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Supporting Information

Cobalt Complexes of Tetradentate, Bipyridine-Based Macrocycles; their Structures, Properties and Photocatalytic Proton Reduction

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1 Materials and Methods

General: All reactions were carried out under nitrogen atmosphere on a standard nitrogen/vacuum line unless otherwise stated. The glassware was dried by the use of a heat gun or in an oven at 120 °C at least overnight. Commercially available reagents were purchased reagent-grade and used without further purification. $CoBr_2$ hydrate was purchased from *Acros Organics* and used directly. Co(acetate)$_2$ tetrahydrate (> 99 %) was purchased from *Sigma Aldrich*. Solvents for reactions were purchased in *p. a.* quality. For extractions or column chromatography normally distilled technical solvents were used. Water for reactions, extractions and catalysis experiments was deionized and doubly distilled prior to usage. Dry DMF was purchased from *Acros* (99.8 %, extra-dry) and dry pyridine (anhydrous, 99.8 %) was purchased from *Sigma Aldrich* and used without further drying. All final products were dried under reduced pressure (at least 10^{-3} mbar) before analytical characterization. Reactions were monitored for completion by analyzing a small sample (after suitable workup) by thin-layer chromatography (TLC) or high-performance-liquid chromatography (HPLC). TLC was carried out on aluminum plates coated with SiO_2-60 UV$_{254}$ from *Merck*. The spots were visualized by UV light at 254 nm and 365 nm. Column chromatography was performed using SiO_2-60 (0.063–0.200 mm. 70–230 mesh ASTM; *Merck*) on normal phase.

HPLC: Measurements were performed on a *VWR Hitachi Elite LaChrome* equipped with a column from *Phenomenex* (Kinetex, reversed phase (C_{18}), 2.6 µm particle size, 100 Å pore size, 75 x 4.6 mm) operated in an oven (*L-2350*) at 40 °C and a PDA detector (*L-2450*). The eluent was a mixture of H_2O/MeOH/TFA (gradient starting with 10 % MeOH, 0.1 % TFA in H_2O to 0.1 % TFA/pure MeOH).

NMR: Spectra for the characterization of the novel complexes **1a**–**4b** were not recorded due to their paramagnetic properties.

Mass Spectra (MS): The samples were dissolved in an appropriate solvent at a concentration of around 1 µmol/mL and measured at a continuous flow of 3 µL/min. The *Bruker maXis QTof* high-resolution mass spectrometer (*Bruker GmbH*, Bremen, Germany) was operated in the positive or negative electrospray ionization mode at 4'000 V capillary voltage, -500 V endplate offset, with a N_2 nebulizer pressure of 0.8 bar and dry gas flow of 4 L min^{-1} at 180 °C. MS acquisitions were performed in the mass range from m/z 50 to 2'000 at 20'000 resolution (full width at half maximum) and 1.0 Hz spectra rate. Masses were calibrated prior analysis and below 2 ppm accuracy between *m/z* 158 and 1450 with a 2 mM solution of sodium formate or between *m/z* 118 and 2721 with a *Fluka* electrospray calibration solution (*Sigma-Aldrich*, Buchs, Switzerland) that has been 100 times diluted with acetonitrile, respectively.

Elemental Analysis (EA): Measurements were performed on a *LecoCHNS-932* elemental analyzer at the University of Zürich, Switzerland.

IR: Spectra were recorded neat by ATR on a *Perkin-Elmer FT-IR Spectrum Two s*pectrometer.

UV/vis: Spectra were recorded on a *Varian Cary 50 Scan* or a *Perkin Elmer Lambda 35* in 1 cm quartz cuvettes. For the measurements for photostability also 1 cm plastic cuvettes were used. For all new compounds the absorption maxima are given; *sh* means shoulder.

Electrochemistry: Differential pulse voltammetry (DP) and cyclic voltammetry (CV) were operated on a *Methrom 757 omputrace* with a glassy carbon electrode (GC; d = 2 mm) or a hanging mercury drop electrode (HMDE; *Metrohm* Multi-Mode Electrode Pro, drop size of 0.15–0.60 mm^2), and a Pt counter electrode versus Ag/AgCl reference electrode. The electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate in DMF or the *Britton Robinson* buffer[1] (0.04 M H_3BO_3, 0.04 M H_3PO_4, 0.04 M CH_3COOH) in water. DP voltammograms were recorded at a scan speed of 15 mV/s (voltage step of 6 mV; $\Delta E = 50$ mV; pulse time 40 ms and voltage step time 400 ms) and CV voltammograms at 100 mV/s. The voltammograms measured in the *Britton Robinson* buffer were referenced to SHE (by measuring $K_3[Fe(CN)_6]$; 430 mV vs. NHE[2] or to ferrocene (in the case of tetrabutylammonium hexafluorophosphate in DMF) by adding the mentioned references to the analyte in the same setup at the end of the measurements.

Magnetization: Measurements were performed with a Quantum Design magnetic properties measurement system (MPMS XL 7 T) equipped with a 7 T magnet and a reciprocating sample option (RSO). The samples were fixated in gelatin capsules to ensure a stable measurement setting with only a minor background signal. The measurements were performed in magnetic fields of 0.1 T and 1 T and in a temperature range between 5 K and 300 K.

X-ray Crystallography: Crystallographic data were collected at 183(2) K with either Mo K_α radiation ($\lambda = 0.7107$ Å) or Cu K_α radiation ($\lambda = 1.54184$ Å). Compounds **3**, **3a** and **4a** were measured on an *Agilent SuperNova*, dual source, with an Atlas detector while compounds **2a** and **5** were measured on an *Oxford Diffraction CCD Xcalibur* system with a Ruby detector. Suitable crystals were covered with oil (*Infineum V8512*, formerly known as *Paratone N*), placed on a nylon loop that is mounted in a *CrystalCap Magnetic*™ (*Hampton Research*) and immediately transferred to the diffractometer. Data were corrected for Lorentz and polarisation effects as well as for absorption (numerical). The program suite *CrysAlis^{Pro}* was used for data collection, multi-scan absorption correction and data reduction.[3] Structures were solved with direct methods using *SIR97*[4] and were refined by full-matrix least-squares methods on F^2 with *SHELXL-97*.[5] The structures were checked for higher symmetry with help of the program *Platon*.[6] CCDC 1434720-1434724 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Computational Methods: The structural and energetic analyses of the molecular systems described in this study were carried out with the BP86[7] and B3P863[8] density functional methods, using an ultrafine grid, together with the Def2-TZVPP basis set.[9] Full geometry optimizations were performed and uniquely characterized via second derivatives (Hessian) analysis to establish stationary points and effects of zero point and thermal corrections. Effects of solvent were included using a cluster-continuum solvation model, where the continuum model is based the original COSMO theory of *Klamt* modified for *ab initio* theory, [10, 11] with a dielectric for DMF and for water. Excited state structure and properties were carried out using B3P86/Def2-TZVPP//BP86/Def2-TZVPP (H_2O) using TD-DFT.[12] Reduction potentials were determined at the BP86/Def2-TZVP (DMF) level using $E° = -\Delta G/nF - E_{ref}$, where $n = 1$, $F = 1$ eV, $E_{ref} = 4.98$. Visualization and analysis of structural and property results were obtained using *Avogadro*.[13]

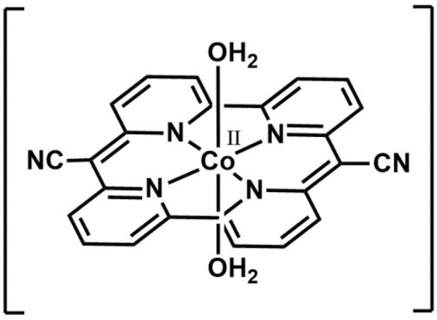
Hydrogen Evolution Measurements: Gas chromatograms were recorded on a *Bruker 450 or Bruker 456 GC* gas chromatograph by using argon as carrier gas (20 mL/min for both reference and sample), a column of 3 m x 2 mm packed with molecular sieves 13X 80-100, an oven operated isothermally at 100 °C and a thermal conductivity detector operated at 150 °C. Automated measurements were performed as described previously (see also Scheme SI1).[14, 15] This setup allowed the detection of H_2 to $2\cdot10^{-5}$ (mole fraction) for GC-450 and $2\cdot10^{-6}$ for GC-456, respectively. At Ar flows of 6 mL/min through the reaction the detection limit was $H_2/s \geq 1\cdot10^{-10}$ for GC-450 or $\geq 1\cdot10^{-11}$ mol s^{-1} for GC-456, respectively. Sample preparation for catalysis was performed by mixing NaHasc (final concentration 0.1 M), TCEP (final concentration 0.1 M), the PS $[Ru(bpy)_3]Cl_2 \cdot 5\ H_2O$ (final concentration 500 µM) and the corresponding WRC (compounds **2a**, **2b**, **3a**, **3b**, **4a** and **4b**, final concentrations of 1, 2, 5 and 10 µM, respectively) in water (approximately 5 mL), and the mixture was titrated (pH-meter from *Mettler Toledo SevenEasy* with an *InLab Semi-Micro pH* electrode) with NaOH (1 M) to a pH of 5 (variation between pH 4.9 and 5.1). At the end H_2O was added to a total reaction volume of 10 mL. Compound **1a** was added as solid (175 µM) due to the insolubility in water. An HPLC sample was measured. The reaction vessel was connected to the Ar line with a controlled flow of 6.0 ± 0.15 mL/min and directly degassed under stirring. The dried purge gas was analyzed by the GC, and when oxygen and nitrogen had been vanished from the solution irradiation with an LED lamp (453 nm, 80 ± 5 mW, photon flux of 0.30 ± 0.02 µE/s) was started from the bottom of the reaction vessel. Hydrogen evolution was continuously monitored by GC. After catalysis the pH of the reaction mixture was measured and an HPLC sample was recorded. Conversions in TCEP were directly measured from the reaction solution by ^{31}P NMR spectroscopy (200 MHz *Varian Mercury* or 300 MHz *Varian Gemini-2000* spectrometer): 15.7 ppm (broad singlet, $[R_3\mathbf{P}\text{-}H]^+$); 56.1 ppm (singlet, $R_3\mathbf{P}{=}O$).

2 Experimental Procedures (Syntheses of 1a, 2a, 2b, 3a, 3b, 4a, 4b)

Ligands **1**, **2**, **3**, **4** and **5** were prepared as described in the literature.[16] Alkylation of **1** afforded a mixture of **2**, **3** and **4**, which was challenging to separate. The optimized procedure for the separation of this mixture is reported here: Column chromatography of the mixture was conducted on SiO_2 with an eluent gradient of CH_2Cl_2/MeOH (100:0) → CH_2Cl_2/MeOH (90:10). Addition of NEt_3 to the eluent did not improve the yields. Compound **2** was eluted first and purely, while the second fraction, **4**, was contaminated with **2**. The third fraction, **3**, was contaminated with an unidentifiable species. A fourth fraction was eluted, which turned out to be protonated **3** as triiodide salt. The dibutyl-species **3** and **4** were finally purified by repeated recrystallization in acetone and EtOH. Interestingly, on reversed phase (C_{18}) HPLC, the order of elution was not inverted but as follows: **4** was eluted first, then **3**, and finally **2**.

In the following, the syntheses of Co^{II} complexes **1a**, **2a**, **2b**, **3a**, **3b, 4a** and **4b** are described, also giving the experimental details.

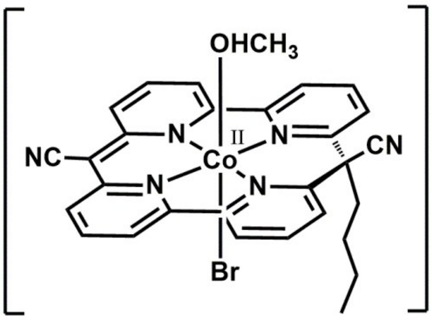
[$Co^{II}(OH_2)_2$(pyr)] (1a):



A suspension of pyrphyrin (**1**) (100 mg, 0.26 mmol) in pyridine (60 mL) was treated with $KO^{t}Bu$ (58 mg, 0.52 mmol) and sonicated for 2 h at 70 °C to afford an orange brown solution. The solution was filtered under exclusion of air and Co(acetate)$_2$ tetrahydrate (72 mg, 0.29 mmol) was then added to instantaneously give a black green solution. The mixture was heated to 100 °C and stirred for 2 h, then heating was stopped and the mixture was cooled to 25 °C. 10 mL water was added to quench the reaction. The dark green solution slowly turned dark red. The solvent was removed under reduced pressure to afford a black solid with low solubility. Water (150 mL) was used to suspend (10 min sonicated) the black solid. The suspension was heated to reflux and stirred overnight to purify the product. The suspension was rigorously washed with water to afford **1a** as a black solid (111 mg, 0.23 mmol, yield: 89 %).

IR (ATR): $\tilde{\nu} \approx$ 3079 (w), 2923 (w), 2851 (w), 2169 (m), 1672 (w), 1672 (w), 1600 (m), 1559 (s), 1547 (m), 1466 (s), 1415 (s), 1366 (m), 1307 (m), 1288 (m), 1246 (s), 1220 (m), 1182 (s), 1112 (w), 1066 (w), 1036 (m), 1017 (m), 993 (m), 869 (w), 780 (s), 758 (m), 734 (m); **HR-ESI-MS**: *m*/*z* (%): 443.0445 (100, $[M - 2\,H_2O]^+$, calcd for $[C_{24}H_{12}CoN_6]^+$: 443.0450), 459.0395 (21, $[(M_2 - 2\,H_2O + O\,]^+$, calcd for $[C_{24}H_{12}CoN_6O]^+$: 459.0399); **SQUID**: T_C (Θ) ≈ -3.93 K, $\mu_{eff} \approx 1.85\ \mu_B$; **EA**: calcd (%) for $[C_{24}H_{16}CoN_6O_2]$ (479.36): C 60.13; H 3.36, found: C 60.06; H 3.052.

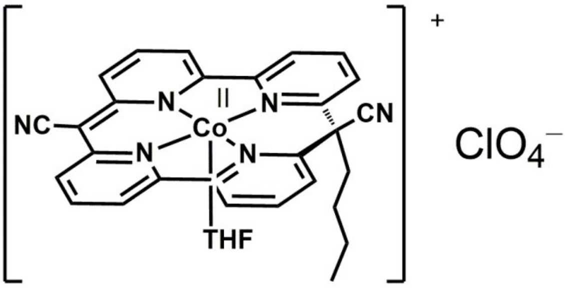
[Co^{II}Br(HOMe)(pyr-bu)] (2a):



A suspension of **2** (70 mg, 0.16 mmol), $CoBr_2$ hydrate (57 mg, 0.17 mmol) and 1M NaOH (158 µL, 0.16 mmol) in MeOH (20 mL) was stirred for 2 d at reflux. The obtained dark red suspension showed complete conversion according to HPLC, therefore the heating and stirring were stopped. The mixture was cooled to 25 °C, filtered and washed with water to yield **2a** as a black solid (76 mg, 0.13 mmol, yield: 83 %). Small dark red single crystals suitable for X-ray analysis were obtained by vapour diffusion with acetone as solvent and isopropyl ether as antisolvent.

IR (ATR): $\tilde{\nu} \approx$ 3059 (w), 2953 (w), 2926 (w), 2860 (w), 2323 (w), 2171 (m), 1983 (w), 1603 (s), 1572 (m), 1558 (m), 1542 (w), 1474 (s), 1447 (s), 1419 (s), 1372 (m), 1310 (m), 1287 (m), 1249 (m), 1220 (m), 1181 (m), 1169 (m), 1101 (w), 1014 (m), 985 (m), 939 (w), 905 (w), 782 (s), 746 (m), 727 (w) cm^{-1}; **UV/vis** (H_2O): λ_{max} (ε, M^{-1} cm^{-1}) ≈ 293 (18770, *sh*), 381 (8980), 472 nm (3676); **HR-ESI-MS**: *m*/*z* (%): 500.1160 (100, $[M - Br - CH_3OH]^+$, calcd for $[C_{28}H_{21}CoN_6]^+$: 500.1154), 1079.1502 (10, $[(M_2 - Br - 2\ CH_3OH)_2]^+$, calcd for $[C_{56}H_{42}Co_2N_{12}Br]^+$: 1079.1497); **SQUID**: T_C (Θ) ≈ -3.48 K, $\mu_{eff} \approx 3.52\ \mu_B$; **EA**: calcd (%) for $[C_{29}H_{25}BrCoN_6O]$ (580.34): C 56.88; H 4.11; N 13.72, found: C 56.73; H 3.97; N 13.65.

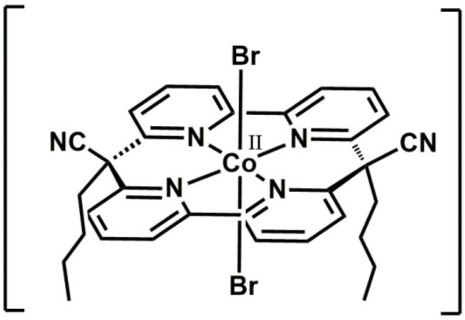
[Co^{II}(THF)(pyr-bu)][ClO_4] (2b):



A suspension of **1** (25 mg, 0.056 mmol), $Co(ClO_4)_2$ hexahydrate (25 mg, 0.068 mmol) and 1 M NaOH (56 µL, 0.056 mmol) in 10 mL MeOH was stirred for 4 d at reflux. Complete conversion to a winered solution was observed by HPLC. Heating and stirring was stopped and the solvent was removed under reduced pressure. Then, the crude black product was dissolved in MeOH (7 mL), and THF (10 mL) was added. After removing of the solvent, the resulting black powder was washed with water and filtered to obtain **2b** as black red solid (20 mg, 0.030 mmol, yield: 53 %).

IR (ATR): $\tilde{\nu} \approx$ 3520 (w), 3094 (w), 2953 (m), 2923 (m), 2853 (m), 2176 (m), 1604 (m), 1563 (m), 1543 (w), 1476 (s), 1456 (s), 1421 (s), 1378 (m), 1308 (w), 1252 (m), 1225 (w), 1186 (m), 1080 (s), 1020 (s), 992 (m), 911 (w), 910 (w), 842 (w), 819 (w), 788 (s), 752 (w), 727 (w) cm^{-1}; **UV/vis** (H_2O): λ_{max} (ε, M^{-1} cm^{-1}) ≈ 294 (17478), 381 (9000), 483 (3623, *sh*); **(+)-HR-ESI-MS**: *m*/*z* (%): 500.1155 (73, [M – ClO_4 – THF]$^+$, calcd for [$C_{28}H_{21}CoN_6$]$^+$: 500.1154); **(-)-HR-ESI-MS**: *m*/*z* (%): 98.9489 (100, [ClO_4]$^-$, calcd for [ClO_4]$^-$: 98.9491), 220.8872 (20, [$(ClO_4)_2$ + Na]$^-$, calcd for [Cl_2O_8Na]$^-$: 220.8873); **EA**: calcd (%) for [$C_{32}H_{29}ClCoN_6O_5$]·(672): C 57.19, H 4.35, N 12.51; found C 57.48, H 4.38, N 12.52.

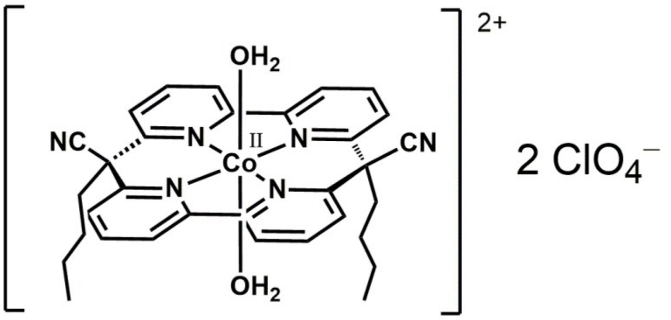
[Co^{II}Br$_2$(*cis*-pyr-bu$_2$)] (3a):



A suspension of **3** (37 mg, 0.073 mmol) in EtOH (4 mL) was stirred and heated to reflux. A solution of $CoBr_2$ hydrate (21 mg, 0.071 mmol) in EtOH (2 mL) was added and the reaction mixture immediately changed to a red solution. Reaction control by HPLC after 5 min showed almost complete conversion and stirring at reflux temperature was continued for 2 h. Heating and stirring were stopped, a dark red precipitate formed, and the suspension was slowly cooled to 25 °C. The mixture was cooled at -18 °C for 3 h, cold filtered over a glass frit (P4) and the precipitate first washed with a mixture of EtOH and Et_2O at 0 °C and then with Et_2O. Drying of the purified precipitate under reduced pressure yielded **3a** as a dark red powder (35 mg, 0.048 mmol, 66 % with respect to Co). The filtrate was concentrated under reduced pressure, dissolved in EtOH and precipitated with Et_2O to afforded further **3a** (9.1 mg, 0.013 mmol, 17 % with respect to Co). Single crystals suitable for X-ray analysis were obtained by covering a saturated KBr solution with an aqueous solution of **3a**.

IR (ATR): $\tilde{\nu} \approx$ 3054 (w), 3020 (w), 2959 (m), 2932 (m), 2869 (w), 2325 (w), 2245 (w), 2164 (w), 2108 (w), 2018 (w), 1910 (w), 1605 (s), 1584 (m), 1573 (m), 1473 (m), 1428 (s), 1394 (m), 1340 (w), 1316 (w), 1265 (m), 1223 (m), 1184 (w), 1157 (w), 1114 (w), 1034 (m), 1016 (w), 950 (w), 912 (w), 804 (s), 756 (m), 745 (m) cm^{-1}; **UV/vis** (H_2O): $\lambda_{\max}$ (ε, M^{-1} cm^{-1}) ≈ 213 (37'000, *sh*), 256 (17'000), 299 (26'100), 332 (5810, *sh*), 433 (1650, *sh*), 468 nm (2630); **HR-ESI-MS**: *m*/*z* (%): 715.0224 (3, $[M]^+$, calcd for $[C_{32}H_{30}Br_2CoN_6]^+$: 715.0225), 662.1074 (4, $[M - Br + CN]^+$, calcd for $[C_{33}H_{30}BrCoN_7]^+$: 662.1073), 636.1043 (97, $[M - Br]^+$, calcd for $[C_{32}H_{30}BrCoN_6]^+$: 636.1042), 592.1548 (9, $[M - 2\,Br + Cl]^+$, calcd for $[C_{32}H_{30}ClCoN_6]^+$: 592.1547), 278.5928 (24, $[M - 2\,Br]^{2+}$, calcd for $[C_{32}H_{30}CoN_6]^{2+}$: 278.5927); **SQUID**: T_C (Θ) ≈ -0.25 K, $\mu_{eff} \approx 4.61$ μ_B; **EA**: calcd (%) for $[C_{32}H_{30}Br_2CoN_6]\cdot\frac{1}{2}\,H_2O$ (726.4): C 52.91, H 4.30, N 11.57; found C 52.57, H 4.26, N 11.50.

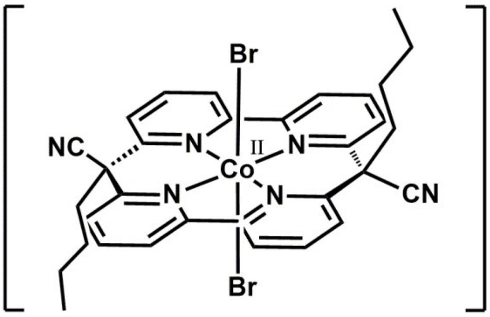
[$Co^{II}(OH_2)_2$(*cis*-pyr-bu$_2$)][ClO_4]$_2$ (3b):



To a suspension of **3** (14 mg, 0.028 mmol) in MeCN (4 mL) a solution of $Co(ClO_4)_2$ hexahydrate (8.2 mg, 0.022 mmol) in MeCN (1 mL) was added at 25 °C and the reaction mixture immediately changed to a yellow solution. Reaction control by HPLC after 4 h showed incomplete consumption of the ligand, thus, the mixture was heated to reflux for 19 h. As HPLC still showed presence of the ligand (ca. 30 % according to HPLC), further $Co(ClO_4)_2$ hexahydrate (in total 3.8 mg, 0.010 mmol), was added until almost full conversion of the reaction was observed. Heating and stirring were stopped, the mixture cooled to 25 °C, and the solvent was evaporated by a stream of N_2. The resulting dark yellow residue was dissolved in water (10 mL) and some drops of MeCN, heated to reflux and cooled to 25 °C overnight. The bright orange solution was filtered over a syringe filter to remove remaining, precipitated ligand. Lyophilisation of the aqueous filtrate gave **3b** as a yellow powder (15 mg, 69 % with respect to **3**).

IR (ATR): $\tilde{\nu} \approx$ 3104 (w), 2936 (w), 2870 (w), 2253 (w), 2164 (w), 2151 (w), 2052 (w), 2030 (w), 1985 (w), 1931 (w), 1835 (w), 1652 (w), 1606 (m), 1586 (w), 1482 (m), 1429 (m), 1401 (w), 1267 (m), 1230 (w), 1194 (w), 1101 (s), 1029 (s), 912 (m), 801 (m), 759 (w), 747 (w); **UV/vis** (H_2O): λ_{max} (ε, M^{-1} cm^{-1}) ≈ 257 (17'500), 300 (26'900), 334 (5470, *sh*), 435 (1680, *sh*), 469 nm (2720); **HR-ESI-MS**: *m/z* (%): 602.1842 (34, [$M - 2\ H_2O + HCOO$]$^+$, calcd for [$C_{33}H_{31}CoN_6O_2$]$^+$: 602.1835), 278.5930 (100, [$M - 2\ H_2O$]$^{2+}$, calcd for [$C_{32}H_{30}CoN_6$]$^{2+}$: 278.5927); **EA**: calcd. (%) for [$C_{32}H_{34}Cl_2CoN_6O_{10}$]·(792.5): C 48.50, H 4.32, N 10.60; found C 48.54, H 4.10, N 10.54.

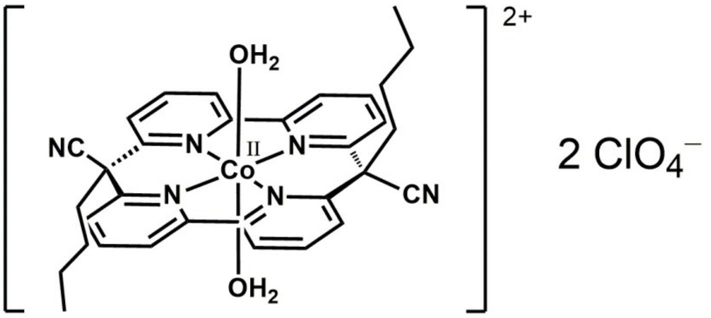
[Co^{II}Br$_2$(*trans*-pyr-bu$_2$)] (4a):



A suspension of **4** (8 mg, 0.016 mmol) in EtOH (2 mL) was stirred and heated to reflux. A solution of $CoBr_2$ hydrate (5 mg, 0.016 mmol) in EtOH (1 mL) was added and the reaction mixture immediately changed to a dark pinkish solution. Reaction control by HPLC after 30 min showed almost complete conversion and stirring at reflux temperature was continued for 2 h. Heating and stirring were stopped, and a dark winered precipitate formed. The suspension was slowly cooled to 25 °C, and then to -18 °C for 3 h, cold filtered over a glass frit (P4) and the precipitate first washed with a mixture of EtOH and Et_2O at 0 °C and then with Et_2O. Drying of the purified precipitate under reduced pressure yielded **4a** as a dark red powder (7 mg, 0.010 mmol, 63 % with respect to Co). Single crystals suitable for X-ray analysis were obtained by vapor diffusion (H_2O/dioxane).

IR (ATR): $\tilde{\nu} \approx$ 3046 (m), 3013 (m), 2961 (m), 2932 (m), 2861 (m), 2384 (w), 2352 (w), 2324 (w), 2247 (w), 2184 (w), 2035 (w), 1991 (w), 1944 (w), 1921 (w), 1842 (w), 1664 (w), 1603 (s), 1581 (s), 1568 (m), 1481 (m), 1470 (s), 1430 (s), 1394 (s), 1313 (m), 1263 (s), 1222 (s), 1193 (m), 1163 (m), 1114 (m), 1075 (m), 1033 (m), 1018 (m), 993 (m), 926 (m), 912 (m), 830 (m), 803 (s), 795 (s), 773 (m), 760 (m), 747 (s), 722 (w); **UV/vis** (H_2O): λ_{max} (ε, M^{-1} cm^{-1}) $\approx$ 213 (34'600, *sh*), 254 (16'000), 299 (26'200), 329 (6520, *sh*), 425 (1660, *sh*), 459 nm (2320); **HR-ESI-MS**: *m*/*z* (%): 636.1052 (3, $[M - Br]^+$, calcd for $[C_{32}H_{30}BrCoN_6]^+$: 636.1042), 616.1872 (40, $[M - 2\ Br + CN + HO_2]^+$, calcd for $[C_{33}H_{31}CoN_7O_2]^+$: 616.1866), 609.1925 (100, $[M - 2\ Br + 2\ CN]^+$, calcd for $[C_{34}H_{30}CoN_9]^+$: 609.1920), 278.5935 (5, $[M - 2\ Br]^{2+}$, calcd for $[C_{32}H_{30}CoN_6]^{2+}$: 278.5927); **SQUID**: T_C ($\Theta \approx -0.28$ K, $\mu_{eff} \approx 4.42$ μ_B; **EA**: calcd (%) for $[C_{32}H_{30}Br_2CoN_6] \cdot \frac{1}{2}\ H_2O$ (726.4): C 52.91, H 4.30, N 11.57; found C 52.62, H 4.27, N 11.45.

[Co^{II}(OH$_2$)$_2$(*trans*-pyr-bu$_2$)][ClO$_4$]$_2$ (4b):



To a suspension of **4** (14 mg, 0.028 mmol) in MeCN (4 mL) a solution of Co(ClO$_4$)$_2$ hexahydrate (9 mg, 0.024 mmol) in MeCN (1 mL) was added at 25 °C and the reaction mixture immediately changed to a yellow solution. Reaction control by HPLC after 18 h showed almost complete conversion, thus, stirring was continued at 25 °C for 24 h, then at reflux temperature for 3 h. Heating and stirring were stopped, the mixture cooled to 25 °C, and the solvent was evaporated by a stream of N$_2$. The resulting dark yellow residue was dissolved in water (10 mL) and some drops of MeCN, heated to reflux and cooled to 25 °C overnight. The bright orange solution was filtered over a syringe filter to remove remaining, precipitated ligand. Lyophilisation of the aqueous filtrate gave **4b** as a yellow powder (13 mg, 71 % with respect to Co).

IR (ATR): $\tilde{\nu} \approx$ 3109 (w), 2961 (w), 2937 (w), 2873 (w), 2252 (w), 2185 (w), 2162 (w), 2110 (w), 2051 (w), 2036 (w), 2013 (w), 1989 (w), 1945 (w), 1607 (w), 1587 (w), 1482 (w), 1472 (w), 1428 (m), 1382 (w), 1267 (w), 1226 (w), 1189 (w), 1097 (s), 1027 (s), 962 (w), 920 (m), 833 (w), 802 (m), 758 (w), 748 (w); **UV/vis** (H$_2$O): λ_{max} (ε, M^{-1} cm^{-1}) ≈ 254 (16'600), 299 (27’100), 329 (6920, *sh*), 428 (1780, *sh*), 459 nm (2430); **HR-ESI-MS**: *m*/*z* (%): 656.1342 (5, [M + ClO$_4$]$^+$, calcd for [C$_{32}$H$_{30}$ClCoN$_6$O$_4$]$^+$: 656.1344), 602.1837 (8, [M – 2 H$_2$O + HCOO]$^+$, calcd for [C$_{33}$H$_{31}$CoN$_6$O$_2$]$^+$: 602.1835), 278.5927 (100, [M – 2 H$_2$O]$^{2+}$, calcd for [C$_{32}$H$_{30}$CoN$_6$]$^{2+}$: 278.5927), 250.0574 (11, [M – 2 H$_2$O – butyl]$^{2+}$, calcd for [C$_{28}$H$_{21}$N$_6$Co]$^{2+}$: 250.0574); **EA**: calcd (%) for [C$_{32}$H$_{34}$Cl$_2$CoN$_6$O$_{10}$] (792.5): C 48.50, H 4.32, N 10.60; found C 48.25, H 4.01, N 10.20.

3 Additional details on Calculated Structures.

B97D/Def2-TZVPP (DMF) calculated structure of cis-pyr-bu$_2$, **3.** The calculated structure reveals the folded shape, with the *cis*-configuration of the alkyl substituents predicted to be more stable than the *trans*-form by 6.7 kcal/mol.

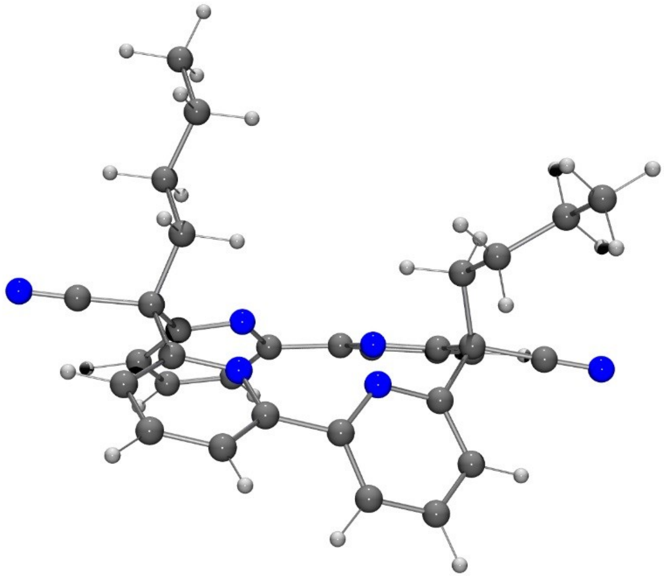
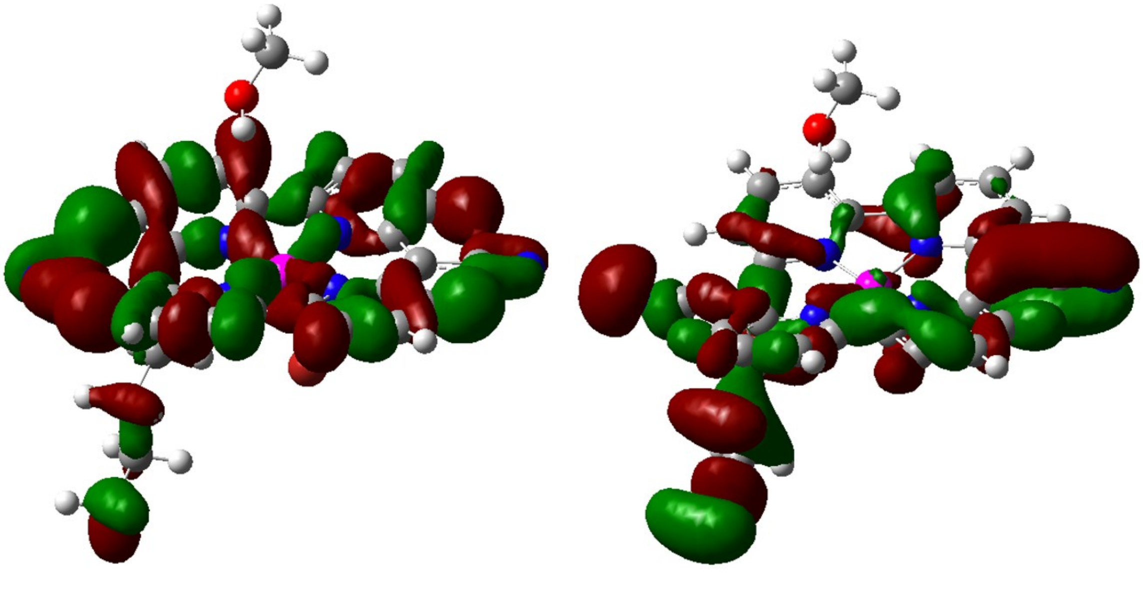


Figure S1. B97D/Def2-TZVPP (DMF) calculated structure of *cis*-pyr-bu$_2$, **3**.



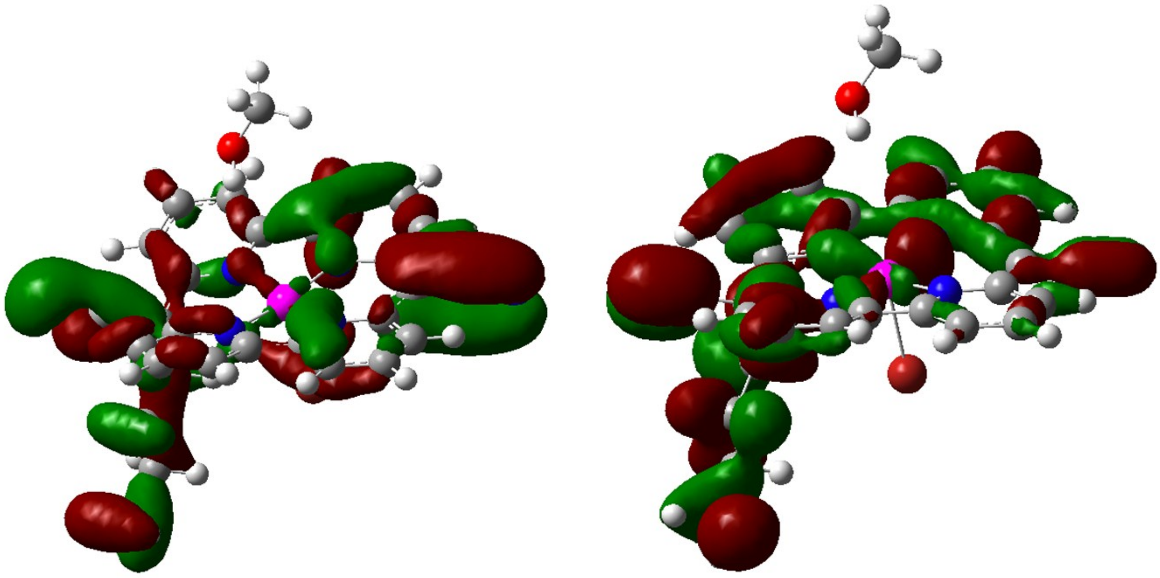
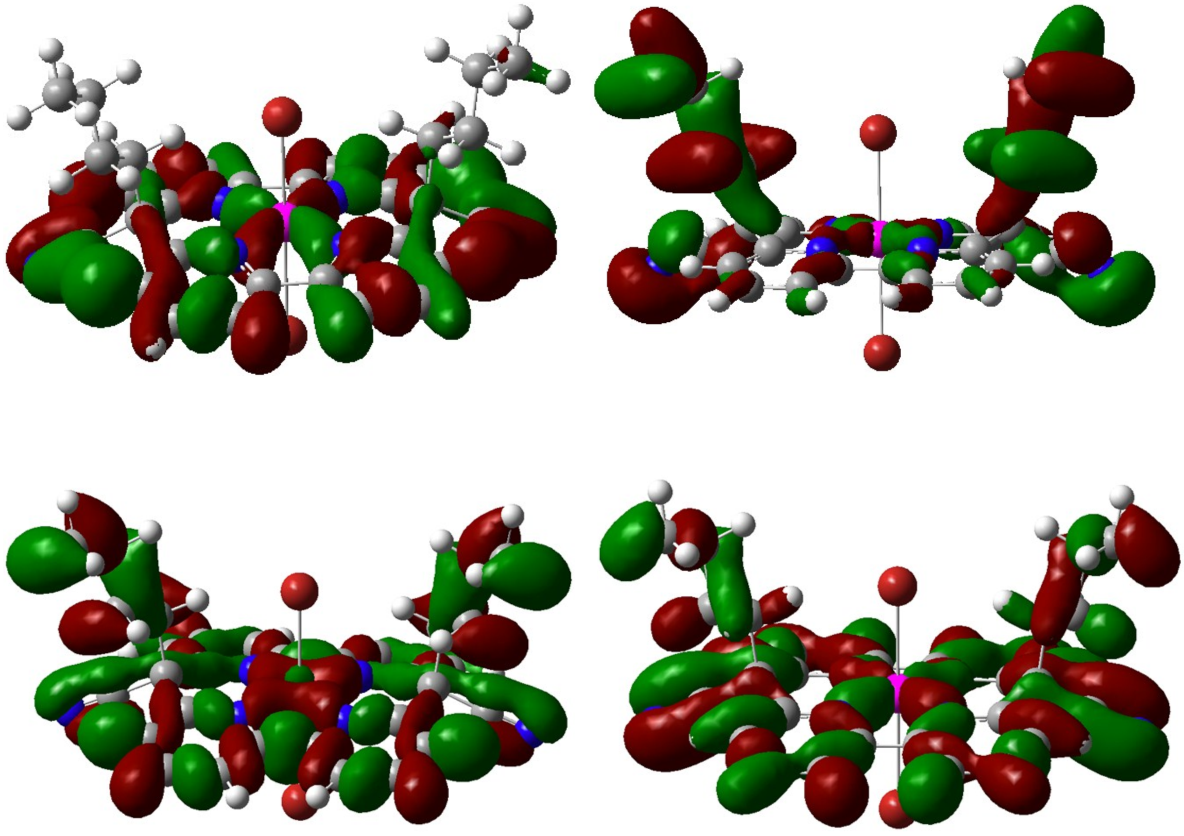


Figure S2 Molecular orbitals 121 and 125 (top) and 126 and 131 (bottom) showing interactions between substuents (i.e., CN) and macrocyclic ring in compound **2**.



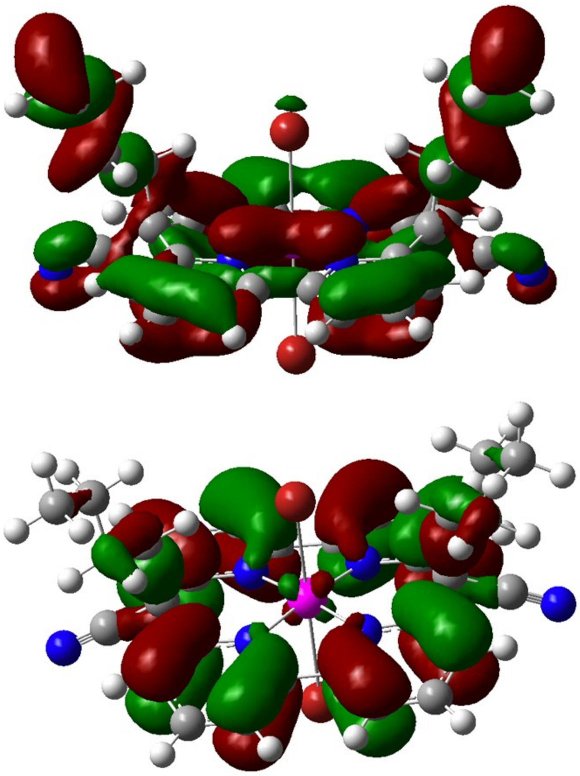


Figure S3 Molecular orbitals 141 and 146 (top), 147 and 148 (middle) and 157 and 172 (bottom) showing interactions between substuents (i.e., CN) and macrocyclic ring in compound **3**.

4 SQUID Measurements of 2a, 3a and 4a

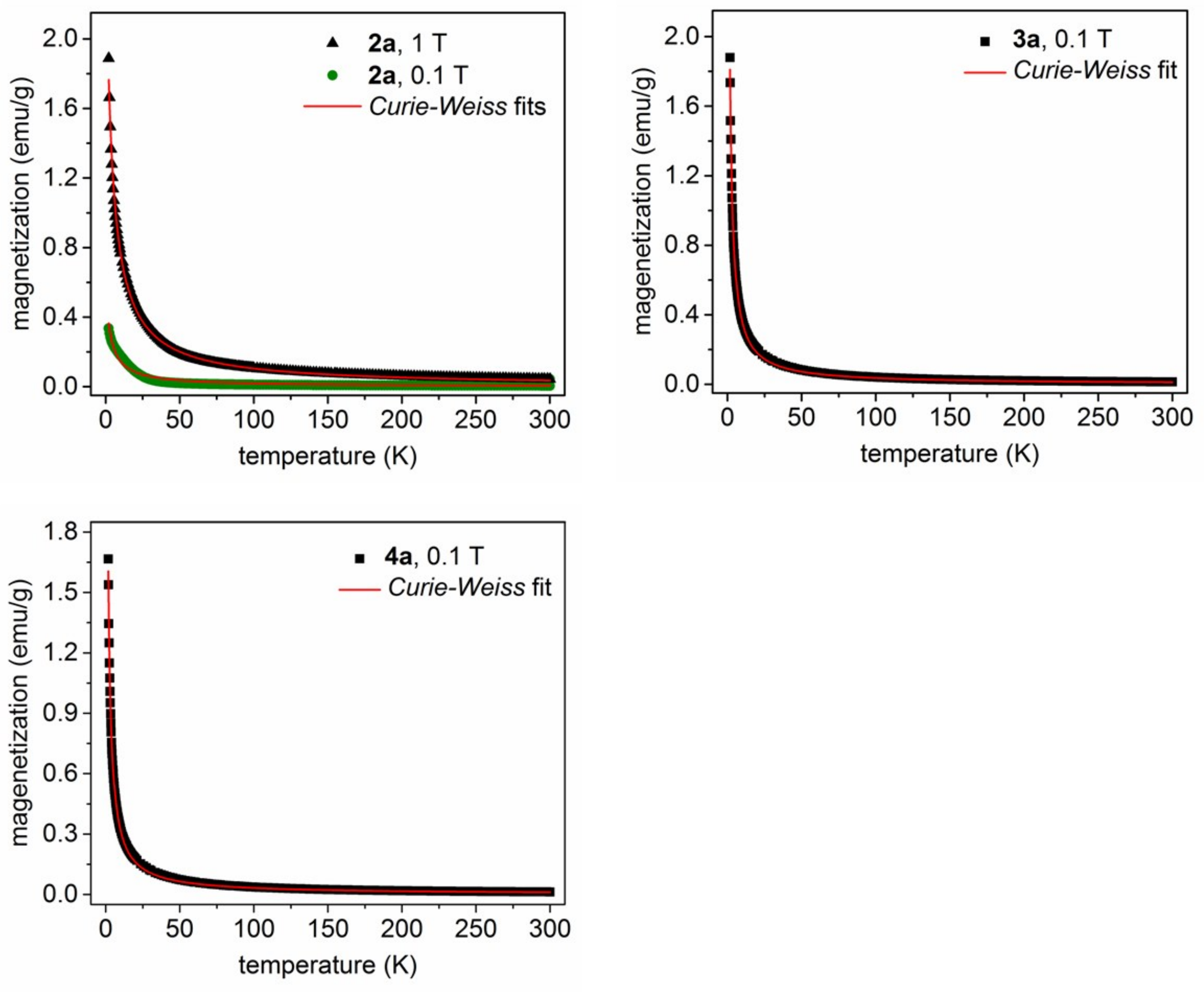


Figure S4. SQUID magnetometry for **2a**, **3a** and **4a** over a temperature range of 300 K at magnetic fields of 0.1 and 1.0 T and the corresponding *Curie-Weiss* fits.

5 Bromide Dissociation of 2a, 3a and 4a in H_2O

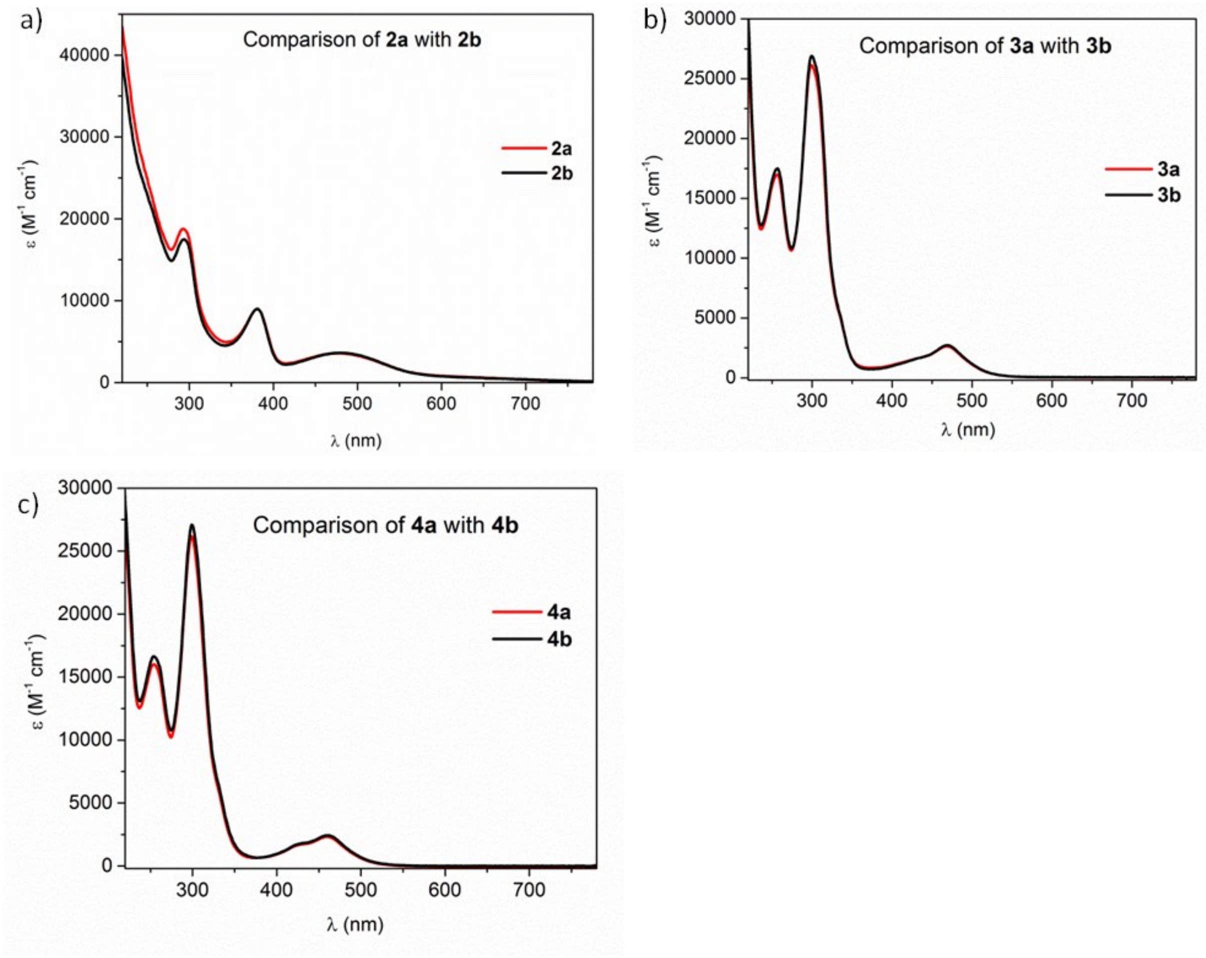


Figure S5. UV/vis spectra of the bromo- and corresponding perchlorato-complexes in water of a) **2a** and **2b**; b) **3a** and **3b**, and c) **4a** and **4b**.

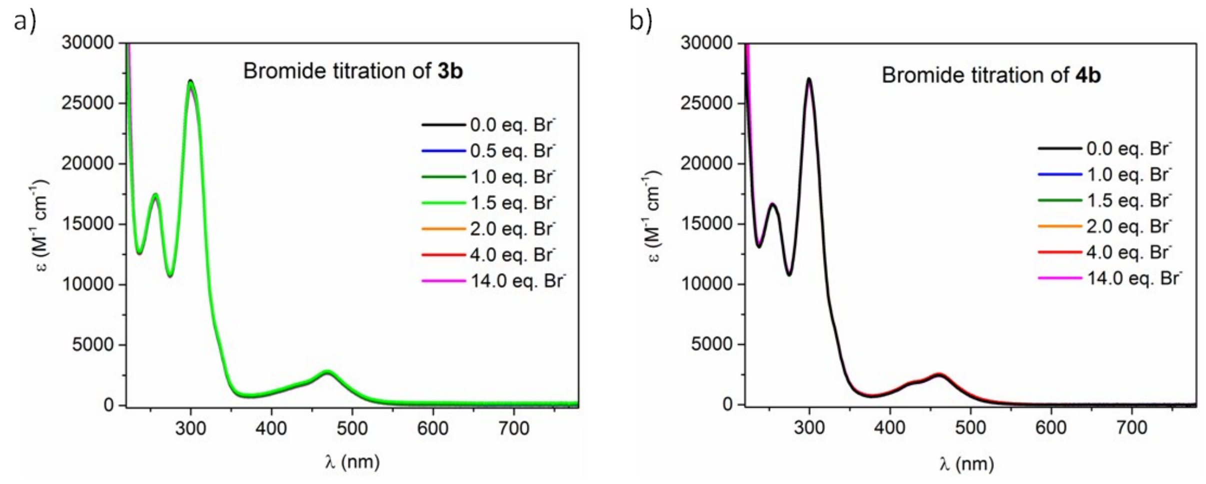


Figure S6. UV/vis spectra of **3b** and **4b** at concentrations of 33 μM in water and upon titration with a solution of aq. KBr (50 mM).

6 Electrochemistry of 2a and 3a in H_2O

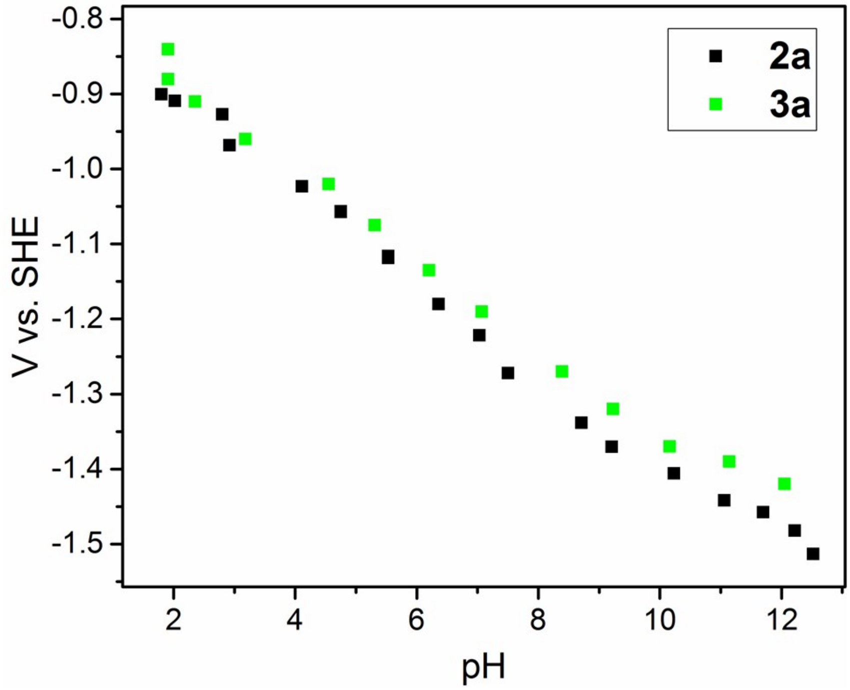


Figure S7. Plot of electrocatalytic potential (I = 1 µA) for **2a** and **3a**. Conditions: **2a**: 180 µM, **3a**: 1 mM; 40 mM AcOH, 40 mM H_3BO_3, 40 mM H_3PO_4, pH adjusted by addition of 2 M NaOH; DP, WE = HMDE, CE = Pt, RE = Ag/AgCl, referenced by measuring $K_3[Fe(CN)_6]$ (430 mV vs SHE).[2]

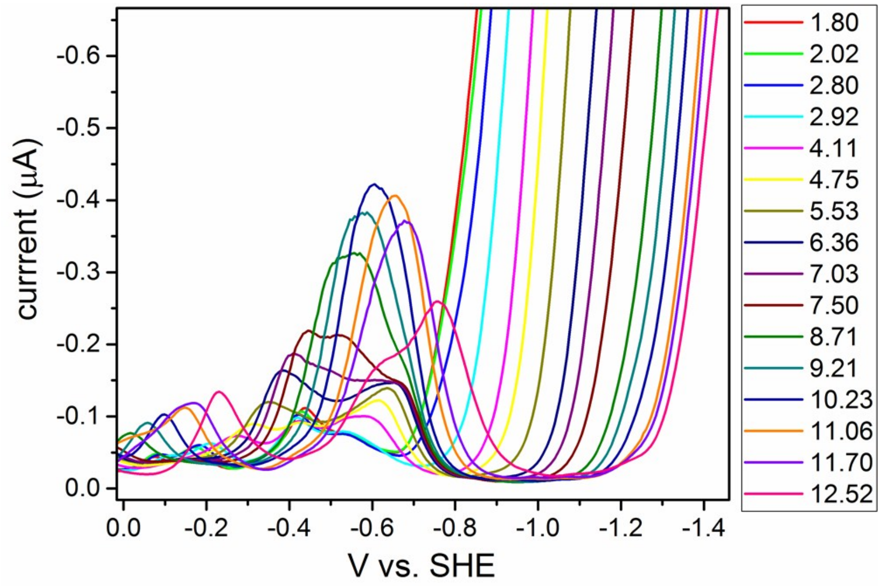


Figure S8. DP scans of **2a** at varying pH. Conditions: 180 µM **2a**, 40 mM AcOH, 40 mM H_3BO_3, 40 mM H_3PO_4, pH adjusted by addition of 2 M NaOH; WE = HMDE, CE = Pt, RE = Ag/AgCl, referenced by measuring $K_3[Fe(CN)_6]$ (430 mV vs SHE).[2]

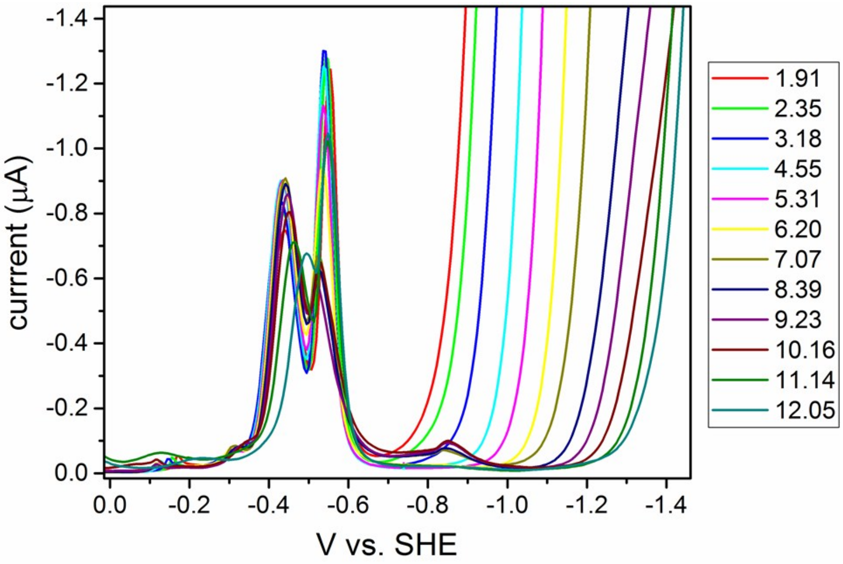


Figure S9. DP scans of **3a** at varying pH. Conditions: 1 mM **3a**, 40 mM AcOH, 40 mM H_3BO_3, 40 mM H_3PO_4, pH adjusted by addition of 2 M NaOH; WE = HMDE, CE = Pt, RE = Ag/AgCl, referenced by measuring $K_3[Fe(CN)_6]$ (430 mV vs SHE).[2]

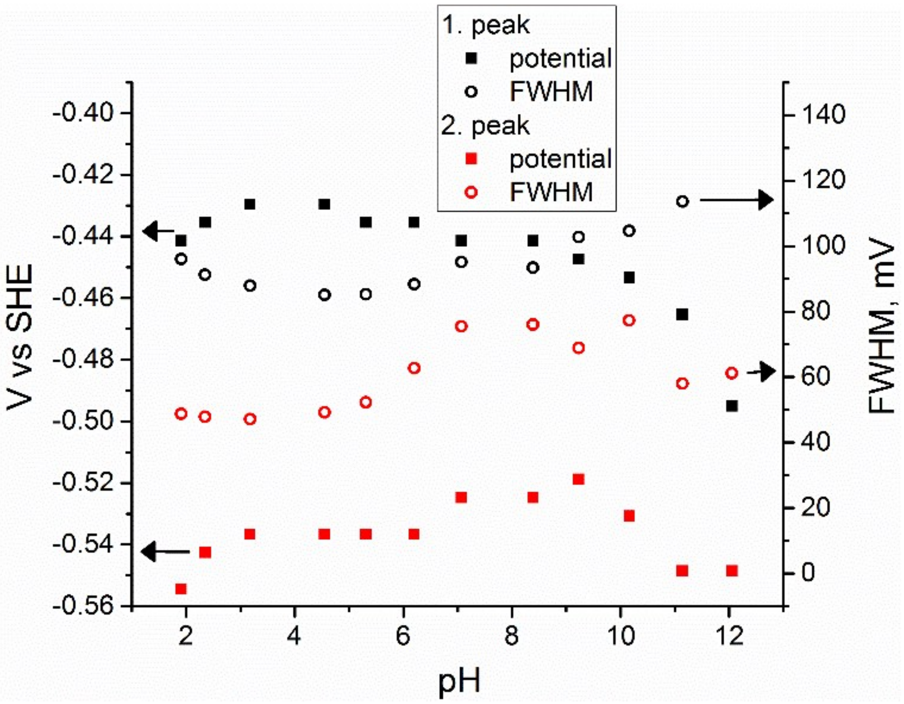


Figure S10. Analysis of DP scans for **3a**: left: peak potential vs SHE, right: full with at half maximum (FWHM), plotted vs pH. Conditions: 1 mM **3a**, 40 mM AcOH, 40 mM H_3BO_3, 40 mM H_3PO_4, pH adjusted by addition of 2 M NaOH; WE = HMDE, CE = Pt, RE = Ag/AgCl, referenced by measuring $K_3[Fe(CN)_6]$ (430 mV vs SHE).[2]

7 Stability of 2a, 3a and 4a in H_2O

The stability of WRCs **2a**, **3a** and **4a** in water was investigated by measuring repeatedly their UV/Vis spectra during a time period of 170 to 500 h. The compounds were dissolved in deionized and bidistilled water (20–33 µM) and transferred into plastic or Quartz cuvettes, respectively, with a path length of 1 cm. Three types of experiments were conducted: I) argon atmosphere, exclusion of light, (blank); II) in normal air atmosphere, exclusion of light; III) argon atmosphere, continuous irradiation at 453 nm by an LED light source (0.30 ± 0.02 µE/s). No stirring was applied. For the experiments under exclusion of light and under normal air atmosphere (experiment type II) the solutions were filled into plastic cuvettes. For the experiments under an argon atmosphere (experiments type I and III) the solutions were transferred into Quartz cuvettes (Q4) with screw caps, degassed with argon for at least 15 min and kept under the inert atmosphere by an argon balloon. Dissolution of **2a** needed time (stirred for one day under normal air atmosphere), hence the experiment in the dark under argon was not conducted. The starting point (0 h) for the experiments of compound **2a** refers to the prepared solution after 1 d of stirring. Since **4a** showed already UV/Vis changes in the absence of light no irradiation experiment was conducted.

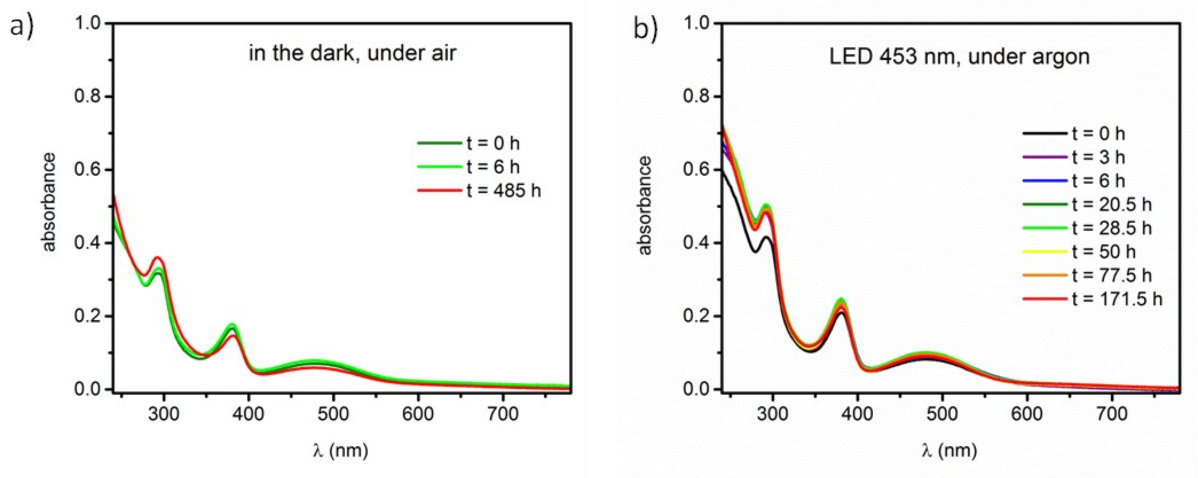


Figure S11. UV/vis spectra of WRC **2a** in water over time. a) in normal air atmosphere, exclusion of light, (20 µM); b) in argon atmosphere, continuous irradiation (25 µM, 3 mL total volume, 453 nm, photon flux of 0.30 ± 0.02 µE/s).

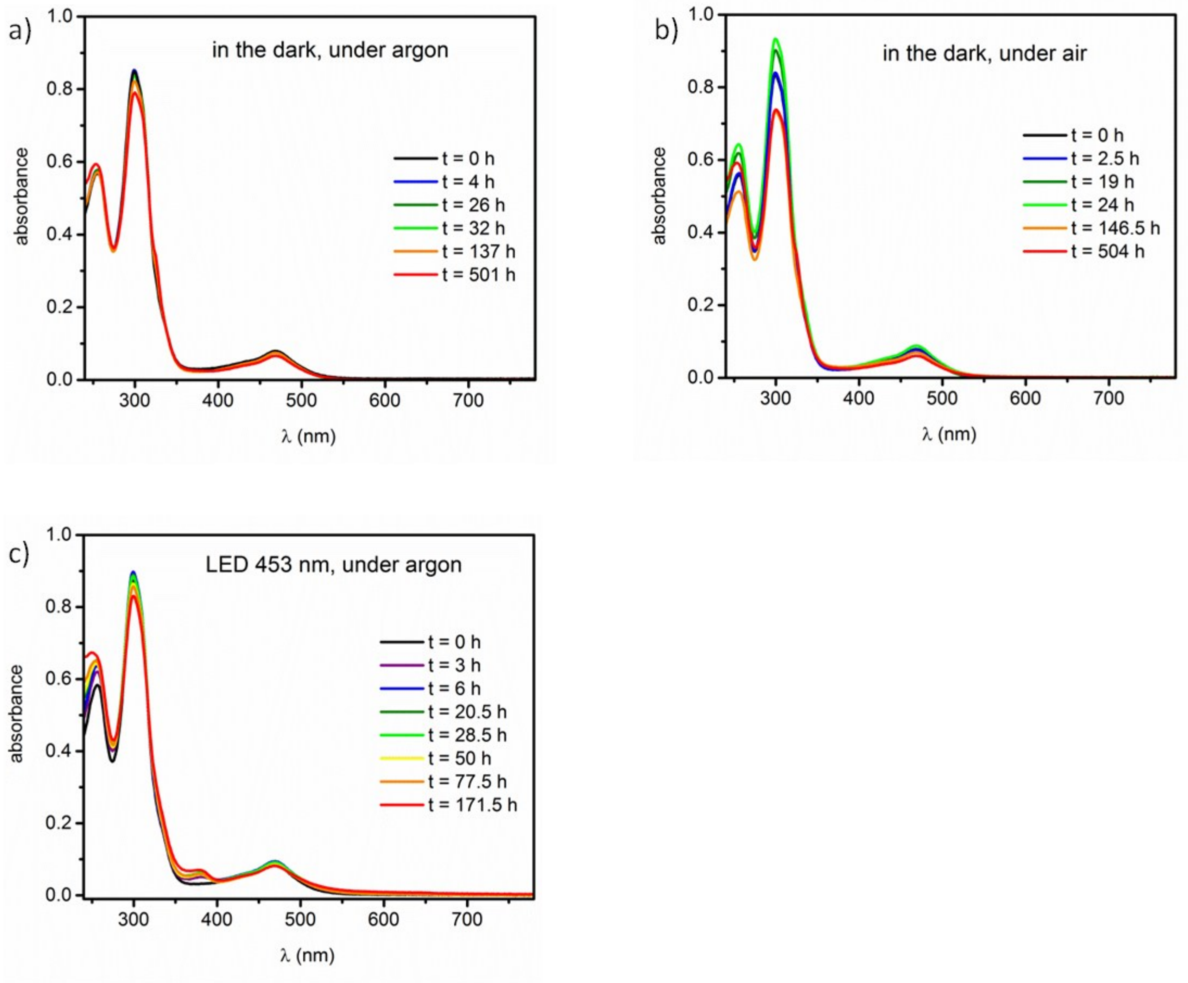


Figure S12. UV/vis spectra of WRC **3a** (33 µM) in water over time. a) in argon atmosphere, exclusion of light, (blank); b) in normal air atmosphere, exclusion of light; c) argon atmosphere, continuous irradiation at (33 µM, 3 mL total volume, 453 nm, photon flux of 0.30 ± 0.02 µE/s).

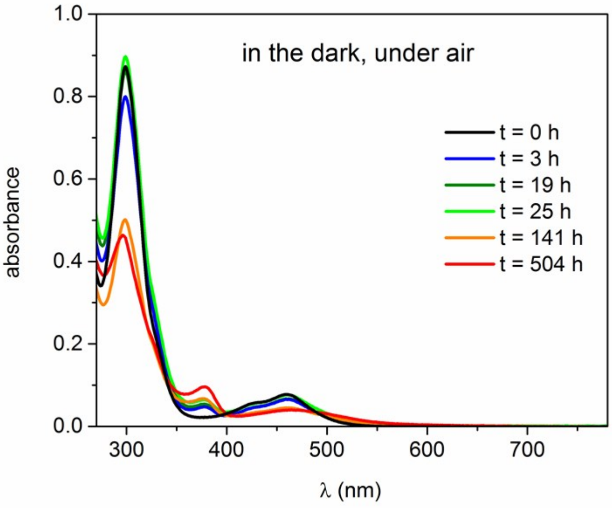


Figure S13. UV/vis spectra of WRC **4a** (33 µM) in water over time in normal air atmosphere and exclusion of light.

8 Photocatalysis of 2a, 2b, 3a, 3b, 4a and 4b

Table S1. Summarized results of all photocatalytic experiments. Conditions: Total volume 10 mL H_2O, PS: 500 µM $[Ru(bpy)_3]Cl_2$, WRC: Co-complexes **2a**–**4b** at various concentrations (1, 2, 5 or 10 µM), 0.1 M TCEP, 0.1 M NaHasc, pH 5, 453 nm LED, photon flux of 0.30 ± 0.02 µE/s. Highlighted in green: Blanks. Highlighted in grey: Bromo-complexes **2a**, **3a** and **4a**. Highlighted in white: perchlorato-complexes **2b**, **3b** and **4b**.

Co-WRC	conc.WRC (µM)	total H_2 [a] (µmol)	Max. rate [a] (nmol/s)	Reaction time [b] (h)	TON_{Co} [a] (H_2/Co)	Max. TOF_{Co} [a] (H_2/Co/h)
-[c]	0	0	0	0	-	-
-[d]	0	3.5 ± 2	0.21 ± 0.03	22	-	-
$CoBr_2$ hydrate	5	5.9 ± 2.5	0.71 ± 0.04	18	120 ± 50	51 ± 3
3a[e]	5	0	0	0	0	0
2a	1	170 ± 20	5.6 ± 0.4	47	17‘200 ± 1800	2000 ± 140
2a	2	340 ± 40	6.4 ± 0.4	84	17‘000 ± 1700	1150 ± 80
2a	5	710 ± 60	8.3 ± 0.5	107	14‘200 ± 1100	590 ± 40
2a	10	800 ± 70	7.8 ± 0.5	91	8000 ± 700	280 ± 20
2b	5	730 ± 40	7.1 ± 0.3	114	14‘600 ± 700	510 ± 30
2b[f]	5	770 ± 40	7.8 ± 0.3	90	15‘500 ± 700	560 ± 30
3a	1	140 ± 20	5.1 ± 0.2	24	13‘800 ± 1500	1820 ± 80
3a	2	130 ± 20	4.7 ± 0.2	37	6600 ± 770	840 ± 40
3a	5	260 ± 40	6.4 ± 0.6	49	5200 ± 640	460 ± 50
3a	10	420 ± 40	4.9 ± 0.2	96	4200 ± 360	180 ± 10
3b	5	330 ± 30	5.5 ± 0.3	71	6500 ± 610	390 ± 20
4a	1	220 ± 20	7.8 ± 0.4	41	21‘900 ± 1200	2800 ± 130
4a	2	370 ± 30	8.4 ± 0.4	80	18‘300 ± 1100	1500 ± 80
4a	5	530 ± 30	6.1 ± 0.2	109	10‘700 ± 500	440 ± 20
4a[f]	5	480 ± 30	6.6 ± 0.2	145	9600 ± 500	470 ± 20
4a	10	650 ± 70	5.9 ± 0.5	111	6700 ± 630	210 ± 20
4b	5	490 ± 30	6.6 ± 0.3	88	9700 ± 450	480 ± 20

[a] Measured by GC.

[b] Time required to form 95 % of totally measured H_2 (GC).

[c] 0.1 M NaHasc and 0.1 M TCEP; no WRC, no PS.

[d] 500 µM $[Ru(bpy)_3]Cl_2$, 0.1 M NaHasc and 0.1 M TCEP; no WRC; according to publication of *C. Bachmann et al.*[15]

[e] 0.1 M NaHasc and 0.1 M TCEP; no PS.

[f] Hg poisoning experiment: Hg was added at the end of the preparation of the catalytic solution (**2b**, 455 mg; **4a**, 477 mg).

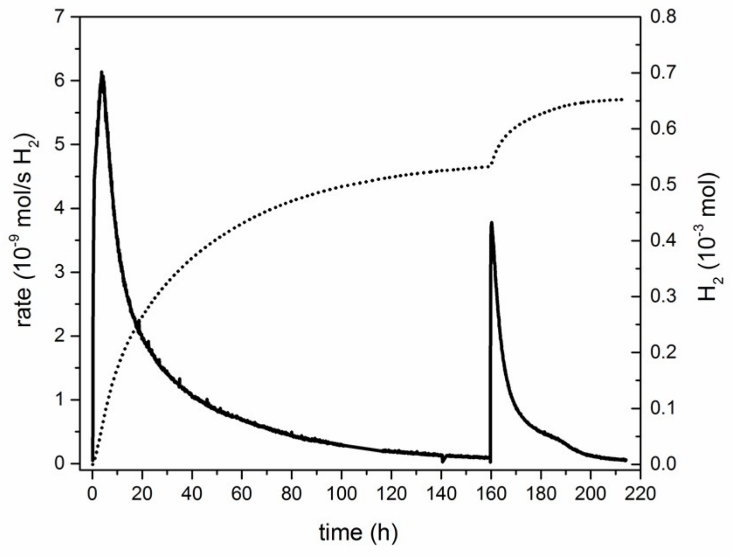


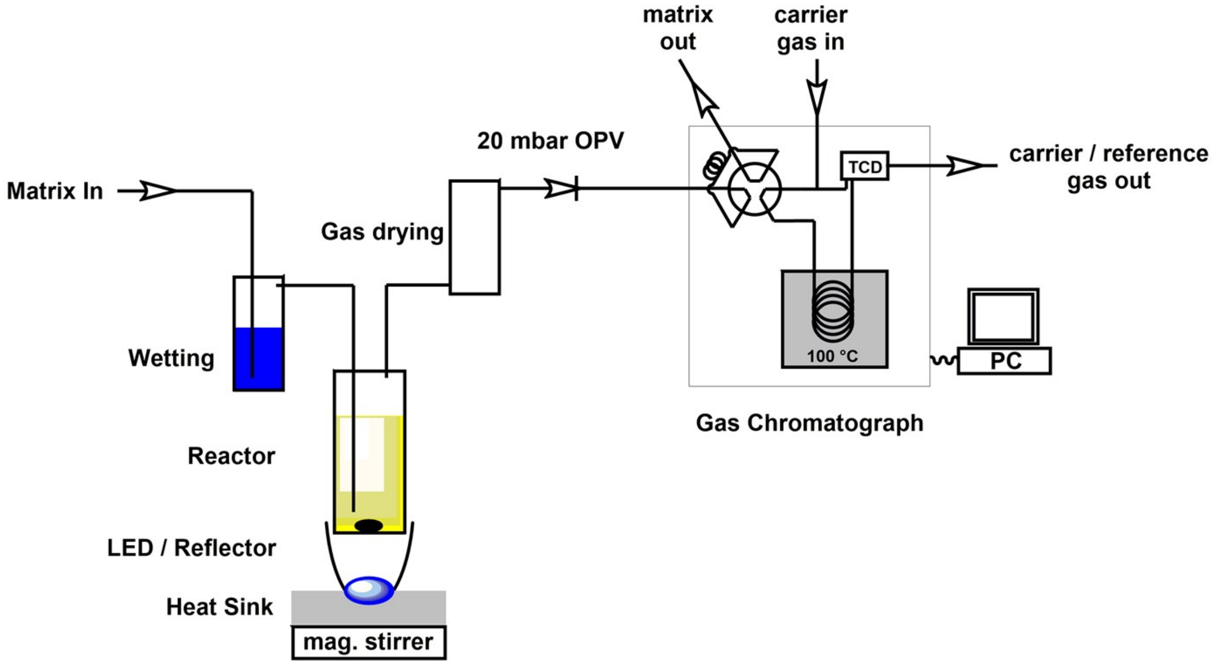
Figure S14. Hydrogen evolution experiment for 10 mL of an aqueous solution of 5 μM catalyst **4a**, 500 μM $[Ru(bpy)_3]Cl_2 \cdot 5\ H_2O$, 0.1 M TCEP, 0.1 M NaHasc, pH 5, 453 nm LED, photon flux of 0.30 ± 0.02 μE/s. Solid line: hydrogen evolution rate, dotted line: amount of H_2 as measured by GC. After t = 160 h further, fresh $[Ru(bpy)_3]Cl_2 \cdot 5\ H_2O$ (3.60 mg, final concentration: 1000 μM) was added and catalysis restarted.

9 Crystal Data of 2, 5, 2a, 3a and 4a

Table S2. Crystal data and data collection of complexes **2a**, **3a** and **4a** as well as the ligands **2** and **5**.

	cis-pyr-bu$_2$ (**3**)	[Co^{II}Br(HOMe)(pyr-bu)] (**2a**)	[Co^{II}Br$_2$(*cis*-pyr-bu$_2$)] (**3a**)	[Co^{II}Br$_2$(*trans*-pyr-bu$_2$)] (**4a**)	*mono*-pyr-bu (**5**)
Empirical formula	$C_{32}H_{30}N_6$	$C_{29}H_{25.25}BrCoN_6O_{1.13}$	$C_{32}H_{32}Br_2CoN_6O$	$C_{44}H_{58}Br_2CoN_6O_8$	$C_{35}H_{36}N_6$
Diffractometer	Agilent SuperNova dual radiation CCD	Xcalibur Ruby	Agilent SuperNova dual radiation CCD	Agilent SuperNova dual radiation CCD	Xcalibur Ruby
Wavelength (Å)	1.54184	0.7107	1.54184	1.54184	0.7107
mol. weight (g/mol)	498.62	614.64	735.39	1017.71	540.70
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P21/n	P-1	P-1	P21/c
a (Å)	8.2048(3)	7.5599(7)	8.2089(9)	8.2358(3)	15.7566(9)
b (Å)	14.7409(5)	14.9746(15)	12.0442(8)	9.0180(3)	15.9366(8)
c (Å)	22.1721(9)	22.551(3)	16.0938(15)	15.1604(6)	11.6429(6)
α (°)	85.744(3)	90	79.730(7)	81.066(3)	90
β (°)	87.213(3)	93.612(9)	85.790(8)	86.679(3)	93.076(5)
γ (°)	89.981(3)	90	74.422(8)	82.895(3)	90
Volume (Å^3)	2671.06(16)	2547.9(5)	1507.6(2)	1102.90(7)	2919.4(3)
Z	4	4	2	1	4
Dens.(calc.) (g/cm^3)	1.240	1.602	1.620	1.532	1.230
Abs. coeff. (mm^{-1})	0.589	2.279	7.859	5.664	0.074
F(000)	1056	1249	742	525	1152
Crystal size (mm^3)	0.28 x 0.18 x 0.04	0.16 x 0.10 x 0.09	0.18 x 0.08 x 0.04	0.18 x 0.04 x 0.02	0.41 x 0.21 x 0.07
Crystal description	yellow plate	black prism	red plate	red needle	pink plate
θ range (°)	2.00 to 76.57	2.79 to 25.35	3.86 to 76.53	2.95 to 76.47	2.89 to 25.35
Index ranges	-10<=h<=10, -14<=k<=18, -27<=l<=21	-9<=h<=7, -17<=k<=18, -27<=l<=21	-10<=h<=10, -13<=k<=14, -20<=l<=20	-7<=h<=10, -11<=k<=11, -19<=l<=18	-15<=h<=18, -19<=k<=16, -14<=l<=13
Refl. collected	36749	14184	23358	15112	14701
Indep. reflections	11019 [R(int) = 0.0236]	4661 [R_{int} = 0.0662]	5864 [R_{int} = 0.0230]	4532 [R_{int} = 0.0218]	5315 [R_{int} = 0.0432]
Reflections obs.	9451	3379	5397	4316	3740
Criterion for obs.	>2sigma(I)	>2sigma(I)	>2sigma(I)	>2sigma(I)	>2sigma(I)
Completeness to θ	98.8 % to 74.33°	99.9 % to 25.35°	93.9 % to 74.33°	99.4 % to 66.97°	99.8 % to 25.35°
Absorption corr.	Semi-empirical from equiv.	Semi-empirical from equiv.	Semi-empirical from equiv.	Gaussian	Semi-empirical from equiv.
Max. and min. transm.	0.9768 and 0.7692	0.8212 and 0.6420	0.7440 and 0.4752	0.918 and 0.617	0.9949 and 0.6469
Data / restraints / param.	11019 / 0 / 689	4661 / 0 / 347	5864 / 0 / 387	4532 / 4 / 296	5315 / 0 / 389
Goodness-of-fit on F^2	1.097	1.057	1.041	1.041	1.025
Fin. R ind. [I>2sigma(I)]	R1 = 0.0780, wR2 = 0.2287	R1 = 0.0652, wR2 = 0.1379	R1 = 0.0219, wR2 = 0.0568	R1 = 0.0235, wR2 = 0.0586	R1 = 0.0551, wR2 = 0.1275
R indices (all data)	R1 = 0.0866, wR2 = 0.2328	R1 = 0.0980, wR2 = 0.1532	R1 = 0.0248, wR2 = 0.0584	R1 = 0.0250, wR2 = 0.0594	R1 = 0.0845, wR2 = 0.1463
Fin. diff. ρmax (e$^-$/Å^{-3})	0.354 and -0.276	0.924 and -0.622	0.309 and -0.326	0.544 and -0.324	0.314 and -0.247

10 Setup for photocatalysis with in-line gas detection to give rates of hydrogen production



Scheme S1: Argon (matrix gas) is first humidified by passing through water, subsequently passed through the (photocatalytic) reaction, dried, passed through an overpressure valve (OVP) and analyzed by GC/TCD in 5 min intervals. The response time of the setup is 15 min, depending on the headspace volume. Integration of the measured rate profile gives total amount of produced gas. Calibration is performed by measurement of known amounts of gas in matrix, and referenced by electrochemical gas production for H_2.

10 References

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