

Supplementary Information

A photoelectrochemical device for visible light driven water splitting by a molecular ruthenium catalyst assembled on dye-sensitized nanostructured TiO₂

Lin Li,^a Lele Duan,^a Yunhua Xu,^a Mikhail Gorlov,^a Anders Hagfeldt,^{a,b} and Licheng Sun^{*a,c}

^a Center of Molecular Devices, Department of Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology (KTH), 10044 Stockholm, Sweden. Fax: +46 8 791 2333; Tel: +46 8 790 8127; E-mail: lichengs@kth.se

^b Department of Physical and Analytical Chemistry, Uppsala University, Box 259, 75105 Uppsala, Sweden.

^c DUT-KTH Joint Education and Research Center of Molecular Devices, State Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), 116012 Dalian, China.

Experimental Section

Materials: RuP was prepared according to the literature.^[1]

[Ru(III)L(pic)₂]₂PF₆ (L=2,2'-bipyridine-6,6'-dicarboxylic acid. Pic=4-picoline) (Complex **1**⁺):

Complex **1** (30 mg, 0.056 mmol) was placed in a solution of acetonitrile (1 mL) with 2mL triflic acid aqueous solution (pH = 1.0). Ammonium cerium nitrate (309 mg, 0.564 mmol) was gradually added to the above solution with vigorous stirring. The colour of the solution changed from dark red to light yellow accompanied by evolution of a large amount of O₂ gas. After removing acetonitrile and adding excess NH₄PF₆ aqueous solution, the mixture was kept stationary to obtain a light yellow precipitate. Filtration and washing with water and diethyl ether gave a yellow solid of [Ru(III)L(pic)₂]₂PF₆. HRMS (ESI, *m/z*⁺): calcd for C₂₄H₂₀N₄O₄Ru, 530.0528; found, 530.0438. Anal. calcd for C₂₄H₂₀F₆N₄O₄PRu·0.6H₂O: C 42.06, H 3.12, N 8.18, found: C 42.1, H 2.95, N 7.71.

Device Fabrication: For devices employing complex **1**, a Nafion film combined with dye sensitized TiO₂ on conducting glass substrates (Pilkington TEC8, sheet resistance 8 Ω/square) was used as the photo-anode. 6 μm thick TiO₂ film electrodes (0.25 cm² active area) were dipped into a 0.2 M dye bath overnight for sensitization. After washing with ethanol and drying by air flow, the dye sensitized TiO₂ electrode was coated with a Nafion solution, using Scotch® tape as a mask (0.25 cm² active area), followed by heating on a hot plate at 120 °C for 3 min. Complex **1**⁺ was introduced into Nafion film by dropping acetonitrile solution of Complex **1**⁺ on the surface of prepared Nafion coated TiO₂ film, followed by drying with air flow, rinsing with acetonitrile, and drying again. The device was charged with 0.1 M Na₂SO₄ electrolyte or pH 7.0 phosphate buffer solution (50 mM) and flushed with nitrogen prior to use.

Experimental Techniques: The photocurrent measurements were carried out in a two electrode cell with an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie), using the above prepared photo-anode as the working electrode, a platinum foil as the counter electrode. 0.1 M Na₂SO₄ was used as the electrolyte. The photoanode was illuminated using a light emitting diode array (spectrum showed in Figure S5) to give a light intensity 1000 Wm⁻² (AM 1.5 irradiation) calibrated by a silicon solar cell.

The oxygen evolution was recorded by a Clark-type oxygen electrode. Normal procedure: a two electrode system, with prepared photo-anode working electrode and Pt-glass counter electrode, charged with pH 7.0 phosphate buffer solution (total 2 mL) as electrolyte. After degassing, the above photoanode was irradiated by a 500 W xenon light source through a 400 nm cut off filter. To detect hydrogen evolution, Micro-GC was used [Micro-GC CP 4900 Quad, Varian]

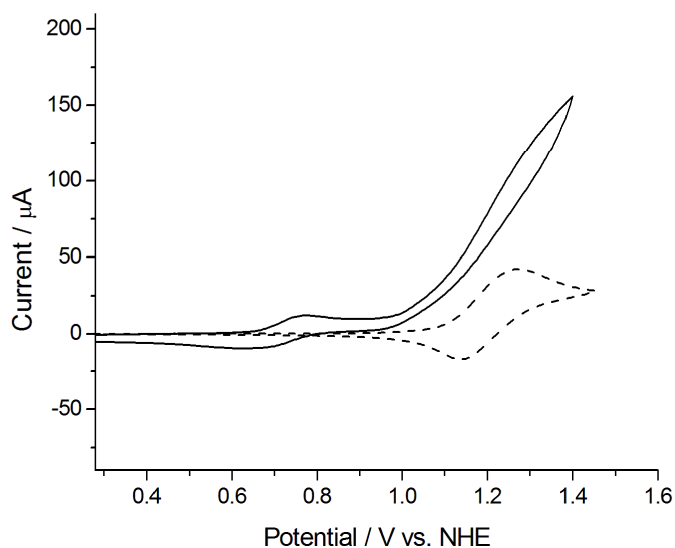


Figure S1. Cyclic voltammograms of **RuP** on TiO₂/FTO glass (dash line) in phosphate buffer (pH 7.0, 50 mM) solution and complex **1** with a glassy carbon disk as the working electrode (solid line) in phosphate buffer (pH 7.0, 50 mM) solution containing 10% acetonitrile, Ag/AgCl is used as the reference electrode and [Ru(bpy)₃]²⁺ as the internal reference.

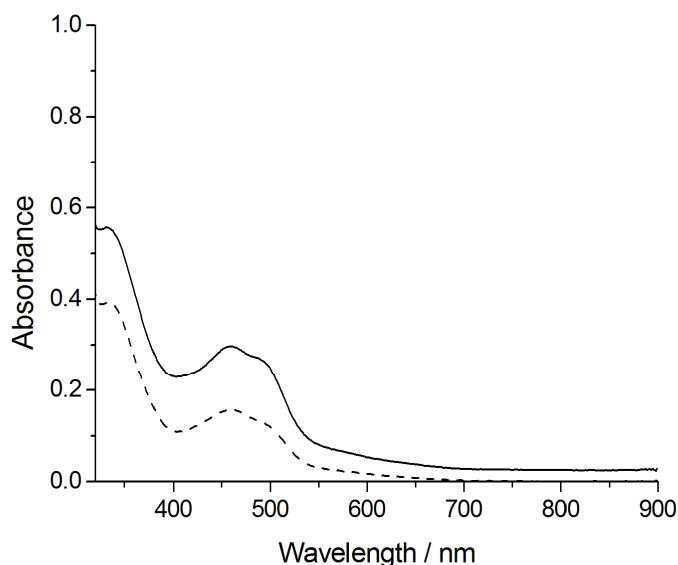


Figure S2. UV-Vis absorption spectra of complex **1**⁺ on Nafion film (solid line) and complex **1**⁺ (5×10^{-5} M) in a solution (water/acetone = 1:1, V/V) (dash line)

Complex **1**⁺ loading on Nafion film: The amount of complex **1**⁺ penetrated into the Nafion membrane can be determined from the absorption of complex **1**⁺ on Nafion film and compared

with a known concentration of complex $\mathbf{1}^+$ (5×10^{-5} M) in the solution (water/acetone = 1:1, V/V), based on the assumption of an equivalent molar extinction coefficient. The total amount of complex $\mathbf{1}^+$ on the Nafion film is estimated to be 1.7×10^{-8} mol.

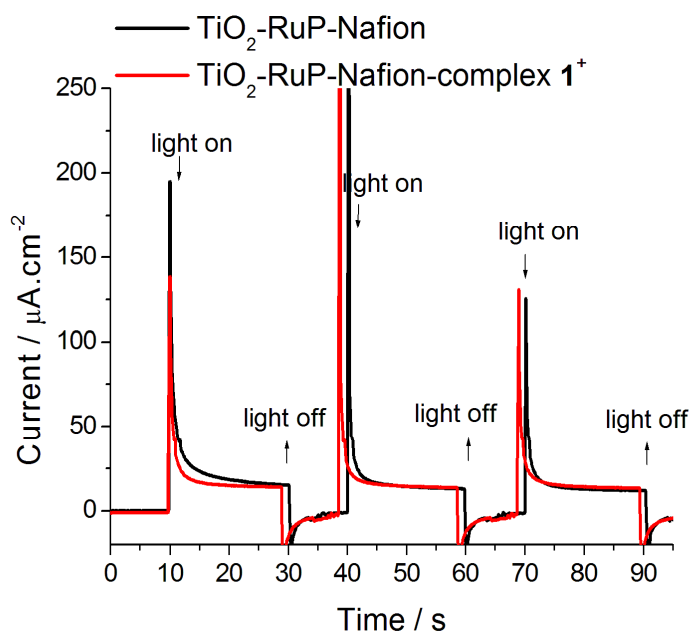


Figure S3. The transient short-circuit current responses to on-off cycles of illumination by a light-emitting diode in a operating PEC device, the anode was a dye-sensitized TiO₂ combined with a Nafion film prepared by a commercial solution with the pH 2; 0.1M Na₂SO₄ aqueous solution as the electrolyte; Pt counter electrode; without complex $\mathbf{1}^+$ in Nafion (black line); with complex $\mathbf{1}^+$ in Nafion (red line)

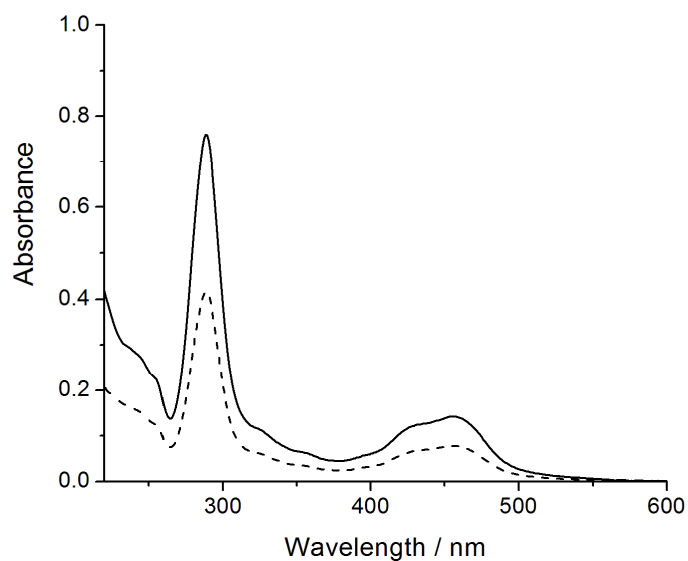


Figure S4. UV-Vis absorption spectra of **RuP** desorbed from sensitized TiO₂ electrodes (dash line); and pure **RuP** (1×10^{-5} M) (solid line) in 0.1 M NaOH solution (water/ethanol = 1:1, V/V)

RuP loading on TiO₂: three identical **RuP** sensitized TiO₂ films were desorbed into 0.1 M NaOH solution in 10ml (water/ethanol = 1:1, V/V) for two hours.^[2] The UV-Vis absorption spectrum of the resultant solution was measured and compared to a known concentration of **RuP** (1×10^{-5} M) to estimate the amount of dye adsorbed on TiO₂. The total amount of dye on each TiO₂ film is estimated to be 1.8×10^{-8} mol.

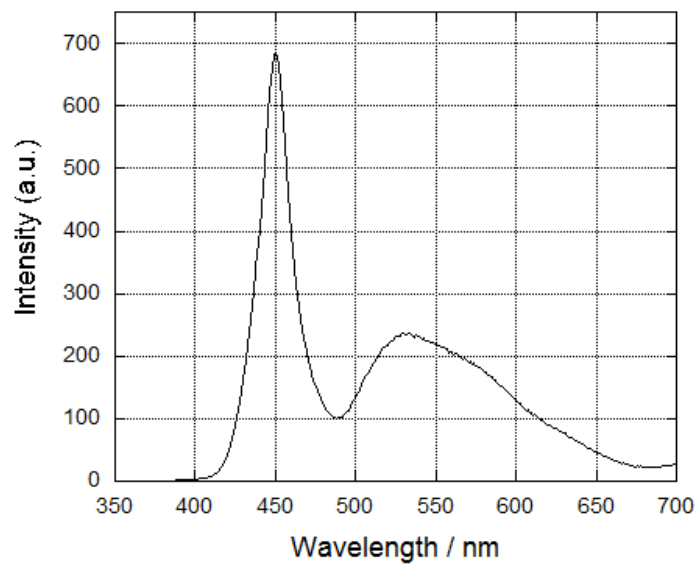


Figure S5. Spectrum of the light-emitting diode (LED)

- [1] I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C. A. Bignozzi, P. Qu, G. J. Meyer, *Inorg. Chem.*, 2001, **40**, 6073.
- [2] Z.-S. Wang, H. Kawauchi, T. Kashima, H. Arakawa, *Coord. Chem. Rev.* **2004**, *248*, 1381.