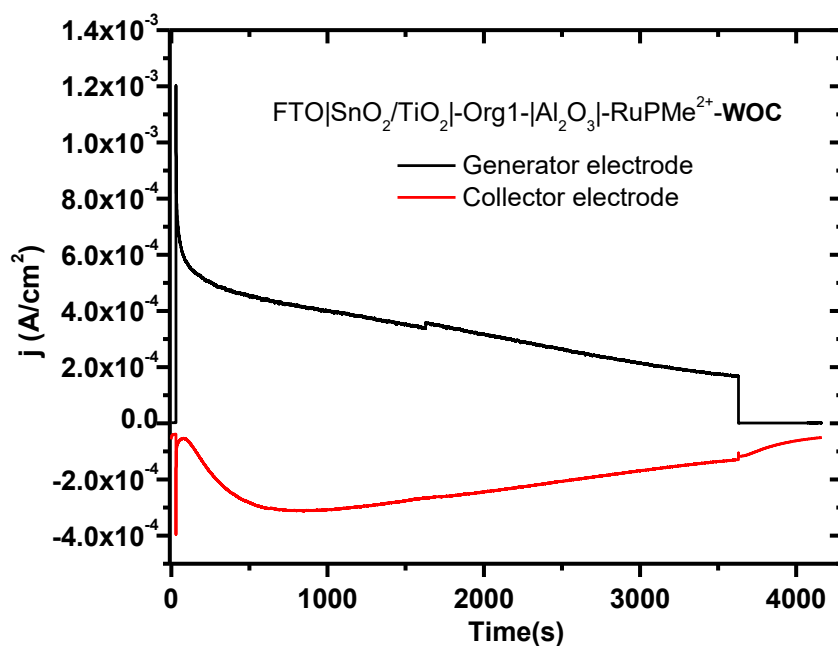


Fig. S22. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Org1-|1.1nm Al₂O₃|-RuCP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 78%.

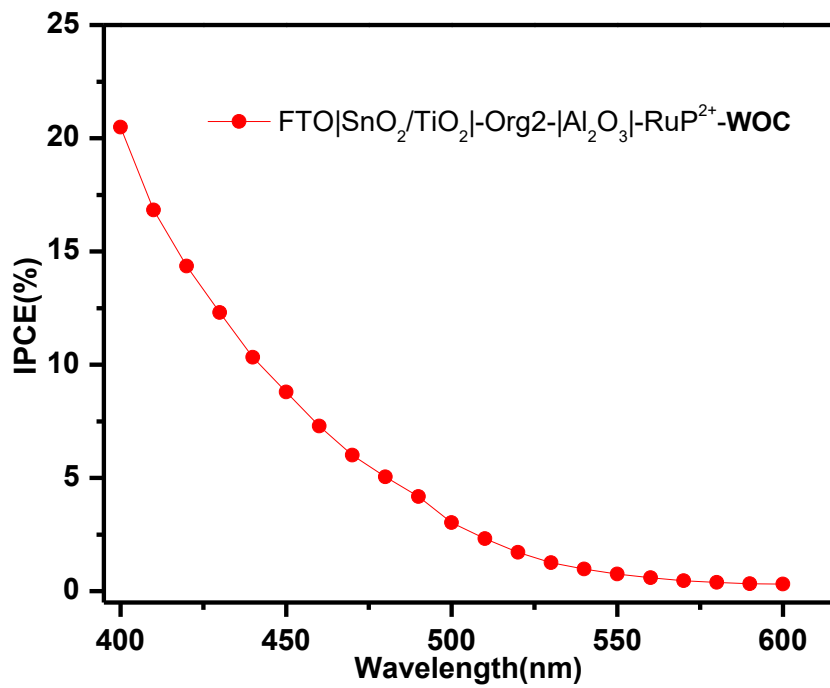


Fig. S23. IPCE results for, **SnO₂/TiO₂|-Org2-|1.1nm Al₂O₃|-RuP²⁺-WOC**, at an applied bias of 0.4 V versus Ag/AgCl at pH = 4.65 0.1 M in acetate, 0.4 M NaClO₄.

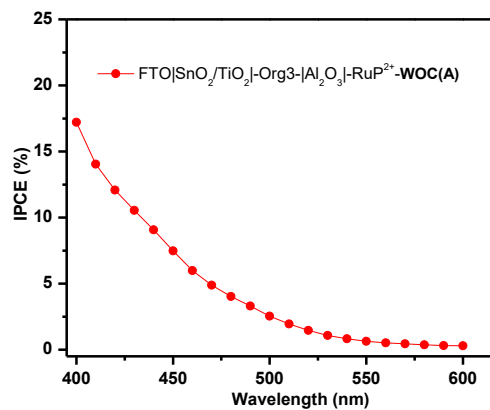


Fig. S24. IPCE results for, **FTO|SnO₂/TiO₂|Org3-|1.1nm Al₂O₃|-RuP²⁺-WOC(A)**, at an applied bias of 0.4 V versus Ag/AgCl at pH = 4.65 0.1 M in acetate, 0.4 M NaClO₄.

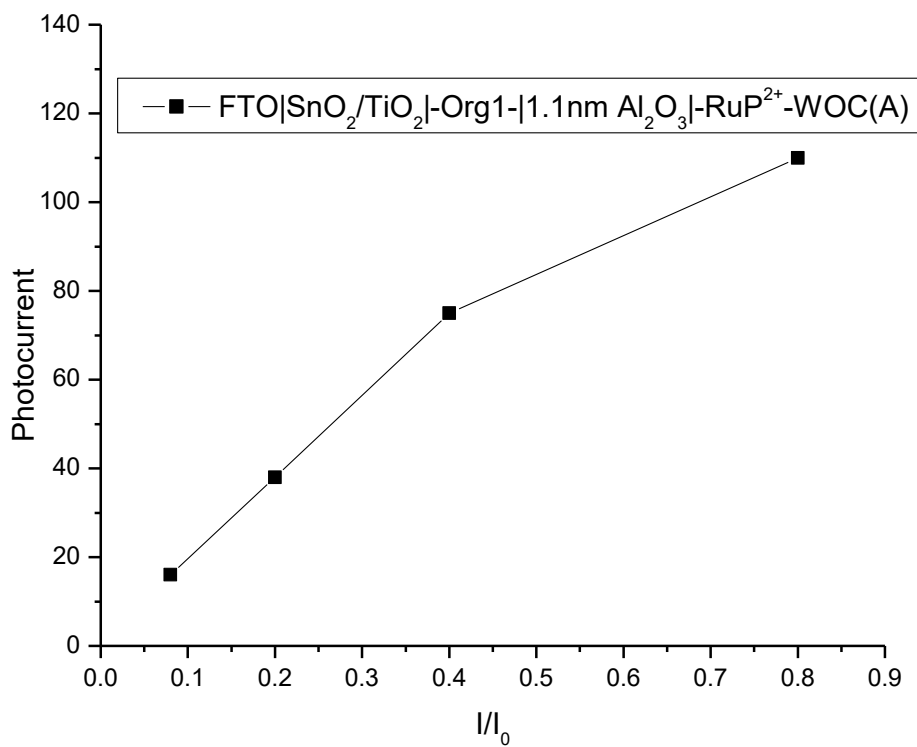


Fig. S25. The photo-responds of the electrode, FTO|SnO₂/TiO₂|Org1-|1.1nmAl₂O₃|-RuP²⁺-WOC under different light intensity. The measurement was performed, at an applied bias of 0.4 V versus Ag/AgCl at pH = 4.65 0.1 M in acetate, 0.4 M NaClO₄. I₀ is the one sun illumination. And the I is the applied light intensity using filter to modulate the photons pass.

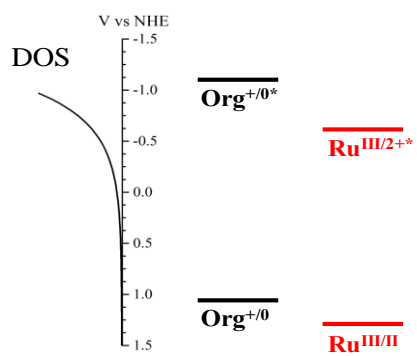


Fig. S26. The energy diagram of the organic dye **Org1** and **RuP²⁺** molecular.

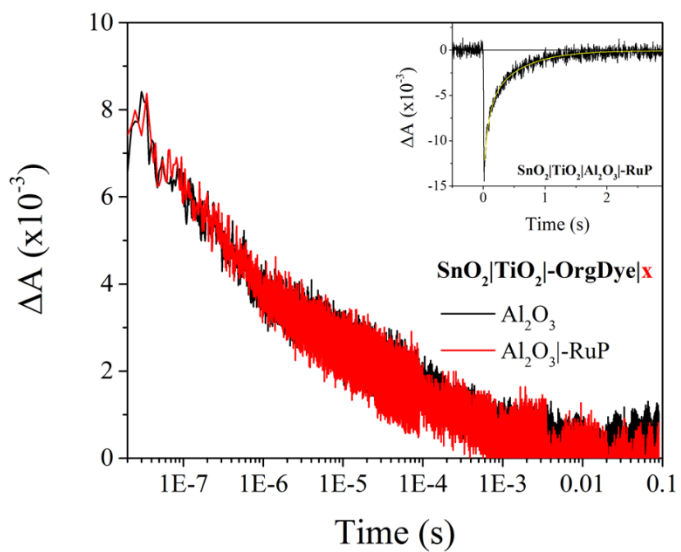


Fig. S27. The Transient absorption spectrum of the electrode: FTO|SnO₂/TiO₂|-Organic dye-|1.1nm Al₂O₃|-X

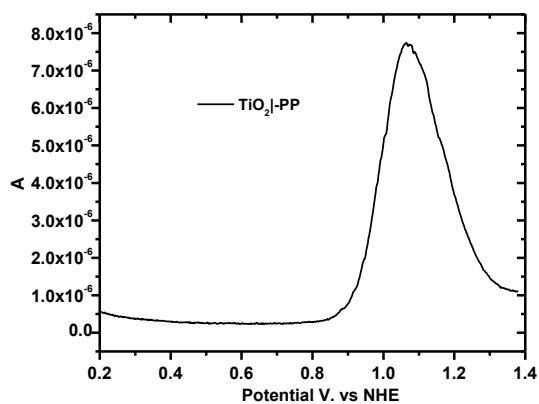


Fig. S28. Differential pulse voltammograms of FTO|TiO₂|PP. The TiO₂/FTO electrodes with a TiO₂ thickness of 4 μ m were prepared by doctor blade technique. The electrochemical measurements were carried out in pH4.65, 0.1M acetate buffer with 0.4M NaClO₄ .

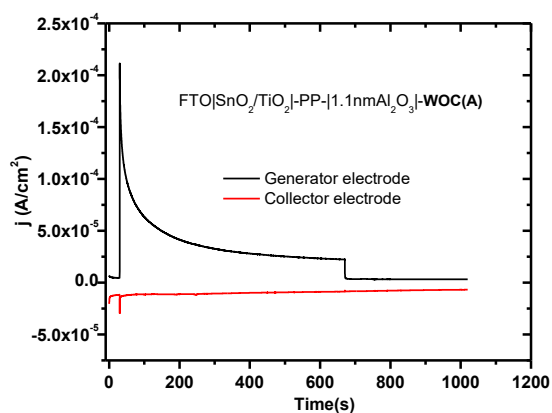


Fig. S29. O₂ measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|-Porphrin-9cycles ALD Al₂O₃|-WOC**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 0%.

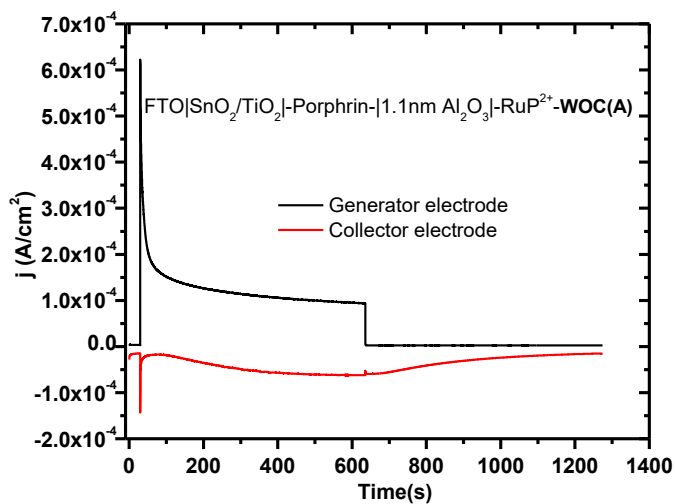


Fig. S30. O_2 measurements for water oxidation from (black), **FTO|SnO₂/TiO₂|Porphrin-[1.1nm Al₂O₃]-RuP²⁺-WOC(A)**, on 1 cm² slides illuminated with 100 mW cm⁻² white light with a 400 nm cutoff filter from 30 to 3630 s at a bias of 0.4 V versus Ag/AgCl. The current-time response in red is for an O₂ sensing electrode, 1 mm from the photoanode biased at -0.85 V versus Ag/AgCl; in 0.1 M acetic acid/acetate buffer at pH 4.65 in 0.4 M NaClO₄. FE of O₂ production is around 78%.

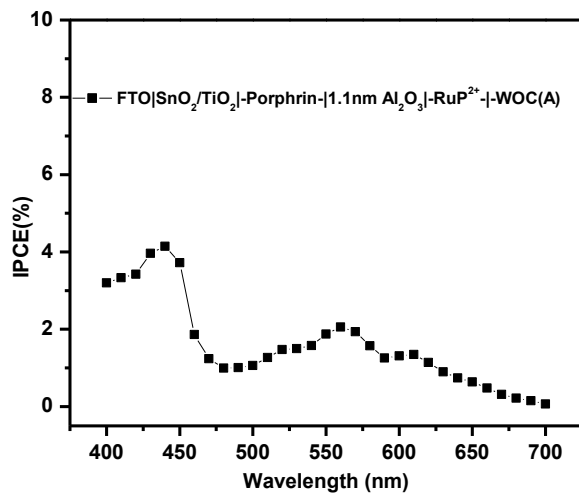


Fig. S31. IPCE results for, **FTO|SnO₂/TiO₂|PP-[1.1nmAl₂O₃]-WOC(A)** at an applied bias of 0.4 V versus Ag/AgCl at pH = 4.65 0.1 M in acetate, 0.4 M NaClO₄. A 400 nm cutoff filter was used.