Supplementary Information

A noble metal-free photocatalytic system based on a novel cobalt tetrapyridyl catalyst for Hydrogen production in fully aqueous medium

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Materials.

Solvents, starting materials and reagents were purchased from Sigma-Aldrich and used without further purification. $Ru(bpy)_3Cl_2$ was purchased from Strem.

The 6,6'-bis-(2-aminopyridyl)-2,2'-bipyridine (bapbpy) ligand,[1] the corresponding zinc complex [Zn(bapbpy)Cl]Cl[2] and the *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin chloride **2Cl$_4$**[3] were synthesized according to reported procedures.

Synthesis of 1(BF$_4$)$_2$. To a suspension of *bapbpy* ligand (100 mg, 0.29 mmol) in methanol (50 mL), a solution of $Co(BF_4)_2.6H_2O$ (99 mg, 0.29 mmol) in methanol (5 mL) was slowly added under continuous stirring. This mixture was stirred 30 min to give a clear yellow solution. The solution was then filtered to remove any remaining ligand. Solvent was removed under reduced pressure and the resulting solid was collected and thoroughly washed with Et_2O. Drying the powder under vacuum afforded the desired compound as a pale yellow solid (150 mg; 85% yield).

ESI-MS: m/z 485.7 $[M\text{-}2H_2O\text{-}BF_4]^+$, 199.5 $[M\text{-}2H_2O\text{-}2BF_4]^{2+}$

UV-Vis (MeOH): λ_{max} in nm (ε in $L.mol^{-1}.cm^{-1}$) = 312 (23817), 373 (10829), 408 (1610).

Elemental Analysis Calcd. for $\{C_{20}H_{16}N_6B_2F_8Co + 0.5\ MeOH + 1.5\ H_2O\}$: C, 39.59; H, 3.40; N, 13.51. Found: C, 39.60; H, 3.25; N, 13.40.

Methods and equipments.

UV-visible spectra were recorded on a Shimadzu UV-1800 spectrophotometer.

Electrospray ionization mass spectra were recorded with a LXQ THERMO SCIENTIFIC spectrometer.

Elemental analyses were performed on a Thermofisher Scientific "Flash 2000" by the "Plateforme d'analyse pour la chimie" (GDS 3648, Strasbourg).

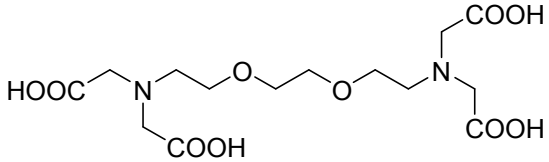
X-ray crystallography. X-ray suitable crystals of **1(BF$_4$)$_2$** were grown by slow evaporation of a THF/H_2O solution. Diffraction data were collected using an Oxford Diffraction XCalibur S Kappa area detector four-circle diffractometer (Mo-K_α radiation λ = 0.71073 Å, graphite monochromator), controlled by the Oxford Diffraction CrysAlis CCD software. Unique intensities with $I > 10\sigma(I)$ detected on all frames using the Oxford Diffraction RED were used to refine the values of the cell parameters. The substantial redundancy in data allows analytical absorption corrections to be applied using crystal shape determination. The space group was determined from systematic absences, and it was confirmed by the successful

resolution of the structure. The structure was solved by direct method using ShelXT[4] software in Olex1.2 environment and all the atoms were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F^2 using ShelXL program[4] while hydrogen atoms were isotropically refined. The asymmetric unit contains Co C_{20} H_{16} N_6 $(H_2O)_2$, 2(BF_4). CCDC 1564999.

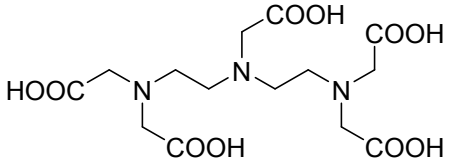
Electrochemical measurements. Electrochemical analysis was performed using a BioLogic SP300 potentiostat fitted with a high current/high voltage board (1 A/48 V) controlled via the EC-Lab® V10 software. The voltammetry experiments were carried out in a three-electrode electrochemical cell using a glassy carbon (GC) working electrode, a platinum wire as auxiliary electrode and a reference electrode based on the Ag/AgCl/KCl 3M couple (Ag/AgCl). This electrode was calibrated after each experiment with the internal reference system Fc^+/Fc, usually found at 0.450 V vs Ag/AgCl in CH_3CN. Solution concentrations were ca. 1 mM for the complex and 0.1 M for the supporting electrolyte ($TBAClO_4$ or $TBAPF_6$) in acetonitrile. For aqueous measurements in Tris-HCl buffer, the reference electrode was externally calibrated in phosphate buffer 0.1 M using the $K_3[Fe(CN)_6]$ reference (found at +0.4247 V vs NHE).

Hydrogen production monitored by a Clark-type hydrogen electrode.[5] The hydrogen concentration was measured in solution with a miniaturized Clark-type electrochemical H_2 sensor (provided by Unisense) consisting of a microsensor monometer (polarization set to +1000 mV) equipped with a hydrogen microsensor. Prior to the experiments, the electrode was calibrated using deionized water bubbled with 100 % N_2, a 40:60 H_2/N_2 mixture, and 100 % H_2 ($[H_2]^{20°C}$ (100 %) = 800 µM, $[H_2]^{20°C}$ (40 %) = 320 µM).

Solutions of $[Eu(EGTA)(H_2O)]^{2-}$ and $[Eu(DTPA)(H_2O)]^{3-}$(20 mM) in 1 M Tris-HCl buffer (pH 8.0) were prepared by mixing a stock solution of $EuCl_2$ (100 mM in 1 M Tris-HCl, pH 8.0) with equivalent volumes of EGTA and DTPA solutions (25 mM in 1 M Tris-HCl, pH 8.0), respectively.



EGTA (Ethylene glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid)

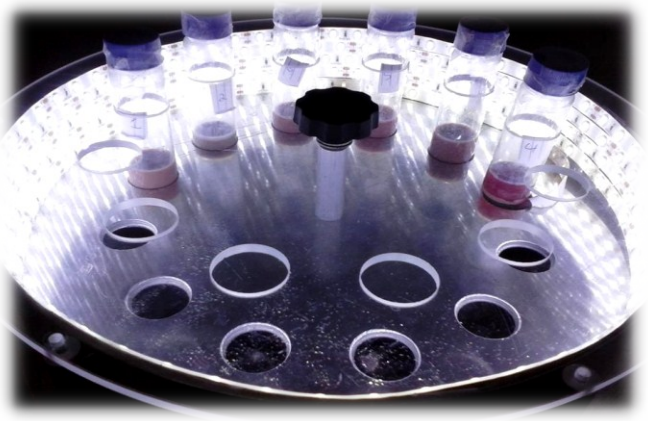


DTPA (diethylenetriamine-N,N,N',N'',N''-pentaacetic acid)

For studying hydrogen production, a solution of **1(BF$_4$)$_2$** (10 μM) in 50 mm Tris-HCl (pH 7.0, 1.1 mL) was prepared and transferred to the microrespiration chamber inside a glovebox. The gas volume above the solution was carefully reduced to less than 50 μL to minimize gas exchange processes and the injection channel through the plunger was sealed with grease. The cell was removed from the glovebox, and the microsensor was plunged into the solution. After an equilibration time of 1–2 min, the Eu^{II} solution (11 μL, 20 equiv.) was added with a Hamilton syringe. It is important to note that a shift in baseline of the [H_2]-trace was occasionally observed when the sensor stabilized after injection. This is, for instance, the case with the blank experiment (no catalyst) presented in Fig. 2 of the manuscript. It is artifact of the microsensor and it does not indicate rapid formation of hydrogen.

For the photocatalytic assays, a 1.1 mL solution of **1(BF$_4$)$_2$** (10 μM) and Ru(bpy)$_3$Cl$_2$ (0.2 mM) in ascorbate buffer (100 mM, pH 4) was prepared inside a glovebox and kept in dark. After equilibrating the sensor for 1 to 2 min, the reaction was initiated by turning on a 300 W xenon lamp (Oriel, ozone free) operating at 280 W coupled with a water-filled Spectra Physics 6123NS liquid filter and a Spectra Physics 59472 UV cutoff filter (λ > 400 nm).

Photocatalytic experiments. The procedure for a typical photocatalytic experiment is as follows. Each sample was prepared in vials. The components (PS and Cat) were weighed and transferred in the vials. Before sample preparation, an aqueous solution of ascorbic acid (AA, 0.2 M), AA/TCEP (0.1 M each) and TEOA (5% v/v) was made. The pH was determined by pH meter and adjusted to the required pH using conc. NaOH or HCl and finally degassed for 10 minutes with nitrogen. 10 mL of the solvent mixture was added in each vial. The sample was sealed and placed at a fixed distance from the white LED lights, which are shown in the image below. The solution was stirred and irradiated. After irradiation, 100 μL samples were taken from the headspace and injected immediately into the GC.



The amounts of hydrogen evolved were measured by gas chromatography (external standard technique) using a Shimadzu GC-2010 plus chromatograph with a TCD detector and a molecular sieve 5 Å column (30 m - 0.53 mm). Control experiments were performed under the same conditions as the hydrogen evolution experiments with removal of one of the components of the hydrogen generating system (i.e. removal of **$2Cl_4$**, **$1(BF_4)_2$**, and/or sacrificial electron donor).

Mercury poisoning experiments were performed by adding an excess of mercury (ca. 40 equiv.) to our solution in order to examine the possibility of formation of metallic nanoparticles or colloids during hydrogen evolution. There was no noticeable change in hydrogen production rate.

Re-activation experiments were run by adding 1 eq of **$1(BF_4)_2$** catalyst or 1 eq of **$2Cl_4$** photosensitizer to our photocatalytic experiments after 4 hours of irradiation.

For the hydrogen evolution experiments the conditions were as follows: Hydrogen production upon irradiation of aqueous solution of AA (0.2 M, pH 4.5) or of aqueous solution of TCEP/AA (0.1 M each, pH 4.5) or of aqueous solution of TEOA (5% v/v, pH 7 or 8) containing $Ru(bpy)_3Cl_2$ ($4.0\ 10^{-5}$ M) or **$2Cl_4$** ($4.0\ 10^{-5}$ M) PS and **$1(BF_4)_2$** ($4.9\ 10^{-4}$ M) catalyst.

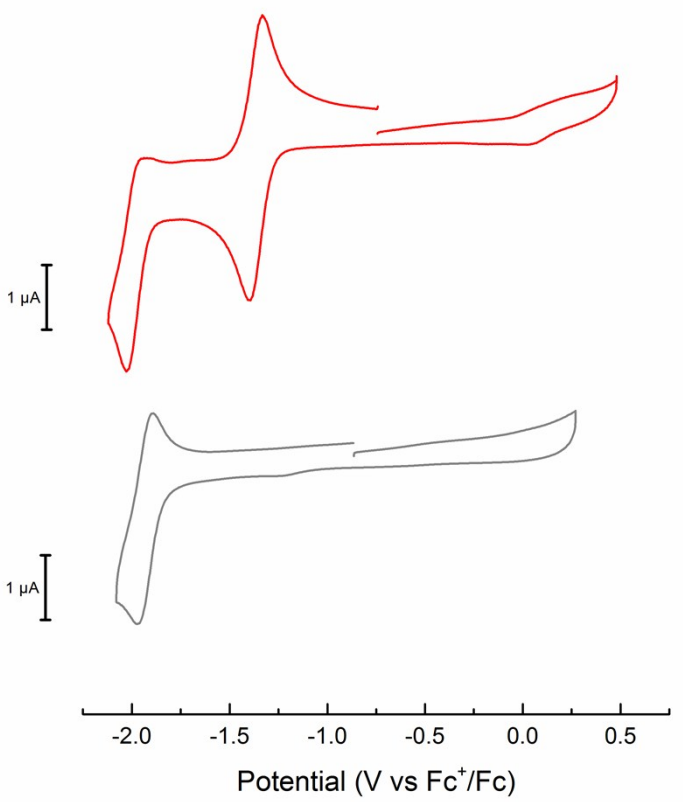


Figure S1. Cyclic voltammograms of $\mathbf{1(BF_4)_2}$ (red line) and of the corresponding zinc complex (grey line) recorded in DMF (containing 0.1 M (n-Bu)$_4$N(BF_4) as supporting electrolyte).

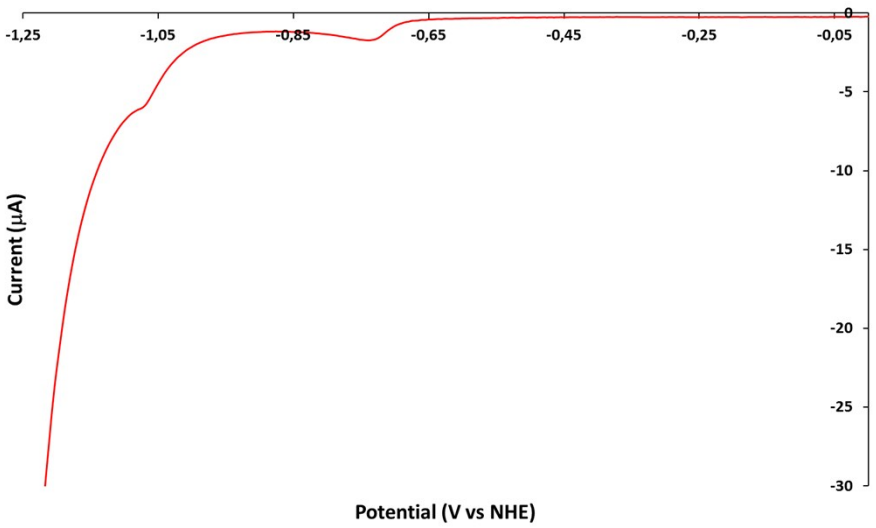


Figure S2. Linear sweep voltammogram of $\mathbf{1(BF_4)_2}$ (1 mM) recorded in Tris-HCl buffer (0.1 M, pH 7) at a scan rate of 10 mV.s^{-1}.
Contribution from direct proton reduction at the electrode surface is observed below -1.2 V vs NHE.

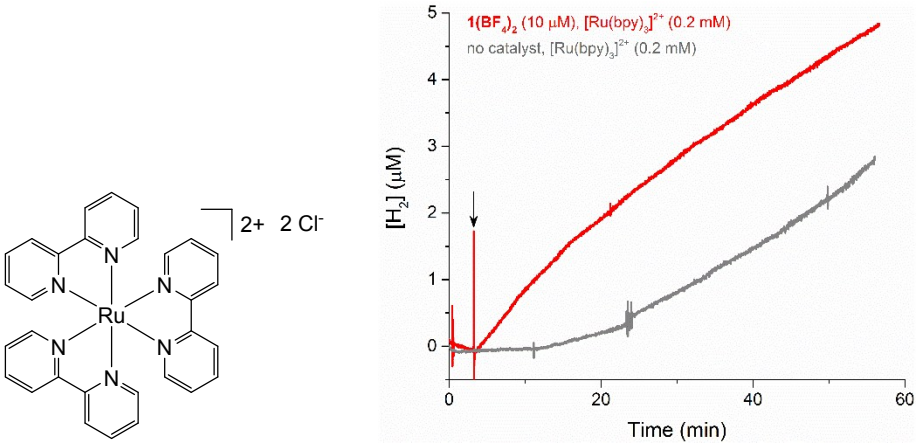


Figure S3. *Left*: Chemical structure of $Ru(bpy)_3Cl_2$; *Right*: Photochemical hydrogen evolution catalyzed by **1(BF$_4$)$_2$** in the presence of $Ru(bpy)_3Cl_2$. The concentration of dissolved H_2 was monitored by a micro-Clark electrode. The arrow indicates start of the irradiation. The photocatalytic assay contained **1(BF$_4$)$_2$** (10 µM), ascorbate buffer (100 mM, pH 4), and $Ru(bpy)_3Cl_2$ (0.2 mM).

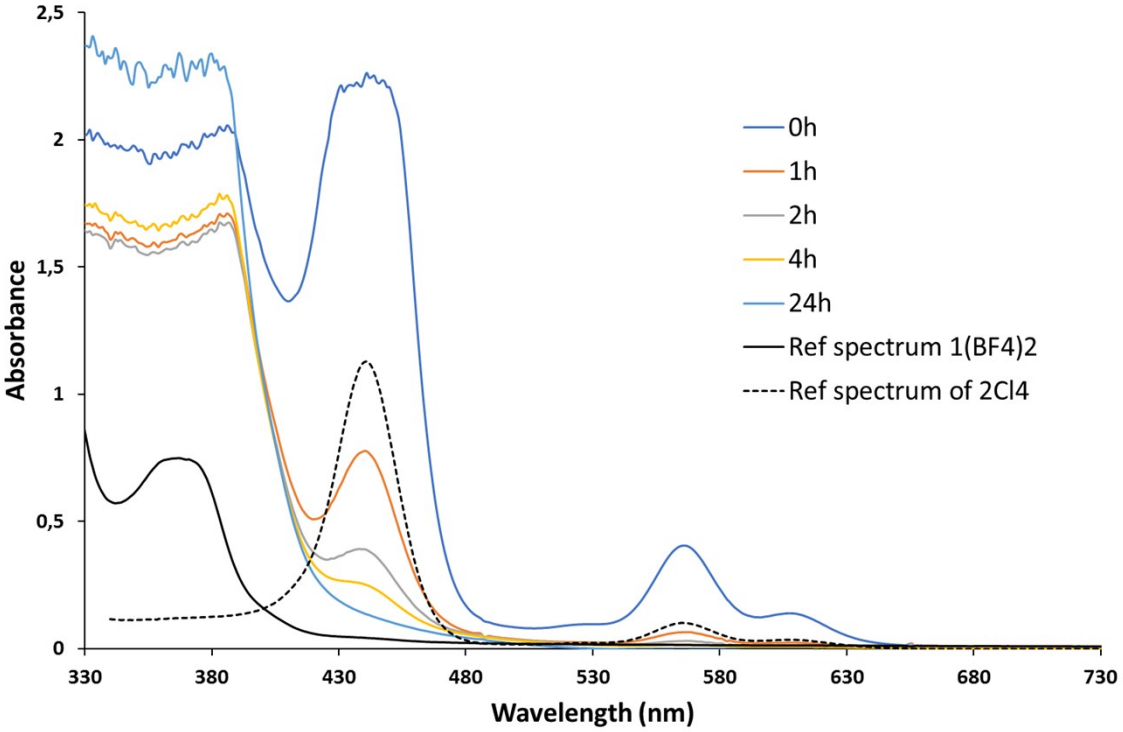


Figure S4. UV-Vis absorption spectra recorded during the course of a photocatalytic test (0 to 24h); Conditions: **1(BF$_4$)$_2$** ($4.9\ 10^{-4}$ M), **2Cl$_4$** ($4.0\ 10^{-5}$ M) in 0.2 M aqueous AA solution, pH 4.5; comparison with reference spectra of diluted solutions of **1(BF$_4$)$_2$** ($6.5\ 10^{-5}$ M, plain dark line) and **2Cl$_4$** ($9\ 10^{-6}$ M, dashed black line) in 0.2 M aqueous AA solution (pH 4.5) is provided.
Extinction of the characteristic absorption bands of **2Cl$_4$** is observed after 24h of irradiation.

Table S1. Selected bond lengths [Å] and angles [°], together with the schematic description of the planes A to D employed to characterize the relevant dihedral angles α, β, γ and γ´ from the structure, as reported elsewhere by Bonnet et al.[6]

Co1-N1	2.1022(14)
Co1-N3	2.0733(13)
Co1-N4	2.0834(14)
Co1-N6	2.0917(14)
Co1-O1	2.1575(13)
Co1-O2	2.1745(13)
N4-Co1-N6	88.55(5)
N3-Co1-N4	78.87(6)
N3-Co1-N1	88.79(5)
N6-Co1-N1	106.69(5)
N4-Co1-N1	160.90(5)
N3-Co1-N6	161.05(5)
α[a]	3.17126(9)
β[a]	41.9774(12)
γ[a]	20.8245(6)
γ'[a]	17.9897(5)

[a] As defined below.

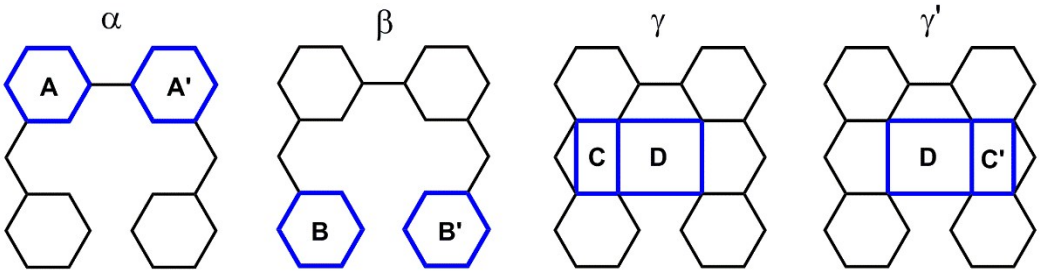


Table S2. Photocatalytic hydrogen production under various experimental conditions.

Catalyst	PS	SED	pH		Time	TON_{PS}
$1(BF_4)_2$	$Ru(bpy)_3Cl_2$	Ascorbate	4.5			**0**
$1(BF_4)_2$	**$2Cl_4$**	Ascorbate	4.5			**19**
Controls:						
$1(BF_4)_2$	**—**	Ascorbate	4.5			**0**
—	**$2Cl_4$**	Ascorbate	4.5			**0**
$1(BF_4)_2$	**$2Cl_4$**	**—**				**0**
$1(BF_4)_2$	**$2Cl_4$**	Ascorbate	4.5	No light		**0**
$1(BF_4)_2$	**$2Cl_4$**	Ascorbate	4.5	Hg (20 eq)		**18**
$1(BF_4)_2$	**$2Cl_4$**	Ascorbate	2			**0**
$1(BF_4)_2$	**$2Cl_4$**	TEOA	7		24h	**0**
$1(BF_4)_2$	**$2Cl_4$**	TEOA	8		24h	**0**
$1(BF_4)_2$	**$2Cl_4$**	**Ascorbate + TCEP (0.1 M)**	4.5		48h	**443**
$1(BF_4)_2$	**$2Cl_4$**	**TCEP (0.1 M) No ascorbate**	4.5			**0**

Table S3. Photocatalytic hydrogen production using **$1(BF_4)_2$** ($4.9\ 10^{-4}$ M) with either $Ru(bpy)_3Cl_2$ ($4.0\ 10^{-5}$ M) or **$2Cl_4$** ($4.0\ 10^{-5}$ M) as photosensitizers (0.2 M aqueous AA solution, pH 4.5) and **$1(BF_4)_2$** ($4.9\ 10^{-4}$ M) with **$2Cl_4$** ($4.0\ 10^{-5}$ M) in presence of the couple AA/TCEP (0.1 M each).

	$Ru(bpy)_3Cl_2$		**$2Cl_4$**		**$2Cl_4$ / 0.1 M TCEP**	
Time (h)	**mL H_2**	**TON_{PS}**	**mL H_2**	**TON_{PS}**	**mL H_2**	**TON_{PS}**
0	0	0	0	0	0	0
1	0	0	0.07	10.0	0.46	68.2
2	0	0	0.08	11.5	1.24	183.9
3	0	0	0.09	12.4	2.02	300
4	0	0	0.10	14	2.45	364
24	0	0	0.13	18.6	2.98	443
48	0	0	0.13	18.7	2.98	443

(1) Bonnet, S.; Siegler, M. A.; Costa, J. S.; Molnar, G.; Bousseksou, A.; Spek, A. L.; Gamez, P.; Reedijk, J. *Chem. Commun.* **2008**, 5619.
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(3) Christensen, P. A.; Harriman, A.; Porter, G.; Neta, P. *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **1984**, *80*, 1451.
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