Electronic Supplementary Information

Effective H₂-producing photocatalytic systems based on cyclometalated iridium- and

tricarbonylrhenium-diimine photosensitizers and cobaloxime catalysts

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Experimental Section

Materials.

2-phenylpyridine (ppy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dmphen), NaBF₄, (*n*-Bu₄N)HSO₄, triethylamine and 4-pyridinecarboxaldehyde were purchased from Aldrich and used without further purification. Ammonium acetate was purchased from Euromedex. IrCl₃.*n*H₂O, RuCl₃.*n*H₂O and [Re(CO)₅Br] were purchased from Strem Chemicals and used as supplied. dimethylglyoxime was obtained from Acros Organics and also used as received. Solvents were degassed by Argon bubbling but not distilled before use. The supporting electrolyte (*n*-Bu₄N)BF₄ was prepared from (*n*-Bu₄N)HSO₄ and NaBF₄ and dried overnight at 80 °C under vacuum. [Co(dmgBF₂)₂(OH₂)₂],¹ [Ru(dmphen)₂Cl₂],² [ReBr(phen)(CO)₃],³ [(Ir(ppy)₂Cl]₂,⁴ [Ir(ppy)₂(phen)(PF₆)],⁵ *p*-cyanoanilinium tetrafluoroborate⁶ and triethylammonium tetrafluoroborate⁷ were prepared according to previously reported literature procedures. 1,10-phenanthroline was oxidized to 1,10-phenanthroline-5,6-dione (phendione) according to literature except for using methanol instead of toluene for recrystallization.⁸

Methods and Instrumentation.

All reactions in solution were carried out under an inert atmosphere of nitrogen or argon using conventional vacuum-line and glasswork techniques. The metal complexes were however handled in air in the solid state.

Electrochemical measurements were carried out under nitrogen. A standard three-electrode configuration was used consisting of a glassy carbon (3 mm in diameter) disk as the working electrode, an auxiliary platinum wire and an Ag/AgCl/ aqueous AgCl_{sat} + KCl 3 mol.L⁻¹ (hereafter named Ag/AgCl) reference electrode closed by a Vicor frit and directly dipped into the solution. In order to take the liquid junction potential between the aqueous and nonaqueous solution into account, this electrode was calibrated with the internal reference system Fc⁺/ Fc, which was found at 0.46 V vs Ag/AgCl in CH₃CN (0.53 V vs Ag/AgCl in DMF). The Fc⁺/Fc couple ($E^0 = 0.400$ V vs SHE) can be used to quote potentials to SHE, when needed.

Cyclic voltammograms were recorded on a EG&G PAR 273A instrument. Solution concentrations were ca. 1 mM for the studied compound and 0.1 M for the supporting electrolyte (*n*-Bu₄N)BF₄. Electrodes were polished on a MD-Nap polishing pad with a 1 μ m monocrystalline diamond DP suspension. Aliquots of 0.05 mol.L⁻¹ *p*-cyanoanilinium in acetonitrile solution were added by syringe. Voltammograms of the supporting electrolyte and of solutions of *p*-cyanoanilinium tetrafluoroborate in the presence of the supporting electrolyte were previously published.

Photocatalytic experiments were carried out in a Schlenk tube made of pyrex. In all experiments, the irradiation was carried out by a 150W mercury lamp coupled with a Spectra-Physics 59470 UV cut-off filter (λ >380 nm).

In a typical experiment, the Schlenk tube (46 cm³) was filled with the photocatalyst (0.55 mmol.L⁻¹), acetone (10 mL), triethylamine (210 μ L, 0.165 mol.L⁻¹, 300 equiv.) and triethylammonium tetrafluoroborate (280 mg, 0.165 mol.L⁻¹, 300 equiv.). The solution was thoroughly degassed by bubbling nitrogen and irradiated under stirring. Three head-space gas samples (50 μ L) were successively taken using a gas-tight syringe and analyzed using a Delsi Nermag DN200 gas chromatograph equipped with a 3 m porapack® column and a thermal conductivity detector. The mean area was used to determine the volume of hydrogen produced, knowing the total volume of the reactor, from a calibration curve.

Quantum yields for H₂ production were measured using an irradiation test bench shown in Figure 1. The main elements of the apparatus are a tightly closed quartz cell (total volume 5 mL; path length = 1cm) in which the solution (0.5 mL) is placed, a 1000W LSH502 xenon lamp (operated at 840W) and a Cornerstone 74000 1/8m monochromator. The image of the monochromator beam output is created on the front cell surface with a confocal optical system. For each wavelength, the average output power is measured using a Newport 1830c power-meter, and the focused beam area is estimated thanks to a CCD camera. The photons flux is then determined by the equation (1), where $\langle P \rangle$ is the average output power in W, λ is the wavelength in cm, S_{Beam} the beam area in cm², *h* the Planck's constant in J.s and *c* the light velocity in cm/s.

$$F_{Photon} = \frac{\left\langle P \right\rangle \lambda}{S_{Beam} hc}$$

For a 412nm-wavelength, the average output power and the focused beam area are respectively $\langle P \rangle = 1,713$ mW and $S_{Beam} = 7,65$ mm², that gives $F_{Photon} = 4,64.10^{16}$ photons.cm⁻².s⁻¹. Compared to the irradiance solar spectrum (ASTM G173-03), the acceleration factor is around 230 (Figure 2).



Figure S1: Experimental set up for the irradiation test of samples

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Figure S2: Irradiance solar and lamp spectra

Under the above conditions the incident light is quantitatively harvested by the photocatalytic system. This was checked by measuring the output power after the sample, which always proved to be below 5% of the incident light power.

The amount of hydrogen produced $n(H_2)$ is estimated from GC measurement and the quantum yield is determined using equation 2:

$$\varphi(1/2H_2) = 2 \frac{n(H_2) \times N}{F_{photon} \times t \times S_{beam}}$$

where N is the Avogadro constant and t the irradiation time (s)

Syntheses

[Ru(dmphen)₂(phen-dione)](PF₆)₂

A mixture of [Ru(dmphen)₂Cl₂] (100 mg, 0.170 mmol) and phen-dione (36 mg, 0.170 mmol) in ethanol (30 mL) was heated to reflux (80 °C) under nitrogen for 6h. After cooling to room temperature, the solution was concentrated under vacuum to 5 mL; a green precipitate was obtained by addition of aqueous NH₄PF₆ (~30 mg) solution (5 mL). Yield: 148 mg, 86%. ¹H NMR (DMSO-d⁶): δ 8.50 (d, 2H), 8.48 (d, 2H), 8.46 (d, 2H), 8.05 (d, 2H), 7.89 (d, 2H), 7.82 (d, 2H), 7.80 (d, 2H), 7.58 (d, 2H), 7.54 (d, 2H), 2.96 (s, 6H), 2.87 (s, 6H). ESI-MS (m/z): 364 (100%, [M]²⁺); 873 (20%, [M+PF₆]⁺).

[Ru(dmphen)₂ (L-pyr)](PF₆)₂ (L-pyr=(4-pyridine)oxazolo-[4,5-*f*]phenanthroline)

A mixture of $[Ru(dmphen)_2(phen-dione)]_2(PF_6)_2$ (164 mg, 0.161 mmol), ammonium acetate (248 mg, 3.22 mmol), and 4-pyridinecarboxaldehyde (46 μ L, 0.48 mmol) in glacial acid acetic (25 mL) was

refluxed at 120°C for 6h and then cooled to room temperature and diluted with water (~50 mL). After neutralisation with concentrated aqueous ammonia (28%), a red precipitate was obtained by addition of aqueous NH₄PF₆ solution. The solution was filtered and the product washed with water and dried diethyl ether. Yield: 125 mg, 70%. Elemental analysis (%) calcd for C₄₆H₃₄F₁₂N₈OP₂Ru[·]H₂0 (1123,83 g.mol⁻¹): C 49.16, H 3.23, N 9.97; Found C 49.50, H 4.21; N 9.13. ¹H NMR (300MHz, acetone): δ 9.14 (d, 2H, J = 8.4 Hz), 8.96 (d, 2H, J = 4.2), 8.55 (m, 4H), 8.5 (dd, 2H, J = 5.4, 1.6 Hz), 8.33 (dq, 2H, J = 4.5, 1.8 Hz), 8.28 (dd, 2H, J = 5.4, 3 Hz), 8.22 (d, 2H, J = 5.4 Hz), 7.95 (dq, 2H, J = 5.1, 1.7 Hz), 7.66 (d, 2H, J = 6.3 Hz), 7.63 (d, 2H, J = 7.8 Hz), 2.98 (s, broad, 6H), 2.97 (s, broad, 6H). ESI-MS (m/z,): 408 (100%, [M]²⁺); 961 (10%, [M+PF₆]⁺).

[Ru(dmphen)₂ (L-pyr)Co(dmgBF₂)₂(OH₂)](PF₆)₂ (1)

[Co(dmgBF₂)₂(OH₂)₂] (120 mg, 0.285 mmol) and [(dmphen)₂Ru(L-pyr)](PF₆)₂ (315 mg, 0.285 mmol) were dissolved in acetone (30 mL) and stirred for 3 h at room temperature. The solvent was removed under vacuum to give an orange solid of **1** which was washed with diethyl ether and dried in vacuo. Yield: 320 mg, 75%. Elemental analysis (%) calcd for $C_{54}H_{48}B_2CoF_{16}N_{12}O_6P_2Ru$ (1509,16 g.mol⁻¹): C 42.99, H 3.21, N 11.14, B 1.43, Co 3.91; Found C 42.31, H 3.64, N 11.16, B 1.50, Co 4.21.

[Ir(ppy)₂(phen-dione)](PF₆)

A mixture of $[(Ir(ppy)_2Cl]_2$ (200 mg, 0.186 mmol) and phen-dione (82 mg, 0.39 mmol) was refluxed (150 °C) in 15 mL of ethylene glycol for 15h. Upon cooling to room temperature, the mixture was transferred to a separating funnel with water (80 mL) and washed with hexanes (3 x 30 mL). The aqueous layer was heated to 85°C for ten minutes to remove residual hexanes. A yellow precipitate was obtained by addition of aqueous NH₄PF₆ solution. The precipitate was filtered and dried diethyl ether Yield: 124 mg, 78%; ¹H NMR (300 MHz, CDCl₃): δ 8.29 (d, 2H), 8.27 (d, 2H), 8.03 (d, 2H), 7.99 (d, 2H), 7.96 (d, 2H), 7.92 (dd, 2H), 7.2 (d, 2H), 7.08 (d, 2H), 7.02 (d, 2H), 6.97 (d, 2H), 6.93 (d, 2H); ESI-MS (m/z,): 711 (100%, [M+PF₆]⁺)

[Ir(ppy)₂ (L-pyr)](PF₆)

A glacial acetic acid solution (30 mL) of $[Ir(ppy)_2(phen-dione)](PF_6)$ (155 mg, 0.181 mmol), ammonium acetate (279 mg, 3.62 mmol), and 4-pyridinecarboxaldehyde (51 µL, 0.54 mmol) was refluxed for about for 6 h. After cooling to room temperature, the solution was diluted with water (~50 mL) and neutralised with aqueous ammonia (28%). A yellow precipitate was obtained by addition of aqueous NH₄PF₆ (~30 mg) solution (5 mL), filtered and washed with water and dried diethyl ether. Yield: 131 mg, 77%.

Elemental analysis (%) calcd for $C_{40}H_{26}F_6IrN_6OP.3H_2O$ (998,14 g.mol⁻¹): C 48.14, H 3.23, N 8.42; Found C 47.74, H 3.50, N 7.71; ¹H NMR (acetone): § 9.3 (d, 2H, J = 8.4 Hz), 8.96 (d, 2H, J = 6 Hz), 8.5 (dd, 2H, J = 5.4, 1.2 Hz), 8.34 (dd, 2H, J = 4.5, 1.5 Hz), 8.27 (dd, 2H, J = 3.9, 1.15 Hz), 8.24 (dd, 2H, J = 3.7, 1.5 Hz), 7.96 (dd, 2H, J = 7.8, 2.2 Hz), 7.92 (dd, 2H, J = 3.9, 1.8 Hz), 7.75 (d, 2H, J = 5.7 Hz), 7.08 (d, 2H, J = 5.5 Hz), 7.03 (d, 2H, J = 7.5 Hz), 6.97 (d, 2H, J = 3.6 Hz), 6.45 (d, 2H, J = 6.5 Hz); ESI-MS (m/z,): 799 (100%, [M+PF₆]⁺).

[Ir(ppy)₂ (L-pyr)Co(dmgBF₂)₂(OH₂)](PF₆) (2)

A solution of $[Co(dmgBF_2)_2(OH_2)_2]$ (90 mg, 0.214 mmol) and $[(ppy)_2Ir(L-pyr)](PF_6)$ (202 mg, 0.214 mmol) in acetone (30 mL) was stirred for 3 h at room temperature. After evaporation of the solvent, an orange powder was obtained which was washed three times with diethyl ether and then dried under vacuum. Yield: 233 mg, 81%. Elemental analysis (%) calcd for C₄₈H₄₀B₂CoF₁₀IrN₁₀O₆P (1347,19 g.mol⁻¹): C 42.81, H 2.99; N 10.40, B 1.61, Co 4.38; Found C 41.80, H 3.23, N 9.70, B 1.42, Co 4.22.

Figure S3: Cyclic voltammograms of $[Co(dmgBF_2)_2(dmf)_2]$ (green), $[(dmphen)_2Ru(L-pyr)](PF_6)_2$ (blue), and **1** (red) recorded in a DMF solution of *n*-Bu₄NBF₄ (0.1 M) on a glassy carbon electrode (100 mV.s⁻¹) starting on reduction (potentials versus Ag/AgCl).



Figure S4: Cyclic voltammograms of $[Co(dmgBF_2)_2(CH_3CN)_2]$ (blue), $[(ppy)_2Ir(L-pyr)](PF_6)$ (green), and **2** (red) recorded in a CH₃CN solution of *n*-Bu₄NBF₄ (0.1 M) on a glassy carbon electrode (100mV.s⁻¹) starting on reduction (potentials versus Ag/AgCl).



Figure S5: Cyclic voltammograms of complex **1** in acetonitrile solutions containing 0.1 M n-Bu₄NBF₄ in the presence of increasing amounts of p-cyanoanilinium tetrafluoroborate. Scan rate: 100 mV.s⁻¹; glassy carbon electrode.

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Figure S6: Cyclic voltammograms of complex **2** in acetonitrile solutions containing 0.1 M n-Bu₄NBF₄ in the presence of increasing amounts of p-cyanoanilinium tetrafluoroborate. Scan rate: 100 mV.s⁻¹; glassy carbon working electrode.



Figure S7: Cyclic voltammogram of $[(Ir(ppy)_2Cl]_2 \text{ recorded in a CH}_3CN \text{ solution of } n-Bu_4NBF_4 (0.1 M) on a glassy carbon electrode (100 mV.s⁻¹) starting on reduction (potentials versus Ag/AgCl).$

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Figure S8: Electronic absorption spectra of $[Re(CO)_3Br(phen)]$ (black), $[Ir(ppy)_2(phen)]PF_6$ (orange), $[Co(dmgBF_2)_2(OH_2)_2]$ (green) $[Ru(bipy)_2(L-pyr)](PF_6)_2$ (blue) $[Ru(dmphen)_2(L-pyr)](PF_6)_2$ (red) at 4.0 10^{-5} mol.L⁻¹ in acetone.



Table S1: Potentials of cobalt-centred electrochemical processes measured versus Ag/AgCl in DMF and CH₃CN ([n-Bu₄NBF₄] = 0.1 M) at a glassy carbon electrode for the compounds of the study (scan rate: 100 mV.s⁻¹).

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	$^{1}/_{2}(E_{pc+}E_{pa})$ Co ^{II} /Co ^I			
	DMF	CH ₃ CN		
$[\mathrm{Co}^{\mathrm{II}}(\mathrm{dmgBF}_2)_2(\mathrm{OH}_2)_2]$	-0.55	-0.45		
1	-0.44			
2		-0.43		

Table S2 Photocatalytic H_2 production from acetone solutions (10 mL) of Et_3N and Et_3NHBF_4 . TON are given with regard to the cobalt moiety.

Run	Photocatalyst ^a	Irrad. timeTON ^b	
1	1	4	9
2	2	1	42
3	2	4	90
4	2	8	140
5	2	15	210°
6	$[Ir (ppy)_2(phen)](PF_6)+[Co(dmgBF_2)_2(OH_2)_2]$	1	52
7	$[Ir(ppy)_2(phen)](PF_6)+[Co(dmgBF_2)_2(OH_2)_2]$	4	96
8	$[Ir(ppy)_2(phen)](PF_6)+[Co(dmgBF_2)_2(OH_2)_2]$	8	132
9	$[Ir(ppy)_2(phen)](PF_6)+[Co(dmgBF_2)_2(OH_2)_2]$	15	165 ^c
10	$[\text{ReBr(phen)(CO)}_3]+[\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2]$	1	53
11	$[\text{ReBr(phen)(CO)}_3]+[\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2]$	4	140
12	$[\text{ReBr}(\text{phen})(\text{CO})_3] + [\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2]$	15	273°
13	-	15	<1
14	$[Co(dmgBF_2)_2(OH_2)_2]$	4	<1
15	$[Ru(dmphen)_2(L-pyr)](PF_6)_2$	4	<1
16	$[Ir(ppy)_2(L-pyr)](PF_6)$	4	<1
17	$[Ir(ppy)_2(phen)](PF_6)$	4	<1
19	[ReBr(phen)(CO) ₃]	4	<1

^{*a*} [Ru], [Ir], [Re] or [Co] = 0.55 mmol.L⁻¹; ^{*b*} irradiation was performed in pyrex glassware using a 150 W Hg lamp equipped with an infrared and UV cut-off filter; unless otherwise stated, 300 equiv. Et₃N and 300 equiv. Et₃NH⁺ were added; ^{*c*} 600 equiv. Et₃N and 600 equiv Et₃NH⁺ were added.

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