Electronic Supporting Information for:

Effect of peripheral bipyridine ligands on the photocatalytic hydrogen production by activity of Ru/Pd catalysts

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Experimental

General: Reagents for synthesis were purchased as reagent grade and were used without further purification. NMR spectra were recorded on a Bruker Advance 400 spectrometer and referenced to the solvent signal. Elemental analysis was carried out on an Exador Analytical CE440 by the Microanalytical Department of the University College Dublin. UV-Vis spectra were recorded on Varian Cary 50 spectrophotometer at $20 \pm 1^{\circ}$ C in a quartz cuvette with an optical path length of 10 mm. Acetonitrile for spectrophotometric measurements was purchased from Aldrich in spectrophotometric grade and used as received. Emission and excitation spectra were obtained on a Perkin Elmer LS 50B at $20 \pm 1^{\circ}$ C. Excited-state lifetimes were measured by time-correlated single photon counting on an Edinburgh Analytical Instruments single photon counter at $20 \pm 1^{\circ}$ C (293 K) in deaerated acetonitrile solution (freeze-pump-thaw triple sequence). Samples were excited with a LED at 360 nm. Cyclic voltammograms and differential pulse voltammograms were recorded against a silver/silver chloride reference electrode (Ag/AgCl) for the mono- and dinuclear complexes. Glassy carbon (GC) electrodes were used as the working electrodes and a platinum wire was employed as the counter electrode. Scans were recorded at room temperature for all complexes. A solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka, electrochemical grade) in acetonitrile (Aldrich, anhydrous, 99.8%) was used as the supporting electrolyte. Typical complex concentrations of 1 mM were used for cyclic voltammetry and differential pulse voltammetry. Electrochemical experiments were carried out using a CHI750C bipotentiostat. Prior to each experiment, the electrochemical cell was purged for at least 25 minutes using argon. The working electrodes were prepared by polishing with 0.05 µm alumina pastes and sonicated in Millipore water for 5 min followed by 5 min of sonication in acetonitrile. Scan rates recorded at 100 mV/s.

2,5-di(pyridin-2-yl)pyrazine

2,5-bis(2-pyridyl)pyrazine was prepared according to the literature.^{1,2}

¹H NMR (CDCl₃): 9.59 (s, 2H, 3-H, 6-H), 8.68 (d, 2H, *J* = 4.7 Hz, 9-H, 15-H), 8.38 (d, 2H, *J* = 7.8 Hz, 12-H, 18-H), 7.91 (t, 2H, *J* = 7.6 Hz, 11-H, 17-H), 7.80 (t, 2H, *J* = 5.0 Hz, 10-H, 16-H).

Synthesis of the mononuclear ruthenium complexes Ru and EtOOC-Ru

 $[Ru(2,2'-bipyridine)_2Cl_2]\cdot 2H_2O$ (0.65 mmol) dissolved in 10 ml of ethanol was added drop-wise to a solution of 2,5di(pyridin-2-yl)pyrazine (0.187 g, 0.80 mmol) in 10 ml of ethanol/water (3:1 v/v). The reaction mixture was heated at reflux for 8 h. Subsequently, the mixture was allowed to cool to room temperature and the solvent was evaporated in vacuo. Then 2 ml of water were added to dissolve the red complex and filtered to remove unreacted 2,5-dpp. The red aqueous solution yielded a precipitate upon addition of a saturated aqueous solution of NH₄PF₆ followed by filtration of the product and washing with 10 ml of diethyl ether. Recrystallization from acetone/water (3:1 v/v) afforded a red solid.

[bis-(2,2'-bipyridine)(2,5-di(pyridin-2-yl)pyrazine)ruthenium(II)] (PF₆)₂ · H₂O (**Ru**)

Yield: 71%. Anal. Calcd. for $C_{34}H_{26}F_{12}N_8P_2Ru \cdot H_2O$ (956.08 g/mol): C, 42.73; H, 2.95; N, 11.73%. Found: C, 43.11; H, 2.94; N, 11.46%. ¹H-NMR (Acetonitrile-d₃, 400 MHz): $\delta = 9.65$ (d, J = 1.2 Hz, 1H, 3-H), 8.74 (d, J = 1.2 Hz, 1H, 6-H), 8.69 (d, J = 8.4 Hz, 1H, 12-H), 8.57 – 8.52 (m, 4H, bpy), 8.51 (d, J = 4.8 Hz, 1H, 15-H), 8.44 (d, J = 8.0 Hz, 1H, 18-H), 8.19-8.08 (m, 4H, bpy), 8.14 (ddd, J = 8.0 Hz, J = 1.6 Hz, 1H, 11-H), 7.97 (ddd, J = 8.0 Hz, J = 1.6 Hz, 1H, 17-H), 7.81 (d, J = 5.6 Hz, 1H, 9-H), 7.82-7.75 (m, 4H, bpy), 7.50-7.44 (m, 4H, bpy), 7.49 (m, 1H, 10-H), 7.46 (m, 1H, 16-H).

[bis-(4,4'-dicarboxyethyl(2,2'-bipyridine))(2,5-di(pyridin-2-yl)pyrazine) ruthenium(II)] $(PF_6) \cdot 2H_2O$ (EtOOC-Ru)

Yield: 78%. Anal. Calcd. for $C_{46}H_{42}F_{12}N_8O_8P_2Ru \cdot 2H_2O$ (1261.90 g/mol): C, 43.78; H, 3.67; N, 8.88%. Found: C, 43.53; H, 3.27; N, 8.49%. ¹H-NMR (Acetonitrile-d₃, 400 MHz): $\delta = 9.69$ (s, 1H, 3-H), 9.12-9.07 (m, 4H, bpy) 8.71 (d, J = 8.3 Hz, 1H, 12-H), 8.64 (s, 1H, 6-H), 8.50 (d, J = 4.8 Hz, 1H, 15-H), 8.44 (d, J = 8.0 Hz, 1H, 18-H), 8.20 (ddd, J = 8.0 Hz, J = 1.5 Hz, 1H, 11-H), 8.13-7.84 (m, 8H, bpy) 7.97 (m, 1H, 17-H), 7.74 (d, J = 5.6 Hz, 1H, 9-H), 7.52 (m, 1H, 10-H), 7.46 (m, 1H, 16-H) 4.54-4.46 (m, 8H, CH₂), 1.50-1.40 (m, 12H, CH₃).

The mononuclear precursor (0.10 mmol) was dissolved in 5 ml of dichloromethane and added drop wise to a solution of $Pd(CH_3CN)_2Cl_2$ (0.026 g, 0.10 mmol) in 5 ml of dichloromethane. The reaction mixture was heated at reflux for 24 h. Subsequently the mixture was allowed to cool to room temperature. The product was precipitated by addition of 10 ml of n-hexane. After filtration and washing with 10 ml of diethyl ether a reddish purple solid was obtained.

[Ruthenium(II)(2,2'-bipyridine)₂(μ -2,5-di(pyridin-2-yl)pyrazine)PdCl₂] (PF₆)₂ · 2 H₂O (**RuPd**)

Yield: 90%. Anal. Calcd for $C_{34}H_{26}Cl_2F_{12}N_8P_2PdRu \cdot 2 H_2O$ (1150.98): C, 35.48; H, 2.63; N, 9.74%. Found: C, 35.30; H, 2.22; N, 9.31%. ¹H-NMR (Acetonitrile-d₃, 400MHz): $\delta = 10.05$ (s, 1H, 3-H), 8.91 (d, J = 4.8 Hz, 1H, 15-H), 8.62 (d, J = 8.4 Hz, 1H, 12-H), 8.57 – 8.52 (m, 4H, bpy), 8.42 (s, 1H, 6-H), 8.15 (ddd, J = 6.0 Hz, J = 1.8 Hz, 1H, 11-H), 8.19-8.08 (m, 4H, bpy), 8.10 (ddd, J = 7.6 Hz, J = 1.2 Hz, 1H, 17-H), 7.81 (d, J = 8.0 Hz, 1H, 9-H), 7.82-7.75 (m, 4H, bpy), 7.66 (d, J = 7.6 Hz, 1H, 18-H), 7.59 (m, 1H, 10-H), 7.61 (m, 1H, 16-H), 7.50-7.44 (m, 4H, bpy).

$[Ruthenium(II)(4,4'-dicarboxyethyl(2,2'-bipyridine))_2(\mu-2,5-di(pyridin-2-yl)pyrazine)PdCl_2] (PF_6)_2 \cdot 2 H_2O (EtOOC-RuPd)$

Yield: 88%. Anal. Calcd. for $C_{46}H_{42}F_{12}N_8O_8Cl_2PdP_2Ru \cdot 2H_2O$ (1439.23 g/mol): C, 38.39; H, 3.22; N, 7.79%. Found: C, 38.22; H, 2.89; N, 7.72%. ¹H-NMR (Acetonitrile-d₃, 400 MHz): $\delta = 10.13$ (s, 1H, 3-H), 9.12-9.08 (m, 4H, bpy), 8.81 (d, J = 4.8 Hz, 1H, 15-H), 8.68 (d, J = 8.4 Hz, 1H, 12-H), 8.42 (s, 1H, 6-H), 8.25 (ddd, J = 8.0 Hz, J = 1.2 Hz, 1H, 11-H), 8.10 (ddd, J = 8.0 Hz, J = 1.8 Hz, 1H, 17-H), 7.92-7.83 (m, 8H, bpy), 7.82 (d, J = 5.6 Hz, 1H, 18-H), 7.79 (d, J = 7.6 Hz, 1H, 9-H), 7.61 (m, 1H, 10-H), 7.59 (m, 1H, 16-H), 4.54-4.46 (m, 8H, CH₂), 1.50-1.40 (m, 12H, CH₃).



Figure S1 UV-Vis absorption (solid) and emission (dashed) spectra in CH₃CN of (left) the mononuclear and (right) heterobimetallic dinuclear complexes.

Photocatalysis

All manipulations were carried out under strict a dinitrogen atmosphere. Acetonitrile was dried over calcium hydride and triethylamine over sodium according to standard procedures and freshly distilled under dinitrogen prior to use. Photocatalytic dihydrogen production experiments were carried out using a home-built air-cooled apparatus for maintaining the temperature (22°C) under constant irradiation of the sample. For a typical photocatalytic experiment, 2 ml of sample solution were added to GC vials (total volume 5 ml, diameter 13 mm, 3 ml headspace) in the dark and under a constant stream of dinitrogen. The vials were closed with gas-tight septum caps and placed in the sample holder of the apparatus for irradiation. A typical sample solution was prepared by mixing 0.1 ml of a $8.16 \cdot 10^{-4}$ M catalyst solution in acetonitrile, 0.6 ml of triethylamine, 0.1 ml (5 vol%) of thoroughly degased water and 1.2 ml of anhydrous acetonitrile. Subsequently, the GC vials were irradiated at 470 nm using light emitting diodes (LEDs, vide infra) for 18 h. After irradiation, 20 µl samples were drawn from the headspace with a gas tight syringe (50 µl, SGE Analytical Science) and injected into a gas chromatograph (GC). The dihydrogen evolved was measured by headspace gas chromatography on a Varian CP3800 gas chromatograph, with a thermal conductivity detector and a CP7536 Plot Fused Silica 25 MX 0.32 MMID column (length 25 m, layer thickness 30 µm) with dinitrogen carrier gas (purity 99.999 %). The GC was calibrated by 100% dihydrogen. The obtained signal (retention time for $H_2 = 1.58$ min) was plotted against the calibration curve and multiplied accordingly to receive the total produced amount of dihydrogen in the headspace. The LED-torch consists of a stick-shaped printed board (19 x 1 cm) with 30 blue LEDs (Kingbright, type L-7113PBC-G, 470 ± 20 nm) with a luminous efficiency of 2000 mcd per LED. LEDs are soldered closely on front and backside in a range of 9 cm.



Figure S2 Irradiation time-dependent evolution of hydrogen with the **EtOOC-RuPd** (blue) and **EtOOC-Ru** + $Pd(CH_3CN)_2Cl_2$ (red).

1 F. Case and E. Koft, *J. Am. Chem. Soc.*, **1959**, 81, 905-906. 2 G. Clemo, T. Holmes and G. Leitch, *J. Chem. Soc.*, **1938**, 753.