Electronic Supporting Information

A Cobalt(II) Polypyridyl Complex as Visible Light-Driven Catalyst for both Water Oxidation and Reduction

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Experimentals

Materials and Methods

The ligand 2,2':6',2":6'',2"'-quaterpyridine (qpy), $[Ru^{II}(bpy)_3]Cl_2$, $[Ru^{III}(bpy)_3](ClO)_3$, $[Ir^{III}(ppy)_2(bpy)]PF_6$, $[Co^{II}(bpy)_3]Cl_2$, $[Ir^{III}(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ and *p*-cyanoanilinium tetrafluoroborate were synthesized according to literature methods.¹⁻⁶ All other chemicals were of reagent grade and were used as purchased.

Synthesis of Catalysts.

Trans-[Co^{II}(qpy)(Cl)₂]·2H₂O. CoCl₂·6H₂O (100 mg, 0.42 mmol) was dissolved in methanol (8 mL). A solution of qpy (130 mg, 0.42 mmol) in chloroform (7 mL) was added slowly with stirring. A brown solid was formed gradually and the mixture was stirred for 2 h. The solid was filtered and washed with methanol and chloroform to remove the unreacted ligand. The solid was dried in air. Yield: 82 mg (41 %). Anal. Calcd. for C₂₀H₁₈Cl₂CoN₄O₂: C, 50.44; H, 3.81; N, 11.76; Found: C, 50.27; H, 3.92; N, 11.67. *m/z* (1:1 H₂O/methanol): 368, [Co(qpy)–H]⁺.

Trans-[Co^{II}(**qpy**)(OH₂)₂](ClO₄)₂. [Co^{II}(**qpy**)(Cl)₂]·2H₂O (80 mg, 0.18 mmol) was dissolved in water (10 mL). LiClO₄ (61 mg, 0.57 mmol) was added to the solution with stirring. A pale brown solid precipitated gradually and the solution was stirred for 30 min. The solid was collected by filtration, washed with water and diethyl ether and dried in air. Yield: 61 mg (56 %). Anal. Calcd. for C₂₀H₁₈Cl₂CoN₄O₁₀: C, 39.76; H, 3.00; N, 9.27. Found: C, 39.89; H, 3.10; N, 9.34. *m/z* (1:1 H₂O/methanol): 368, [Co(**qpy**)–H]⁺; 468, [Co(**qpy**)+ClO₄]⁺.

Cis-[Co^{II}(bpy)₂(Cl)₂]. CoCl₂·6H₂O (100 mg, 0.42 mmol) was dissolved in 10 mL ethanol. 2,2'bipyridyl (131 mg, 0.84 mmol) was added with stirring. The pink microcrystalline solid formed was collected by filtration after 30 min of stirring. The solid was air-dried. Yield: 103 mg (55 %). Anal. Calcd. for C₂₀H₁₆N₄Cl₂Co: C, 54.32; H, 3.65; N, 12.67. Found: C, 54.25; H, 3.71; N, 12.58. m/z (1:1 H₂O/methanol): 406, [Co(bpy)₂(OH)(OH₂)]⁺. *Cis*-[Co^{II}(bpy)₂(OH₂)₂](ClO₄)₂. Co(bpy)₂Cl₂ (80 mg, 0.19 mmol) was dissolved in water (10 mL). LiClO₄ (61 mg, 0.57 mmol) was added to the solution with stirring. After 30 min, the orange brown precpitate was collected by filtration, washed with water and diethyl ether, and dried in air. Yield: 74 mg (64 %). Anal. Calcd. for C₂₀H₂₀N₄O₁₀CoCl₂: C, 39.62; H, 3.33; N, 9.24. Found: C, 39.64; H, 3.26; N, 9.21. m/z (1:1 H₂O/methanol): 406, [Co(bpy)₂(OH)(OH₂)]⁺; 470, [Co(bpy)₂+ClO₄]⁺.

Chemical water oxidation

8 mL aqueous solution of $[Ru^{III}(bpy)_3](ClO_4)_3$ (6.3 µmol) were placed in a round-bottom flask (total volume = 17 mL). The flask was sealed with rubber septum and deaerated with argon for 20 min. A 250 µL deaerated buffer solution (0.5 M) of $[Co^{II}(qpy)(OH_2)_2](ClO_4)_2$ or $[Co(bpy)_2(OH_2)_2](ClO_4)_2$ (6.6 nmol) in aqueous buffer (0.5 M) was then injected into the flask with a syringe, affording a 8.25 mL solution (reported concentrations of the reacting species are based on this volume). The solution was rigorously stirred for 10 min. The oxygen content in the headspace was determined by a HP5890 GC-TCD fitted a Chrompack 5Å molecular sieve column (25 m × 0.32 mm). A calibration curve was prepared by injecting known volume of pure oxygen gas into the reaction flask. The reported turnover number is based on the catalyst.

Measurement of oxygen evolution was also conducted with a YSI Clark-type electrode. The gas permeable membrane of the electrode was replaced prior to each measurement to ensure the highest sensitivity. The electrode, secured in a Teflon tube, was inserted into a gas tight-fitting water-jacketed glass vessel kept in a 25°C water bath. In a typical experiment, 8 mL of deaerated aqueous solution of $[Ru^{III}(bpy)_3](ClO_4)_3$ (6.3 µmol) was allowed to equilibrate with stirring for 5–10 min until a steady baseline was attained. 250 µL of deaerated solution of $[Co^{II}(qpy)(OH_2)_2](ClO_4)_2$ or $[Co(bpy)_2(OH_2)_2](ClO_4)_2$ (6.6 nmol) was then injected, and data were taken at 5 s intervals. The total volume of the solution is 8.25 mL.

Visible light-driven water oxidation

Photocatalytic oxygen generation was conducted in a round bottom flask (total volume = 17 mL) containing 8.25 mL solution of $[Co^{II}(qpy)(OH)_2](CIO_4)_2$ (0.2 μ M), $[Ru^{II}(bpy)_3]Cl_2$ (0.128 mM),

and $Na_2S_2O_8$ (5 mM) at pH 8 in sodium borate buffer (15 mM). The flask was sealed with a rubber septum and deaerated for 20 min. The flask was then irradiated at 457 nm with a Newport 500 W mercury arc lamp equipped with a monochromator (457 nm) and the oxygen content in the headspace was determined by GC-TCD as above at regular intervals. Calculation of the turnover number was based on the catalyst.

Photocatalytic hydrogen generation

Photocatalytic hydrogen generation was conducted in a Pyrex pear-shape flask (volume = 40 mL) containing a solution (10 mL) of $[Co^{II}(qpy)(OH_2)_2](CIO_4)_2$ or $[Co^{II}(bpy)_2(OH_2)_2](CIO_4)_2$ or $[Co^{II}(bpy)_3]Cl_2$ (0.6 mM), $[Ir^{III}(ppy)_2(bpy)]PF_6$ or $[Ir^{III}(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.03 mM), 0.025 M *p*-cyanoanilinium tetrafluoroborate and 0.2 M TEOA in acetonitrile. The flask was sealed with a rubber septum and purged with argon which is saturated with acetonitrile for 20 min at room temperature. The solution was then irradiated by a Newport 500 W mercury-xenon lamp (Model 67005) equipped with a quartz liquid filter of circulating water and a Pyrex filter or a cut-off filter (420 nm). The hydrogen content in the headspace was determined similarly as above at regular time intervals. The reported turnover number is based on the Ir photosensitizer.

Dynamic Light scattering Measurement

The light source for the scattering experiments was a He-Ne laser emitting vertically polarized light at a wavelength of 638 nm and operating at 4 mW. Data were collected at 20 °C with the scattering angle set to 173 degrees (Non-Invasive Back-Scatter), using an Avalanche photodiode detector and connected to a correlator (Zetasizer Nano particle analyser series, Nano ZS, ZEN 3600, Malvern Instruments).

Luminescence Quenching Measurement

All luminescence quenching experiments were carried out by adding known amounts of quencher to the iridium or ruthenium complex solution at room temperature. The concentration of iridium (0.03 mM) or ruthenium complex (0.006 mM) solution was the same as that used in photocatalytic experiments. The solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with at least four successive freeze pump-thaw cycles. Steady-state

luminescence spectra of each sample were then recorded on a SPEX FluoroLog 3-TCSPC spectrofluorometer. The relative emission intensity or lifetime of the characteristic emission of the iridium or ruthenium complex in the presence of the different concentrations of the quencher was used to calculate the quenching rate constant (k_q) by the Stern-Volmer equation.⁷

$$\frac{\tau_o}{\tau}$$
 or $\frac{I_o}{I} = 1 + k_q \tau_o[Q]$

where I_o and I are the emission intensities in the absence and presence of quencher, respectively, τ_o and τ are the emission lifetimes in the absence and presence of quencher, and [Q] is the concentration of the quencher.

Transient Absorption Spectroscopy

Transient absorption spectra at room temperature were recorded using the spectral mode on an Edinburgh Instruments LP920-KS spectrometer equipped with an ICCD detector. The excitation source for the transient absorption measurement was the third harmonic output (355-nm; 6-8 ns fwhm pulse width) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd-YAG laser (10 Hz).



Figure S1. Plot of k_{obs} vs. concentration of catalyst for oxygen evolution from visible lightdriven (457 nm) water oxidation in aqueous borate buffer at pH = 8.0 by $[Co(qpy)(OH_2)_2]^{2+}$ / $[Ru(bpy)_3]Cl_2(128\mu M)$ /Na₂S₂O₈ (5 mM) under argon at 23 °C. Slope = (7.6± 0.3) × 10⁶ M⁻¹ h⁻¹, R² = 0.997.



Figure S2. Time traces of oxygen evolution at various concentrations of Na₂S₂O₈ (mM): a) 5, b) 2.5 and c) 10 in aqueous borate buffer (15 mM, 8.25mL; pH = 8.0) containing $[Co(qpy)(OH_2)_2]^{2+}$ (0.6 µM) and $[Ru(bpy)_3]Cl_2$ (128 µM) under argon at 23 °C.



Figure S3. Stern-Volmer plot for the oxidative quenching of $[Ru(bpy)_3]Cl_2$ (0.07 mM) with $[Co(qpy)(H_2O)_2](ClO_4)_2$ in borate buffer (15 mM) solution [slope = (47.1 ± 3.6) × 10³; y-intercept = 1.003 ± 0.005; r² = 0.988].



Figure S4. UV/Vis absorption spectral change of (a) $[Ru(bpy)_3]^{2+}$ (0.07 mM), Na₂S₂O₈ (2.7 mM) and $[Co(qpy)(OH_2)]^{2+}$ (0.33 μ M) in sodium borate buffer (15 mM, pH 8) upon light irradiation at 455 nm and (b) UV-vis absorption spectrum of $[Ru(bpy)_3]^{3+}$.



Figure S5. ESI/MS of a reaction solution of $[Co(qpy)(H_2O)_2]^{2+}$ (0.2 mM) with 12 mol equiv. of $[Ru(bpy)_3]Cl_2$ and 20 mol equiv. of $Na_2S_2O_8$ at pH 8.0 in borate buffer (15 mM) after irradiation with light at $\lambda = 457$ nm for 30 min at 23 °C. The solution was diluted with 3 vol. of acetonitrile before electrospraying. Insets show the expanded and simulated isotopic mass distribution.

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Figure S6. Particles size distribution of a solution containing 0.05 mM of $[Co(qpy)(OH_2)_2]^{2+}$ (red) and no catalyst (blue), with $[Ru(bpy)_3]^{2+}$ (0.5 mM) and $Na_2S_2O_8$ (10 mM) at pH 8 in 15 mM sodium borate buffer, determined by dynamic light scattering (DLS) measurements, after 30 min irradiation (457 nm).



Figure. S7. Particles size distribution of a solution containing $[Co(qpy)(H_2O)_2]^{2+}$ (0.6 mM) and $[Ru(bpy)_3]^{3+}$ (7.2 mM) (red), and only $[Ru(bpy)_3]^{3+}$ (7.2 mM) (blue), at pH 8 in 15 mM sodium borate buffer determined by DLS measurements.



Figure S8. Plot of k_{obs} vs. [PS] for the H₂ evolution from $[Co(qpy)(OH_2)_2]^{2+}$ (0.6 mM)/TEOA (0.2 M)/CA (0.025 mM)/ $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ in acetonitrile (10 mL) [slope = (3.73 ± 0.29) × 10³; y-intercept = (3.58 ± 10.2) × 10⁻³; r² = 0.9815].



Figure S9. UV/Vis spectra of an acetonitrile solution containing TEOA (0.2 M), $[Co(qpy)(OH_2)_2](ClO_4)_2$ (0.2 mM) and $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 μ M) at a) 0 s and b) 80 s after photolysis with visible light by using a LED lamp (10 W).



Figure S10. (a) Transient absorption spectrum of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (0.03 mM) in the presence of TEOA (0.6 mM) at 23 °C in MeCN solution recorded at 3.5 µs after 355-nm laser excitation. (b) UV-vis absorption difference spectrum of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ in MeCN after controlled-potential reduction at -1.4 V *vs*. Ag/AgNO₃.

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