## **Supporting Information**

# Light-Driven Water Oxidation using Polyelectrolyte Layer-by-Layer Chromophore-Catalyst Assemblies

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#### **Experimental Methods**

**Materials and General.** All chemicals were purchased from the indicated suppliers and used without purification: polydiallyldimethylammonium chloride (PDADMAC,  $M_w = 200,000$ -350,000), polyacrylic acid (PAA,  $M_v \sim 450,000$ ), and perchloric acid were purchased from Sigma-Aldrich Chemical Co. Deionized water was purified by using a Millipore purification system. PS-Ru (degree of polymerization ~ 80) and [Ru(tpy)(2-pyridyl-N-methylbenzimidazole)(OH<sub>2</sub>)]<sup>2+</sup> (RuC) were prepared as described in the literature.<sup>1,2</sup> UV-visible absorption spectra were recorded using a Shimadzu UV-1800 dual beam absorption spectrophotometer. Cyclic voltammetry experiments were performed using a CH Instruments 760E bipotentiostat. An SEM instrument (SU5000, scanning electron microscope) was used to observe the morphology of bare FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>), FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)//((PAA/PS-Ru)<sub>5</sub>, and FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)//((PAA/PS-Ru)<sub>5</sub>//(PAA/RuC)<sub>5</sub> films. This instrument was performed at an accelerating voltage of 10 kV and additional carbon conductive layers were coated on the samples.

**Preparation of the Photoelectrodes.** A SnO<sub>2</sub>/TiO<sub>2</sub> mesoporous film on a fluorine doped SnO<sub>2</sub> (FTO) electrode (FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)) was prepared according to the previous report.<sup>3</sup> To initiate multilayer deposition, the FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>) electrode was dipped into a solution of PDADMAC (pH ~6.6) for 15 min., followed by deposition of PAA (pH ~4.2) and PS-Ru (pH ~6.8) for 15 min. each. These polyelectrolyte solutions of 1 mM with respect to the polymer repeat unit were prepared by dissolution in Millipore water and adjusted pH with HCl. After dipping with a polyelectrolyte solution, the electrodes were rinsed three times with Millipore water. Multilayers were constructed by continuing to deposit alternate layers of PAA polyanion and PS-Ru polycation on the electrode, FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)//((PAA/PS-Ru)<sub>n</sub> (where n = the number of bilayers).

Subsequently, alternate deposition of PAA and the cationic water oxidation catalyst, RuC (1 mM, pH ~6.6) atop the FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)//(PAA/PS-Ru)<sub>n</sub> assembly leads to the "chromophore-catalyst" multilayer structure, FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)//(PAA/PS-Ru)<sub>n</sub>//(PAA/RuC)<sub>m</sub>.

To investigate the visible absorption and cyclic voltammetry of the multilayers onto Sn(IV)doped In<sub>2</sub>O<sub>3</sub> (ITO) (Sigma-Aldrich Chemical Co.) glass substrates, the ITO electrodes with loading polychromophores, catalyst, or polychromophore-catalyst assemblies were using the same procedure as above and denoted as ITO//(PAA/PS-Ru)<sub>5</sub>, ITO//(PAA/RuC)<sub>5</sub> and ITO//(PAA/PS-Ru)<sub>5</sub>/(PAA/RuC)<sub>5</sub>.

**Transient Absorption Measurements.** Transient absorption measurements were conducted using a pump-probe technique based on a Ti:Sapphire chirped pulse amplification (CPA) laser system (Clark-MXR CPA2210). The amplifier produces 150 fs pulses at 775 nm and 1 kHz repetition rate. The 420 nm pump pulse was generated in a 2 mm BBO crystal by sum frequency generation of the 775 nm fundamental and the second harmonic of the 1840 nm idler from an optical parametric amplifier (Light Conversion TOPAS-C). The femtosecond probe pulse is generated by focusing 3 mW of the 775 nm amplifier output into a translating CaF2 window. The pump beam is focused onto the sample using a 300 mm lens and the probe beam is focused and overlapped with a 250 mm spherical aluminum mirror. Time-resolved spectra are collected by varying the delay between pump and probe pulses using a computer controlled delay stage. Spectra are collected on a shot-by-shot (1 kHz) basis over the range of 350 to 800 nm resulting in a high signal to noise ratio and an instrument sensitivity of up to 0.1 mOD. The angle between the pump and probe polarization vectors was set to magic angle (~54.7°) to avoid polarization effects and ensure that only excited-state population dynamics were being monitored. The films samples were

raster scanned at a rate of 1mm/s to prevent photodegradation of the samples. Following data collection, the frequency chirp in the probe pulse was characterized using the optical Kerr response of liquid CCl4 in a 2 mm cuvette in a polarization gating geometry. The spectra were chirp corrected using a data processing program written in LabVIEW.

#### Collector-Generator O<sub>2</sub> Detection.

A detailed description of the collector-generator method can be found in reference 19 of the manuscript. Briefly, two working (FTO based) electrodes were held in place 1 mm apart with a glass spacer on both the lateral edges. The spacer was bonded to each piece of FTO with epoxy (Hysol) forming a seal on each side. The electrodes were independently controlled using a CH Instruments 760E bipotentiostat. With gaps at the top and bottom of the electrode assembly, the internal volume between the electrodes fills by capillary action when placed in solution. Dioxygen  $(O_2)$  formed at the photoanode under study diffuses between the two electrodes and is reduced at the collector when a sufficiently negative bias is maintained at this electrode during the measurement. Under the neutral pH conditions used in this study, an applied potential of -1.1 V vs. NHE was used to sense for  $O_2$ . Any observed cathodic current observed above a background measurement was attributed to  $O_2$ .



Figure S1. SEM images (plane view) of (a) as-prepared  $FTO//(SnO_2/TiO_2)$  film and (b)  $FTO//(SnO_2/TiO_2)//(PAA/PS-Ru)_5$  film, and (c)  $FTO//(SnO_2/TiO_2)//(PAA/PS-Ru)_5$  (PAA/RuC)<sub>5</sub> film.



Figure S2. (Top) Transient absorption spectra following 420 nm laser excitation for the PS-Ru complex on  $TiO_2$  ( $TiO_2$ //PAA/PS-Ru)\_4 at 0.65, 25, 50, 250, 650, and 1300 ps. (Bottom) ( $TiO_2$ //PAA/PS-Ru)\_4 kinetics trace at 450 nm.



**Figure S3.** (Top) Current–time trace (30–630 s) with the illumination (1 sun, 100 mW cm<sup>-2</sup>; 400 nm cut-off filter) on FTO//(SnO<sub>2</sub>/TiO<sub>2</sub>)//(PAA/PS-Ru)<sub>5</sub> in 0.1 M phosphate buffer at pH 7 with an applied bias of 0.44 V versus NHE. (Bottom) current–time traces at an FTO collector electrode, ~ 1mm from the photoanode at an applied bias of -1.1 V versus NHE measured concurrently with the photoelectrochemical–time trace.

### References

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