

Supporting Information

High-throughput screening of earth abundant water reduction catalysts towards photocatalytic hydrogen evolution

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Table of Contents

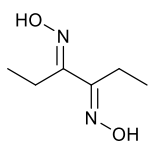
General methods: materials, literature synthesis	S3
Ligand and complex synthesis	S3
Photoreactor setup.....	S8
Reaction optimization data	S9
Figure S1: Reaction traces for Co WRC concentration and water fraction variation	S9
Figure S2: Water to WRC ratio against incubation time of reactions.....	S10
Figure S3: Reaction traces for Co WRC concentration and Eosin concentration variation ...	S10
Figure S4: Reaction traces for Co WRC concentration and pH variation	S11
Uniform plate data	S12
Figure S5: Reaction traces for a uniform reaction plate.....	S12
Control reactions	S13
Figure S6: Reaction traces for negative control experiments.....	S13
Ligand screening.....	S13
Table S1: Identities, structures and activity of all ligands used in Co WRC screening.....	S14
Gas chromatography data	S16
Table S2: Gas chromatography of select WRCs at 10x scale of screen	S16
Figure S7: Reaction traces for comparison of <i>in situ</i> and pre-synthesized WRCs	S17
Mercury Testing Images and Data.....	S17
Figure S8: Traces from Mercury Poisoning Testing in parallel reactor.....	S18

Table S3: Gas chromatography of Mercury Poisoning Testing at 10x scale of screen	S19
Figure S9: Images of mercury testing vials and wells after completing illumination	S20
References	S21

General methods: materials, literature synthesis

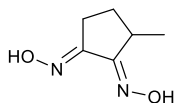
All reagents and solvents were commercially sourced and used without further purification. Nuclear magnetic resonance (NMR) spectra were obtained using 500 Bruker Avance III or a 500 Bruker Avance Neo (^1H , 500 MHz; ^{13}C , 125.8 MHz); spectra were referenced to residual solvent peaks. Ligands **GL11**,¹ **NH1**,² **NH2**,³ **NH3**,⁴ and **NH4**⁵ were synthesized according to previously reported procedure. The cobalt complexes $[\text{Co}(\text{GL1})_2\text{pyCl}]$ and $[\text{Co}(\text{GL1BF}_2)_2\text{pyCl}]$ were synthesized according to previously reported procedures.⁶

Ligand and complex synthesis



GL2

3,4-hexadione (7.5 mL, 61 mmol) was added to a solution of hydroxylamine hydrochloride (10.6 g, 153 mmol) in ethanol (34 mL) and water (4mL). Ground sodium hydroxide (6.1 g, 153 mmol) was added to this in small portions, yielding an exothermic reaction. After addition the solution was left to stir for one hour then dilute with iced water and filtered. Precipitate was washed with water and dried *in vacuo* to yield a white solid.(7.8 g, 89%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 11.27 (s, 1H), 2.50 (q, $J = 7.5$ Hz, 2H), 0.95 (t, $J = 7.5$ Hz, 3H).

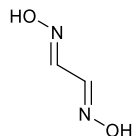


GL3

2-acetylcyclopentan-1-one (1.0 mL, 7.3 mmol) was added to a solution of hydroxylamine hydrochloride (3.0 g, 77 mmol), and sodium acetate (2.0 g, 24 mmol) in methanol (15 mL). The solution was heated to reflux and left stirring overnight. After cooling in air, cold water was added forming a precipitate which was then filtered and washed with water yielding an off-white powder (0.4 g, 42%).

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 10.59 (br s, 2H), 3.19 – 3.09 (m, 1H), 2.61 (ddd, $J = 18.2, 9.0, 2.4$ Hz, 1H), 2.42 (ddd, $J = 18.7, 10.4, 8.9$ Hz, 1H), 1.82 (dddd, $J = 12.8, 10.4, 9.2, 8.0$ Hz, 1H),

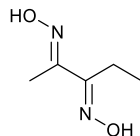
1.47 (ddt, $J = 13.0, 8.9, 2.3$ Hz, 1H), 1.06 (d, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 159.5, 155.7, 33.3, 27.6, 24.7, 16.5.



GL5

Diacetyl (40% w/w aqueous, 13.4 mL, 92 mmol) was added to a solution of sodium hydroxide (7.5 g, 186 mmol), and hydroxylamine hydrochloride (12.9 g, 186 mmol) in water (30 mL). After stirring at room temperature for 10 minutes, the solution was placed in the fridge overnight. The resulting yellow precipitate was then filtered and recrystallized in methanol. (7.1 g, 87%).

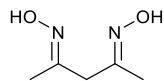
^1H NMR (500 MHz, DMSO) δ 11.63 (s, 2H), 7.73 (s, 2H).



GL6

2,3-pentanedione (5 mL, 48 mmol) was added to a solution of hydroxylamine hydrochloride (16.6 g, 239 mmol) and sodium acetate (9.9 g, 120 mmol) in methanol (50 mL). The solution was left stirring at reflux overnight. After cooling in air, cold water was added forming precipitate which was then filtered and washed with water revealing a white powder (3.8 g, 61%).

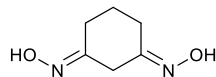
^1H NMR (500 MHz, DMSO- d_6) δ 11.36 (s, 1H), 11.30 (s, 1H), 2.53 (t, $J = 7.5$ Hz, 2H), 1.91 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 157.7, 152.0, 16.5, 10.9, 9.4.



GL7

Acetylacetonate (8.2 mL, 70 mmol) was added to a stirred suspension of sodium acetate (16.4 g, 200 mmol) and hydroxylamine hydrochloride (13.9 g, 200 mmol) in methanol (50 mL). The suspension was stirred for five hours then sat overnight. Solids were removed by filtration and washed with methanol. The filtrate was concentrated then diluted with cold water and filtered after

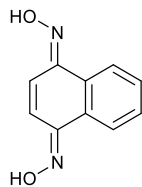
vigorous stirring. The precipitate was washed with cold water and dried in vacuo to yield colourless solid (4.4 g, 48%). ^1H NMR (500 MHz, DMSO- d_6) δ 10.49 (s, 2H), 2.93 (s, 2H), 1.69 (s, 6H).



GL8

1,3-cyclohexanedione (9.0 g, 80 mmol) was added dropwise into a solution of hydroxylamine hydrochloride (16.7 g, 240 mmol) and potassium carbonate (15.9 g, 115 mmol) in cold water (50 mL). This was left stirring at room temperature overnight and the precipitate formed was filtered and recrystallized in ethanol, revealing a brown sticky powder (8.4 g, 74%).

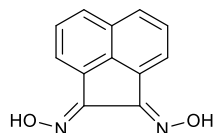
^1H NMR (500 MHz, DMSO) δ 10.41 (s, 2H), 3.43 (s, 2H), 2.33 – 2.27 (m, 4H), 1.67 – 1.58 (m, 2H).



GL10

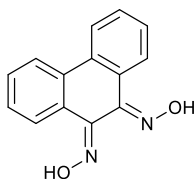
1,4-Napthoquinone (2.0 g, 13 mmol) was added to a solution of hydroxylamine hydrochloride (5.7 g, 82 mmol) and sodium hydroxide (8.6 g, 216 mmol) in ethanol (70 mL). This solution was heated to reflux and left stirring overnight. After cooling to room temperature in air, cold water was added. Filtering and washing with cold water revealed a brown powder. This was then recrystallized in ethanol, revealing a yellow powder (1.6 g, 68%).

^1H NMR (500 MHz, DMSO- d_6) δ 12.18 (s, 1H), 8.07 (dd, J = 6.0, 3.4 Hz, 1H), 7.46 (dt, J = 6.1, 3.5 Hz, 1H), 7.40 (s, 1H). ^{13}C NMR (126 MHz, DMSO) δ 146.3, 128.9, 128.8, 122.3, 118.5.



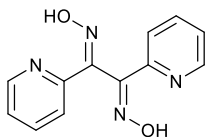
GL12

Acenaphthene quinone (5.5 g, 30 mmol) was added to a mixture of sodium acetate (10 g, 122 mmol) and hydroxylamine hydrochloride (7 g, 101 mmol) in ethanol/water (2.5:1, 305 mL). Solution was heated at reflux overnight before cooling to room temperature and diluting with iced water. The precipitate formed was filtered and recrystallised from ethanol to give a brown crystalline solid (2.3 g, 36%). ^1H NMR (500 MHz, DMSO- d_6) δ 12.35 (d, J = 1.3 Hz, 1H), 8.38 – 8.32 (m, 1H), 8.05 – 7.99 (m, 1H), 7.69 (ddd, J = 14.4, 8.3, 7.1 Hz, 1H).

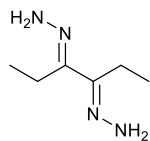
**GL13**

Phenanthrene-9,10-dione (1.3 g, 6 mmol) was added to a solution of hydroxylamine hydrochloride (2.1 g, 31 mmol) and sodium hydroxide (6.5 g, 162 mmol) in ethanol (30 mL). This solution was heated to reflux and left stirring overnight. After cooling to room temperature in air, cold water was added. Filtering and washing with cold water revealed a yellow powder (67 mg, 4.7%).

^1H NMR (500 MHz, DMSO- d_6) δ 8.30 (d, J = 8.0 Hz, 1H), 8.05 – 8.00 (m, 1H), 7.82 – 7.75 (m, 1H), 7.53 (t, J = 7.5 Hz, 1H). Hydroxylamine protons are not observed in ^1H spectra, likely as result of exchange with residual water. ^{13}C NMR (126 MHz, DMSO) δ 179.5, 135.9, 135.8, 131.7, 129.8, 129.6, 124.9.

**GL16**

2,2'-Pyridil (1 g, 5 mmol) was added to an aqueous solution (20 mL) of hydroxylamine hydrochloride (1.3 g, 19 mmol) and sodium hydroxide (4 g, 100 mmol) and stirred at ambient temperature for 40 h. Concentrated HCl was added until precipitate formed (pH ~ 4) then cooled in ice and filtered. Precipitate was with small amount of cold water to yield white product (0.4 g, 33%). ^1H NMR (500 MHz, DMSO- d_6) δ 11.69 (s, 1H), 8.60 (dt, J = 4.9, 1.4 Hz, 1H), 7.84 (td, J = 7.7, 1.8 Hz, 1H), 7.49 (dt, J = 7.8, 1.2 Hz, 1H), 7.39 – 7.28 (m, 1H).



MC2

Hydrazine hydrate (3.5 mL, 109 mmol) was dissolved in ethanol (10 mL) and 3,4-hexadione (4 g, 35 mmol) added dropwise with stirring. Upon addition the solution was heated at reflux for three hours. After cooling to $\sim 0^\circ\text{C}$ for several hours the precipitate was collected, washed with cold ethanol and dried *in vacuo* to yield a slightly yellow crystalline solid (1.9 g, 38%). ^1H NMR (500 MHz, DMSO- d_6) δ 6.14 (s, 2H), 2.41 (q, $J = 7.5$ Hz, 2H), 0.86 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 148.4, 15.1, 9.7.

[Co(GL2)₂(py)Cl]

The complex was synthesized by a modified procedure previously described.^{7, 8} Cobalt (II) chloride (1 g, 8 mmol) and diethylglyoxime (2.2 g, 16 mmol) were dissolved in ethanol (50 mL) and heated to reflux for 30 min. Pyridine (1.3 mL, 16 mmol) was added and the solution was cooled to room temperature then bubbled with air for 20 min. After evaporation of the solvent, the product was extracted with dichloromethane, and the organic layer was dried over anhydrous magnesium sulfate. The product obtained after removal of dichloromethane was recrystallized in acetone/ether mixture (0.33 g, 9%). ^1H NMR (500 MHz, CDCl_3) δ 8.28 – 8.22 (m, 1H), 7.71 (tt, $J = 7.6, 1.4$ Hz, 0H), 7.25 – 7.18 (m, 1H), 2.85 (dq, $J = 13.4, 7.6$ Hz, 2H), 2.72 (dq, $J = 13.4, 7.5$ Hz, 2H), 1.05 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.8, 150.8, 139.1, 125.5, 20.3, 10.5.

[Co(GL3)₂(py)Cl]

The complex was synthesized by a modified procedure previously described.^{7, 8} Cobalt (II) chloride (0.5 g, 4 mmol) and 3-methylcyclopentane-1,2-dione dioxime (1 g, 7.5 mmol) were dissolved in ethanol (25 mL) and heated to reflux for 30 min. Pyridine (0.6 mL, 8 mmol) was added and the solution was cooled to room temperature then bubbled with air for 20 min. After evaporation of the solvent, the product was extracted with dichloromethane, and the organic layer was dried over anhydrous magnesium sulfate. The product obtained after removal of dichloromethane was recrystallized in acetone/ether mixture (0.25 g, 14%). ^1H NMR (500 MHz,

CDCl₃) δ 8.31 – 8.22 (m, 2H), 7.83 – 7.72 (m, 1H), 7.34 – 7.27 (m, 2H), 3.40 – 3.28 (m, 1H), 3.22 – 3.11 (m, 1H), 2.93 (dddt, J = 43.5, 18.4, 9.1, 5.9 Hz, 2H), 2.80 – 2.63 (m, 2H), 2.56 – 2.46 (m, 1H), 2.37 (dtdd, J = 17.6, 8.9, 6.3, 2.9 Hz, 1H), 2.00 – 1.89 (m, 1H), 1.83 – 1.71 (m, 1H), 1.41 (dd, J = 7.2, 5.4 Hz, 3H), 1.26 – 1.10 (m, 3H). Mixtures of isomers complicate the ¹³C spectra. ¹³C NMR (126 MHz, CDCl₃) δ 163.98, 163.88, 163.79, 163.61, 163.59, 163.39, 160.0, 159.73, 159.67, 159.64, 159.45, 151.6, 151.5, 151.4, 139.29, 139.22, 139.15, 125.86, 125.84, 125.80, 125.78, 125.76, 33.84, 33.81, 33.77, 33.74, 33.62, 33.60, 33.58, 33.56, 33.54, 33.51, 33.49, 24.64, 24.61, 24.60, 24.57, 24.54, 16.66, 16.64, 16.19, 16.17.

Photoreactor setup

Our photoreactors, as previously described,^{9, 10} comprise a reactor plate of 96 or 108 wells for 1.1 mL shell vials illuminated from below with 440 nm light emitting diodes. Hydrogen production was measured using a colorimetric hydrogen sensitive tape (DetecTape Hydrogen Detection Tape – Midsun Specialty Products, Item DT-H210015-PF4). Images of the plate and tape were taken throughout the reaction under white light at ten minute intervals for at least 970 minutes. Image data processing was conducted using Wolfram Mathematica by calibration of tape darkness aligned with each vial to known H₂ concentrations. Maximum H₂ produced in μ mol, maximum rate (derivative) of H₂ production, and incubation time can be determined and kinetic traces of H₂ production over time can be constructed.

Reaction vials contained 650 μ L of total solution volume; once solution water fraction was optimized, this included 130 μ L of a 30% (w/w) TEOA in water solution and 520 μ L of 2-ethoxyethanol.

Reaction optimization data

Water fraction was optimized by adding a fixed amount of concentrated TEOA in water and varying volumes of pure water. WRC and EY concentration were optimized by varying the volume of concentrated stock solution added and diluting to volume with pure ethoxyethanol.

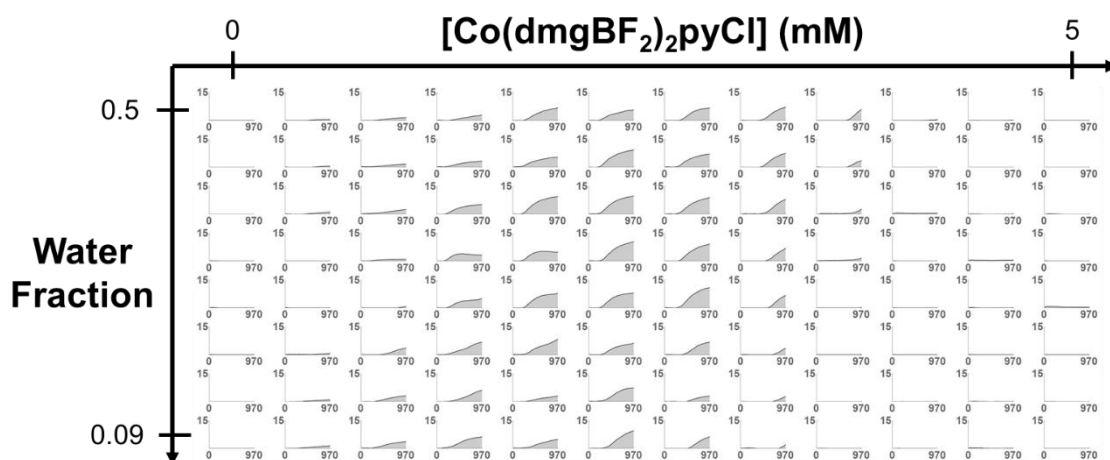


Figure S1: Hydrogen (μmol) produced over time (minutes) in each reaction well for varying cobalt catalyst concentration (increasing across rows) and water fraction (decreasing down column).

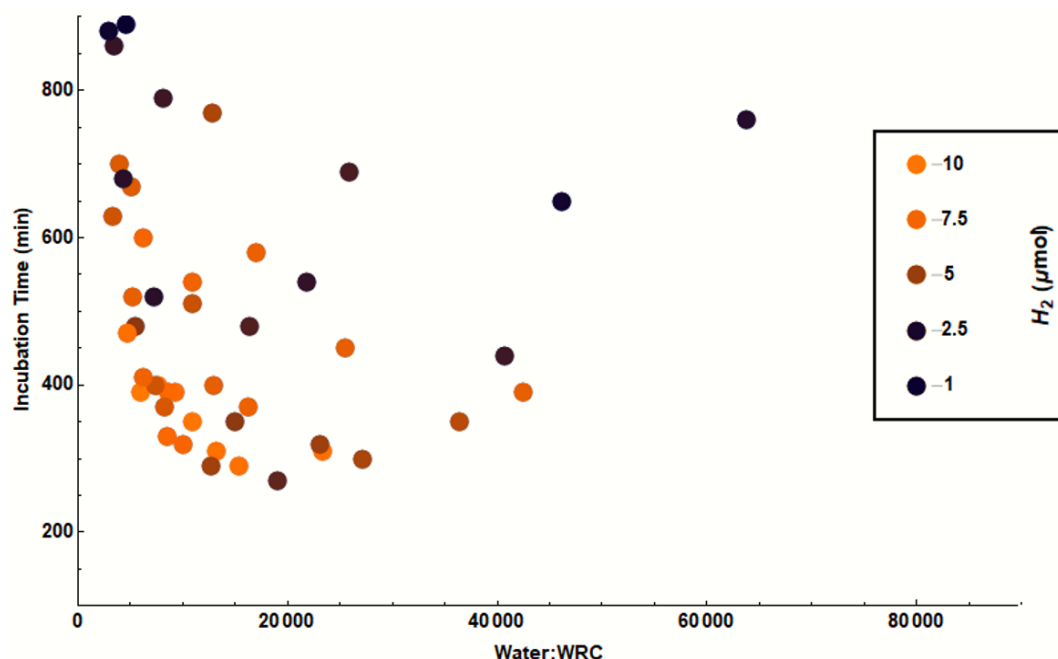


Figure S2: WRC and water optimization expressed as water to cobalt complex mole ratio demonstrating a minimum in incubation time at approximately 20,000 and the most productive systems appearing at 7,000. Incubation times measured were the first timestamp where the system surpassed 1.5 μmol of H_2 and remained above that threshold for at least the next 30 minutes. This period is meant to demonstrate how long the reaction is being illuminated prior to beginning a significant production of H_2 .

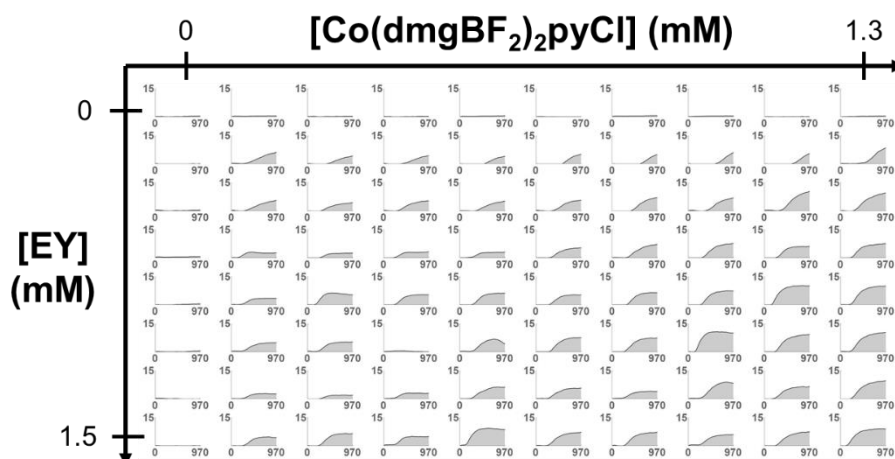


Figure S3: Hydrogen (μmol) produced over time (minutes) in each reaction well for varying cobalt catalyst concentration (increasing across rows) and Eosin Y concentration (increasing down column).

Reaction solution pH was optimized by substituting varying portions of the water fraction with concentrated potassium hydroxide or hydrochloric acid. pH of solution mixtures using the average WRC concentration at approximately 7x scale of reaction vials was measured prior to irradiation using a pH meter connected to an Arduino.

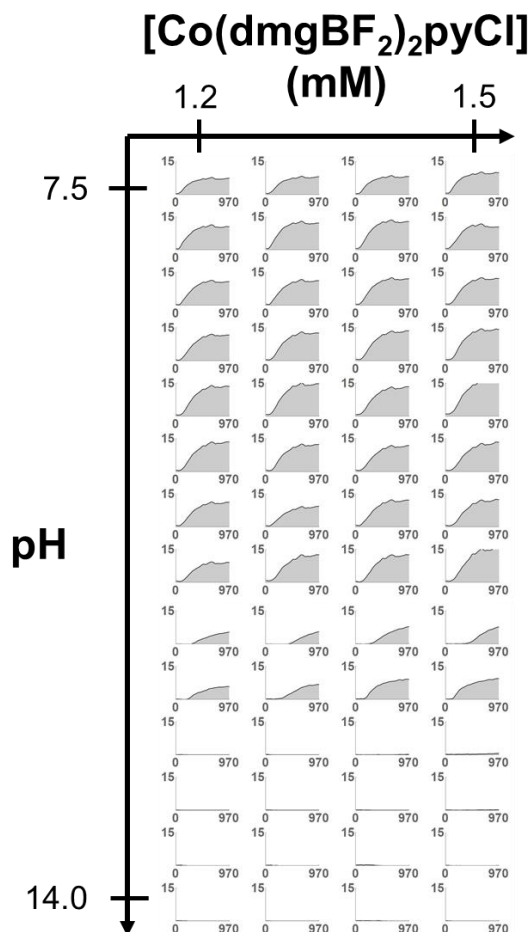


Figure S4: μmol hydrogen produced over time (minutes) for each reaction well for plate varying cobalt catalyst concentration (increasing across rows) and pH (increasing down column).

Uniform plate data

The reaction tested used 0.6 mM Eosin Y, 1.2 mM [Co(**GL1**BF₂)₂pyCl], and 130 μ L of a 30% (w/w) TEOA in water solution and was a total of 650 μ L in volume. Stock solutions were mixed together before being pipetted into the wells to ensure the concentrations were constant across the plate. The resulting traces of generated hydrogen can be seen in **Figure S5** (data points every 10 min)

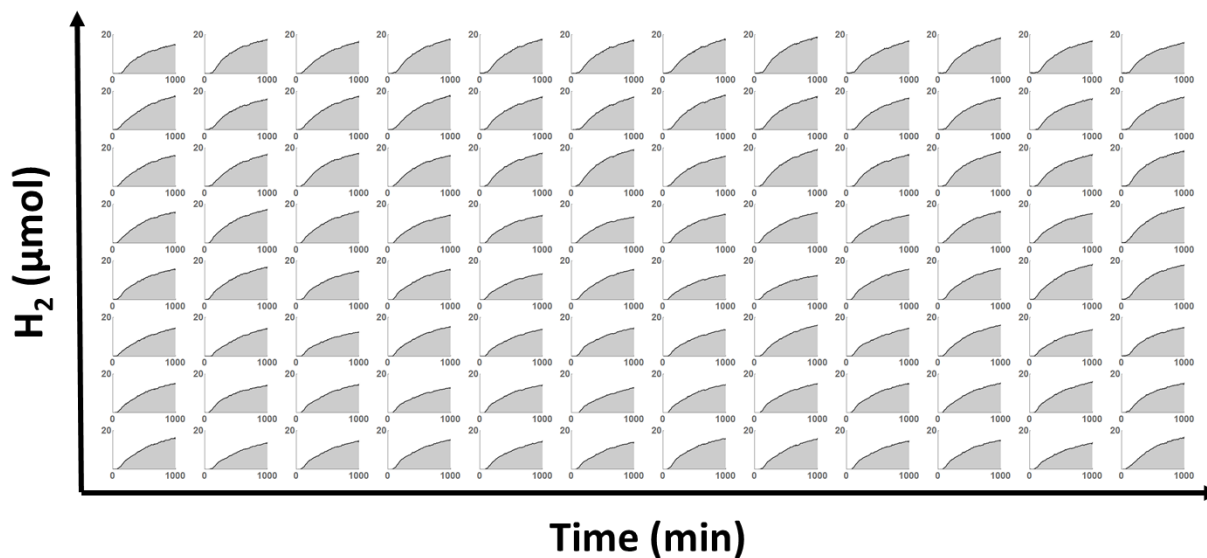


Figure S5. Traces of H₂ evolution from a uniform plate using EY and [Co(**GL1**BF₂)₂pyCl], tested at determined optimized reaction conditions.

Control reactions

Reactions tested included 0.6 mM Eosin Y, 1.2 mM [Co(**GL1**BF₂)₂pyCl], and 130 μ L of a 30% (w/w) TEOA in water solution and was a total of 650 μ L in volume and were irradiated for 1000 minutes. Traces of the reaction of hydrogen produced over time without EY, without the WRC, and without exposure to light compared to that of the optimal reaction conditions are shown in **Figure S6**.

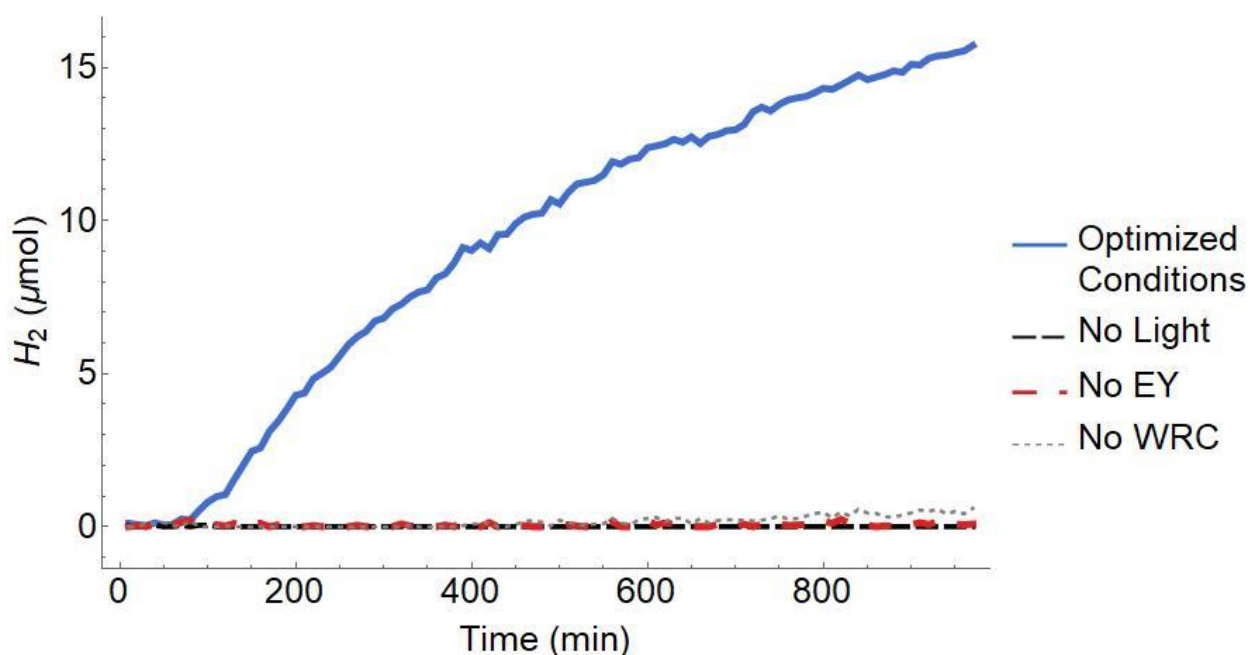


Figure S6: Negative controls kinetic traces; without light, photosensitizer, or co-catalyst, the system is unproductive.

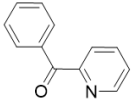
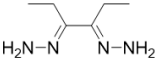
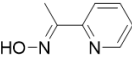
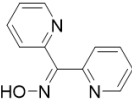
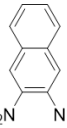
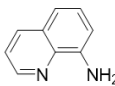
Ligand screening

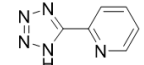
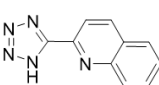
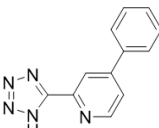
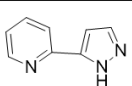
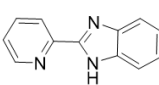
Novel WRC complexes were synthesized *in situ* and screened via our photoreactors. Appropriate equivalents of cobalt chloride, ligand, and pyridine solutions in 2-ethoxyethanol were added in aliquots to reaction vials, with approximately 10 minutes to stand after addition of ligand(s) and after addition of pyridine. Subsequently, EY in solution with 30% TEOA in water was pipetted in and reactions were run.

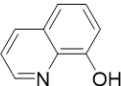
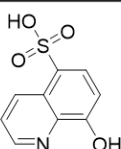
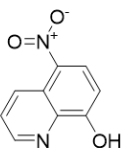
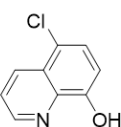
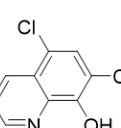
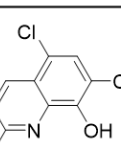
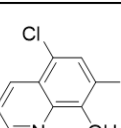
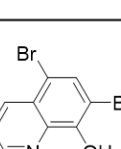
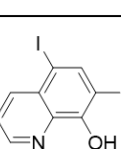
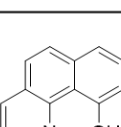
Table S1: Ligand screening of [Co(LL)₂pyCl] complexes, with maximum H₂ production in micromoles for reactions run at optimal conditions for 1000 minutes

Ligand	Structure	H ₂ (μmol)	TON	TOF
GL1		15.6	20.0	9.7
GL2		13.4	17.2	8.3
GL3		7.1	9.1	3.9
GL4		12.2	15.6	7.2
GL5		1.1	1.4	0.6
GL6		3.3	4.2	1.7
GL7		0.2	0.3	0.0
GL8		0.2	0.3	0.0
GL9		0.5	0.6	0.1
GL10		0.3	0.4	0.0
GL11		0.2	0.3	0.0
GL12		0.3	0.4	0.0
GL13		0.3	0.4	0.0
GL14		0.3	0.4	0.0
GL15		0.3	0.4	0.0
G16		0.3	0.4	0.0

Ligand	Structure	H ₂ (μmol)	TON	TOF
BP1		0.3	0.4	0.0
BP2		0.7	0.9	0.3
BP3		0.4	0.5	0.0
BP4		0.5	0.6	0.0
BP5		0.3	0.4	0.0
BP6		0.8	1.0	0.1
BP7		0.4	0.5	0.0
BP8		0.6	0.8	0.0
BP9		0.5	0.6	0.1

Ligand	Structure	H ₂ (μmol)	TON	TOF
MC1		0.5	0.6	0.1
MC2		0.0	0.0	0.0
MC3		0.0	0.0	0.0
MC4		0.0	0.0	0.0
MC5		0.5	0.6	0.0
MC6		0.3	0.4	0.0

Ligand	Structure	H ₂ (μmol)	TON	TOF
NH1		0.2	0.3	0.0
NH2		0.4	0.5	0.1
NH3		0.1	0.1	0.0
NH4		0.3	0.4	0.0
NH5		0.2	0.3	0.0

Ligand	Structure	H ₂ (μmol)	TON	TOF
HQ1		0.3	0.4	0.0
HQ2		0.4	0.5	0.0
HQ3		0.4	0.5	0.0
HQ4		0.1	0.1	0.0
HQ5		0.4	0.5	0.0
HQ6		0.2	0.3	0.1
HQ7		1.0	1.3	0.3
HQ8		0.4	0.5	0.0
HQ9		0.2	0.3	0.0
HQ10		0.4	0.5	0.0

Gas chromatography data

Larger scale reactions were performed for a select set of WRCs (Table S2), as additional confirmation of the consistency of the *in situ* synthesized complexes. Reaction conditions were the same as parallel synthesis and reactivity, but all volumes were increased tenfold. This meant a total solution volume of 6.5 mL, containing 0.6 mM Eosin Y, 1.2 mM WRC, and 1.3 mL of 30% (w/w) TEOA in water. Each vial was sealed (leaving 1 atm of ambient air pressure as an internal standard) and illuminated by blue LEDs (460 nm, 500 +/- 50 mW, Luxeon V Dental Blue, Future Electronics and Fraen, FHS-HNB1-LL01-H) and agitated at 100 rpm (IKA, KS 260 Orbital Shaker) over the course of 10 hours. The reaction was then removed from the light and agitation and 1 mL was removed from the headspace in the vials (Hamilton SampleLock Syringe) and injected into a flow of Argon in the Gas Chromatograph (Perkin-Elmer 3920 chromatograph with Alltech 13X 80/100 mesh molecular sieve column, thermal conductivity detector). Pure ambient pressure H₂ was used for calibration at the injection volumes listed in Table S2.

Table S2: Gas chromatography of select WRCs at 10x scale of screen

Identity	Hydrogen Production (μmoles)
[Co(GL1) ₂ pyCl]	458
[Co(GL2) ₂ pyCl]	404
[Co(GL1BF ₂) ₂ pyCl]	352
Co(GL3) ₂	0
CoCl ₂	0
No WRC	0

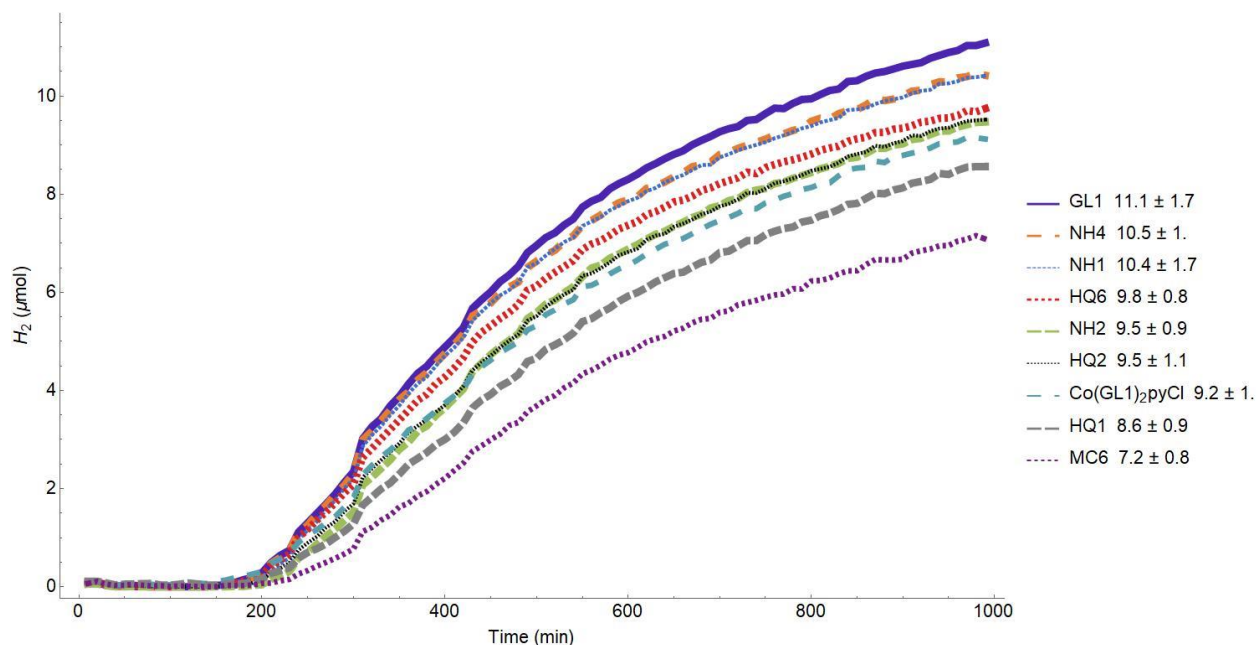


Figure S7: Traces of select WRC averaged over 12 replicates with average maximum hydrogen evolved; ligand listed in legend was combined with **GL1** *in situ*, and [Co(**GL1**)₂pyCl] was synthesized externally.

Mercury Poisoning Testing Data and Images

Mercury Poisoning Test Protocol for Parallel Reactor

Solutions were made for presynthesized WRCs [Co(**GL1**BF₂)₂pyCl] and [Co(**GL1**)₂pyCl] in 2-ethoxyethanol to a concentration of 1.6 mM. A solution of Eosin Y in 2-ethoxyethanol was made to a concentration of 2.4 mM, and a TEOA solution in water was made to a mass percent of 30% TEOA. To each well in the parallel reactor, 390 microliters of WRC, 130 microliters of Eosin Y, and 130 microliters of TEOA solution were added in that respective order. To a series of these wells, a few drops of liquid mercury were added. The plate was capped according to previously reported protocol and illuminated over blue LEDs for 1000 minutes.

Mercury Poisoning Test Protocol for GC Measured mL Scale Testing

Solutions were made for presynthesized WRCs [Co(**GL1**BF₂)₂pyCl] and [Co(**GL1**)₂pyCl] in 2-ethoxyethanol to a concentration of 1.6 mM. A solution of Eosin Y in 2-ethoxyethanol was made to a concentration of 2.4 mM, and a TEOA solution in water was made to a mass percent of

30% TEOA. To each 20 mL EPA vial, 3.9 mL of WRC, 1.3 mL of Eosin Y, and 1.3 mL of TEOA solution were added in that respective order. To an EPA vial of each WRC, 5 to 6 grams of liquid mercury were added. The vials were sealed and illuminated over blue LEDs and agitated at 100 rpm for 24 hours. Measurement was taken after the completion of illumination according to the GC procedure communicated above with greater Ar pressure to reduce effluence times.

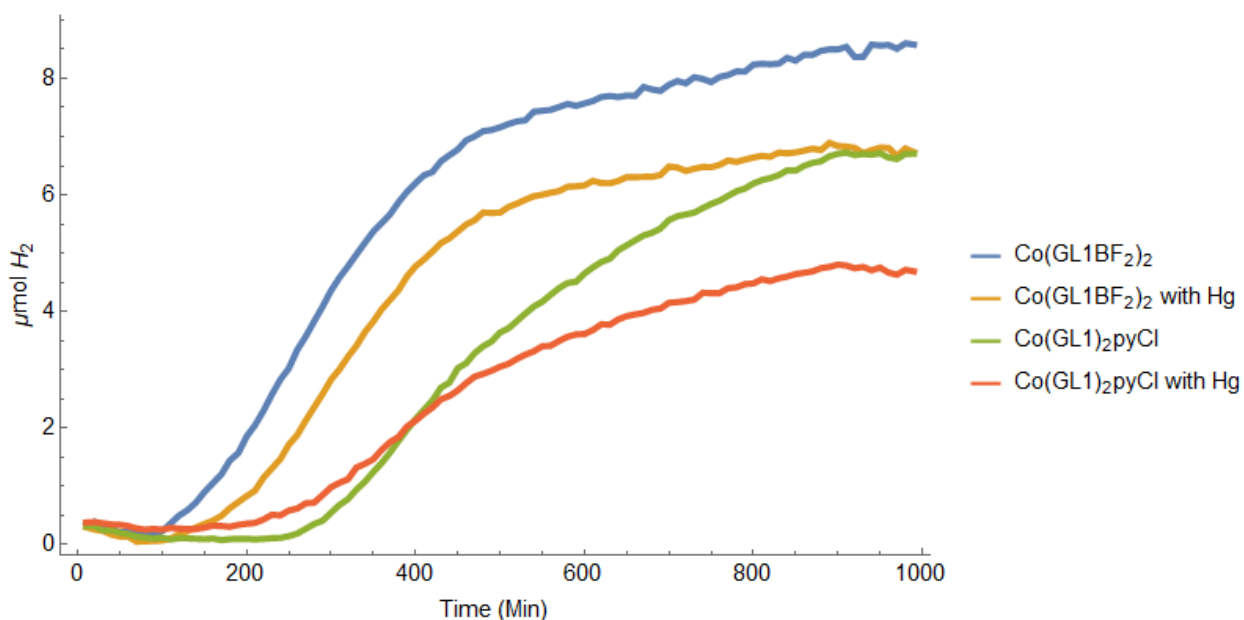


Figure S8: Traces from Mercury Poisoning Testing in parallel reactor. Traces of [Co(**GL1**BF₂)₂pyCl] and [Co(**GL1**)₂pyCl] each represent averages of 6 replicates, [Co(**GL1**)₂pyCl] with Hg represents an average of 5 replicates, and [Co(**GL1**BF₂)₂pyCl] represents an average of 3 replicates.

Table S3: Gas chromatography of Mercury Poisoning Testing at 10x scale of screen.

Identity	Hydrogen Production (μmoles)
[Co(GL1BF ₂) ₂ pyCl]	261
[Co(GL1BF ₂) ₂ pyCl] w/ Hg	252
[Co(GL1) ₂ pyCl]	240
[Co(GL1) ₂ pyCl] w/ Hg	180



Figure S9: Images of mercury testing vials and wells after completing illumination, retained appearance of the pure mercury indicates the complete lack of amalgam formation. *Top-Left;* Reaction vial containing $[\text{Co}(\text{GL1})_2\text{pyCl}]$ after 24 hours of illumination. *Top-Right:* Reaction well containing $[\text{Co}(\text{GL1})_2\text{pyCl}]$ after 1000 minutes of illumination. *Bottom:* Images taken from above and underneath the 108 well plate containing samples of $[\text{Co}(\text{GL1BF}_2)_2\text{pyCl}]$ (Left three columns), and $[\text{Co}(\text{GL1})_2\text{pyCl}]$ (Right 5 columns). Top row does not contain mercury, bottom row represents several small drops being added to each well (approx. 50 microliters).

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