Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information for:

Enhancing the Stability of Photocatalytic Systems for Hydrogen Evolution in Water by using a tris-Phenyl-Phenanthroline Sulfonate Ruthenium Photosensitizer

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1. General experimental details

Disodium (1,10-phenanthroline-4,7-diyl)bis(benzenesulfonate) tris-hydrated (**SPhphen**, 98%, Aldrich), N,N'-Dimethylformamide (DMF, Fisher, 99.9%, Carlo Erba), tetra-*n*-butyl-ammonium perchlorate ($[Bu_4N]ClO_4$, > 99%, Sigma-Aldrich), $[Ru(bpy)_3]Cl_2$ (**Rubpy**, 99%, Aldrich), L-ascorbic acid (H_2A, 99%, Acros), sodium L-ascorbate (NaHA, 99%, Acros), and reference gas (1% and 5% H_2 in N_2, Air Liquide) were purchased from commercial suppliers. All reagents and solvents were used as received. The $[Co(CR14)Cl_2]Cl$ catalyst (**Co**) was prepared according to the literature procedure.[1]

Purification of water (15.0 MΩ cm, 24°C) was performed with a milli-Q system (Purelab option, Elga). ^1H NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer. Chemical shifts for the ^1H NMR spectrum are referenced relative to residual protium in deuterium oxide (D_2O, $\delta = 4.80$ ppm). The electrospray ionization mass spectrometry (ESI-MS) spectra were registered on a Bruker Esquire 3000 plus and Amazon speed ion trap spectrometer equipped with an electrospray ion source. The samples were solubilized in a mixture of methanol/water and analyzed in negative ionization mode by direct perfusion in the ESI-MS interface.

^1H NMR and mass spectrometry were performed within the ICMG Chemistry Nanobio Platform, Grenoble.

2. Synthesis of $Na_4[Ru((SO_3Ph)_2phen)_3]$ (RuSPhphen)

The tetrasodium Tris[(1,10-phenanthroline-4,7-diyl-κN,κN')bis(benzenesulfonato) (2-)]ruthenate(4-) complex has been synthetized according to a procedure adapted from literature.[2] $Ru^{III}Cl_3 \cdot 3H_2O$ (40.4 mg, 0.2 mmol) was dissolved in a 1:1 ethanol/water mixture (total volume of 20 mL) under an argon atmosphere. After 5 minutes, the disodium (1,10-phenanthroline-4,7-diyl)bis(benzenesulfonate) ligand (406 mg, 0.70 mmol) was added to the reaction mixture which was then purged of oxygen by three vacuum/argon cycles. The reaction mixture was heated under reflux (100°C) under argon for 5 hours. The mixture's color turned from black to dark orange. [3] [3] [3] [3] Then, the mixture was cooled to room temperature, and concentrated to reach a volume of about 3 mL. To the resulting solution, 5 mL of cold EtOH were then added. The resulting solution was added dropwise to a cold acetone solution (35 mL) and an orange precipitate was formed. The precipitate was filtered off, washed with cold acetone, and then dried under vacuum overnight. The orange solid was then redissolved in 4 mL of water and then precipitated by addition of cold ethanol. The orange precipitate was filtered off, washed with ethanol and with acetone and then dried under vacuum for one day, affording the $Na_4[Ru((SO_3Ph)_2phen)_3]$ complex (**RuSPhphen**) (313 mg, Yield 95%). ^1H NMR (D_2O); 400 MHz; δ (ppm): 9.04 (d, J = 4.0 Hz, 2H), 8.28 (d, J = 4.0 Hz, 6H), 8.12 (s, 6H), 7.95 (m, 9H), 7.81 (s, 2H), 7.72 (m, 8H), 7.59 (d, J = 4.0 Hz, 6H), 7.55 - 7.50 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H) (Figure S1). ESI-MS, negative mode *m/z* (%) for $Na_4C_{72}H_{42}N_6O_{18}RuS_6$ ($Na_4[Ru((SO_3Ph)_2phen)_3]$ (M)): 531.89 (7.8) $[M-3Na]^{3-}$, 524.24 (9.5) $[M-4Na]^{3-}$, 392.92 (100) $[M-4Na]^{4-}$ (Figure S2).

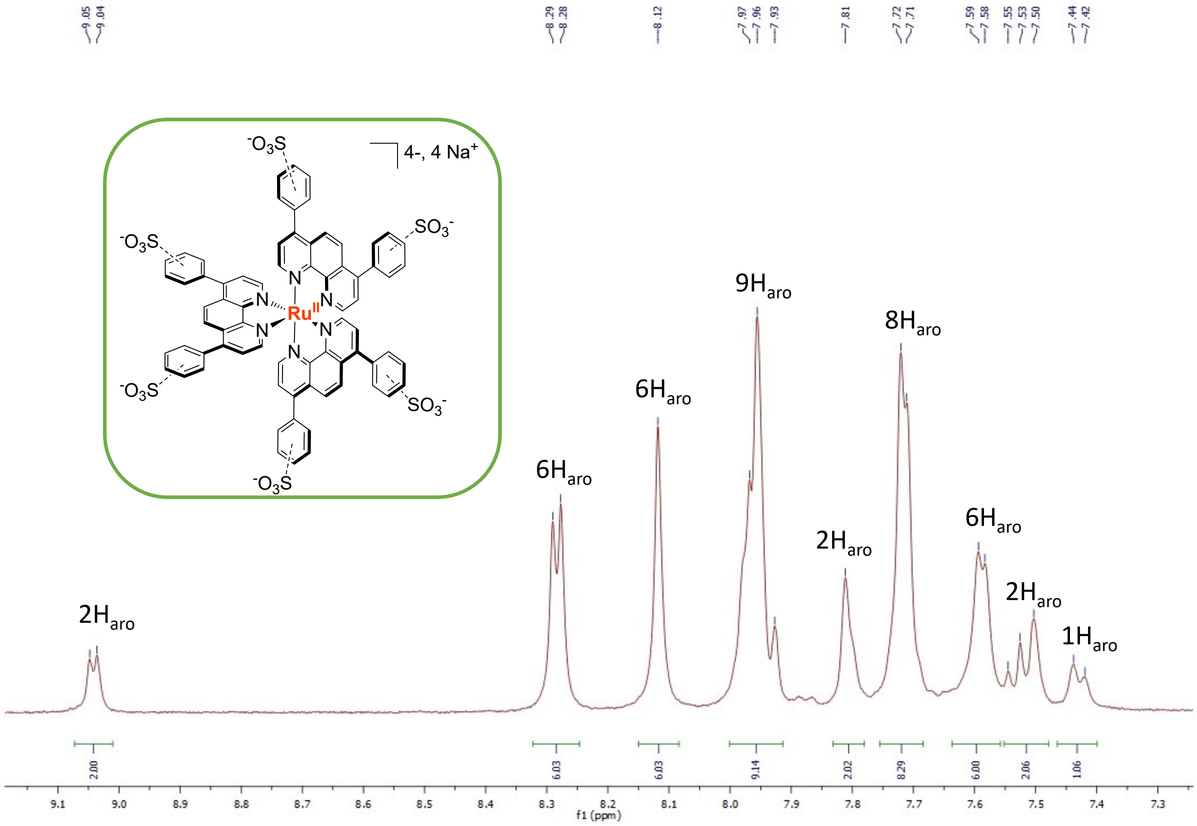

Fig. S1. ^{1}H RMN spectrum (400 MHz) of **RuSPhphen** in D_2O.

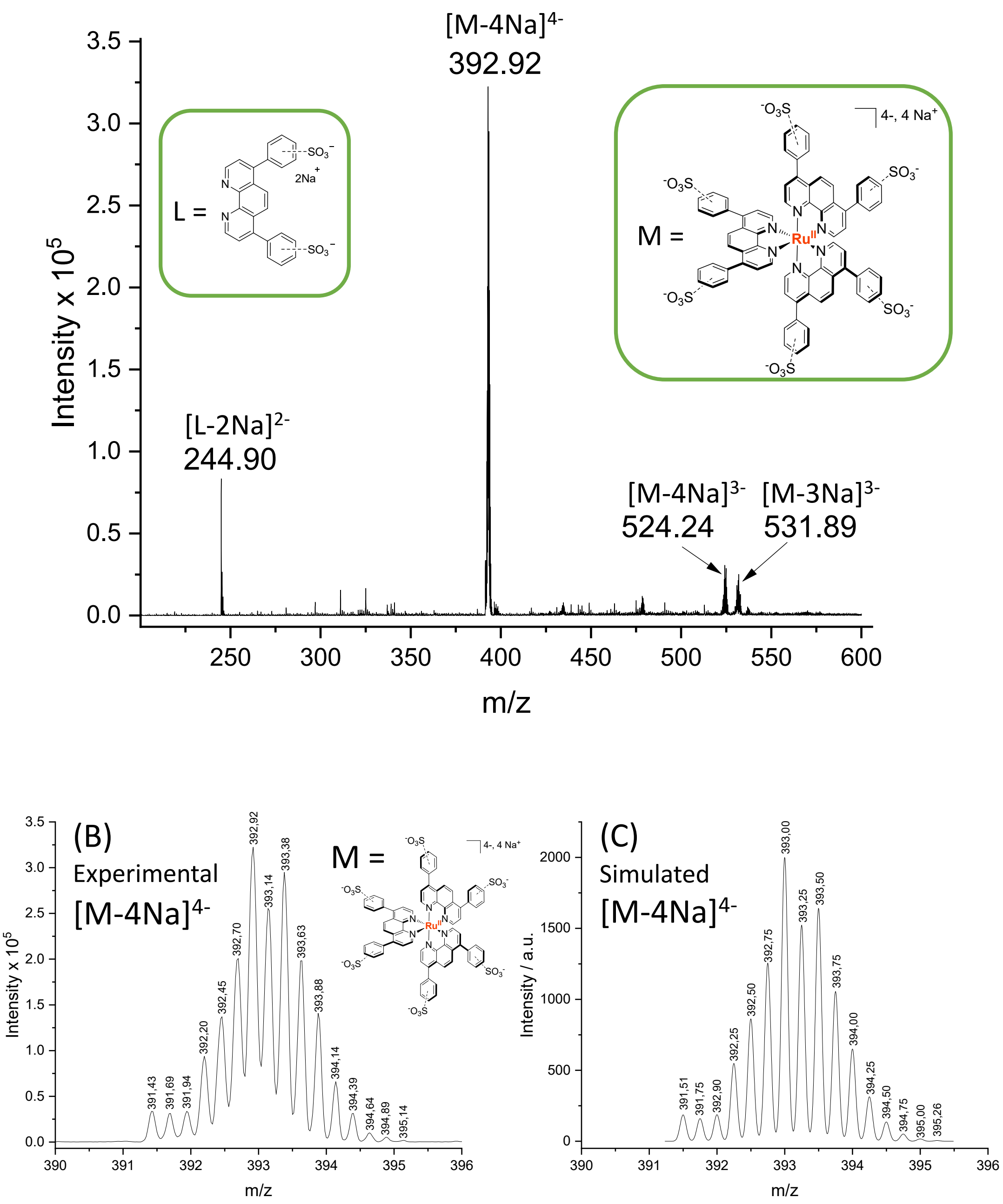

Fig. S2. ESI-MS spectrum in negative mode of **RuSPhphen** in MeOH/H_2O (A) and enlargements of the $[M\text{-}4Na]^{4-}$ isotopic massif at *m/z* = 392.92 (B) and the corresponding simulation (C).

3. Electrochemistry and UV-visible absorption spectroscopy.

The electrochemical measurements were run under an argon atmosphere in a dry glove-box at room temperature. Cyclic voltammetry experiments were recorded using a Solartron Analytical Instrument potentiostat (Modulab XM MTS) with XM-studio as software. A standard three-electrode electrochemical cell was used. In DMF, electrochemical experiments were carried out with 0.1 M $[Bu_4N]ClO_4$ as electrolyte. The working electrode, polished with 2 µm diamond paste (MecaprexPresi), was a carbon vitreous disk (3 mm in diameter) for cyclic voltammetry ($E\text{p}_a$, anodic peak potential; $E\text{p}_c$, cathodic peak potential; $E_{1/2} = (E\text{p}_a + E\text{p}_c)/2$; $\Delta E\text{p} = E\text{p}_a - E\text{p}_c$). Exhaustive electrolyses were carried out on a reticulated vitreous carbon electrode 60 PPI (the electrosynthesis Co. Inc.) three-dimensional meshes (1.8 cm x 0.7 cm x 0.4 cm). The auxiliary electrode was a Pt wire in DMF, 0.1 M $[Bu_4N]ClO_4$. Potentials were referred to an $Ag/AgNO_3$ 0.01 M reference electrode in CH_3CN + 0.1 M $[Bu_4N]ClO_4$. With this reference electrode, the potential of the ferrocenium/ferrocene ($Fc^{+/0}$) couple (reversible wave) is located at $E_{1/2} = 60$ mV.

The UV-Vis absorption spectra were recorded with a MCS 501 UV-NIR (Carl Zeiss) spectrophotometer equipped with an automatic shutter. The light sources are halogen (CLH 500 20 W) and deuterium lamps (CLD 500). The spectrophotometer was equipped with optic fibers (041.002–UV SN 012105) in order to perform the spectroelectrochemical experiments into the glove box with a 1 mm path-length cell (Figures 2 and S3). To record UV-Vis absorption spectra of the photocatalytic solutions containing **Ru**/**Co**/HA^-/H_2A or **Ru**/**Co**, in order to monitor the PS degradation during photocatalysis, a quartz cuvette of 1 mm was used (Figures 4 and 7).

Table S1. Potentials of the Ru PSs in DMF solvent and in water. In DMF, 0.1M $[Bu_4N]ClO_4$, the ferrocene/ferrocenium couple *vs* the reference electrode Ag/0.01 M $AgNO_3$ has been measured at $E_{1/2}$ = +60 mV. In water, the reference electrode Ag/0.01 M $AgNO_3$ can be converted to SCE by adding 298 mV.

Compound	Solvent	Redox potentials $E_{1/2}$ /V *vs* Ag/0.01 M $AgNO_3$(ΔEp/mV)			
		$Ru^{III/II}$	Ligand-centered reduction process ($L/L^{\bullet -}$)		
$[Ru(bpy)_3](PF_6)_2$ (**Rubpy**)[This work]	DMF	+0.88 (110)	-1.65 V (80)	-1.82 V (80)	-2.09 (80)
$(Na)_4[Ru((SO_3Ph)_2phen)_3]$ (**RuSPhphen**)[This work]	DMF	+0.80 (90)	-1.61 V (120)	-1.78 (100)	-2.00 (90)
Compound	Redox potentials/V (ΔEp/mV) *vs* SCE				
$[Ru(bpy)_3]Cl_2$ (**Rubpy**)[4-5]	H_2O (pH 7)	+1.03 ($Ru^{III/II}$)	-1.50 ($Ru^{II}/Ru^{\bullet -}$)		
***Rubpy**[4-5, a]	H_2O (pH 7)	-1.07 ($Ru^{III}/{*Ru^{II}}$)	+0.60 ($*Ru^{II}/Ru^{\bullet -}$)		
***RuSPhphen**[This work,a]	DMF	-0.92 V ($Ru^{III}/{*Ru^{II}}$)	+0.71V ($*Ru^{II}/Ru^{\bullet -}$)		
$[Co^{III}(CR14)Cl_2](ClO_4)$ or $[Co^{III}(CR14)Cl_2]Cl$[b] (**Co**)[6]	H_2O, 0.1M CF_3CO_2Na	+0.23 (128) ($Co^{III/II}$)	-0.85 (69) ($Co^{II/I}$ or $CR/CR^{\bullet -}$)	-[c]	

[a] Oxidation and reduction potentials of the excited state of the Ru complexes (marked by *) are estimated by using the formula : $E_{1/2}(Ru^{III}/{*Ru^{II}}) = E_{1/2}(Ru^{III}/Ru^{II}) - E_{0,0}$ and $E_{1/2}(*Ru^{II}/Ru^{\bullet -}) = E_{1/2}(Ru^{II}/Ru^{\bullet -}) + E_{0,0}$. $E_{0,0}$ is the energy level of the relaxed triplet excited state (^{3}MLCT) of the Ru complexes in water, which is equal to 2.1 eV for **Rubpy**, and 2.02 eV for **RuSPhphen**, the latter having been determined from λ_{em}^{max} value of 590 nm for **Rubpy** in H_2O[5] and 615 nm for **RuSPhphen** in H_2O (mesured in deaerated solution in this work, Fig. S6).

[b] In water, the choride ligands are substituted by water molecules

[c] This wave is not clearly observable in water.

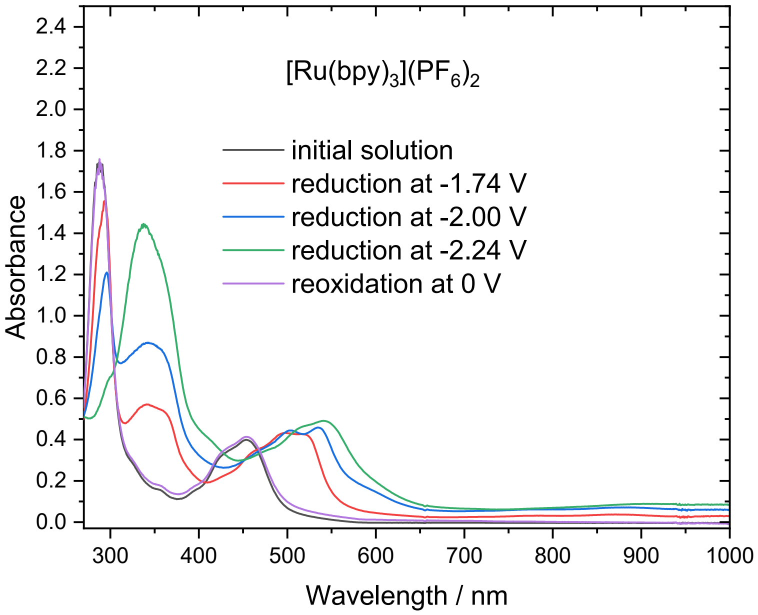

Fig. S3. UV-visible absorption spectra changes of a 0.30 mM solution of $[Ru(bpy)_3](PF_6)_2$ (**Rubpy)** in DMF, 0.1 M $[Bu_4N]ClO_4$, after three successive exhaustive reductions at (a) E = -1.74 V (formation of $[Ru^{II}(bpy)_2(bpy^{\bullet-})]^+$ (**Rubpy**$^{\bullet-}$), (b) E = -2.00 V (formation of $[Ru^{II}(bpy)(bpy^{\bullet-})_2]^0$), and (c) E = -2.24 V (formation of $[Ru^{II}(bpy^{\bullet-})_3]^-$) and (d) after a reoxidation at 0.0 V (reformation of **Rubpy**). Optical path of 1 mm.

4. General procedure for photocatalytic hydrogen generation.

Samples preparation. For experiments performed in an aqueous solution with 1.1 M NaHA/H_2A at pH 4.0, a 5 mL graduated flask was charged with the **Rubpy** or **RuSPhphen** PS weighted as a solid in order to obtain the concentrations of 100, 50 and 25 µM. More precisely, for **Rubpy**, 0.37, 0.19 and 0.09 mg of PS were weighted for the respective concentrations of 100, 50 and 25 µM, and for **RuSPhphen**, 0.94, 0.47 and 0.24 mg of PS were weighted for the respective concentrations of 100, 50 or 25 µM. Then 53, 106, 530 and 1059 µL of a $[Co^{III}(CR14)Cl_2]Cl$ (**Co**) catalyst solution at 472 µM in Milli-Q water were added into the 5 mL flask containing Ru in order to obtain a catalyst concentration of 5, 10, 50 and 100 µM, respectively. After completing the volume to 5 mL with Milli-Q water, the Ru PS concentration (100, 50 and 25 µM) was checked by UV-Vis absorption spectroscopy using a cuvette of 1 mm optical pathlength. Absorbances of 0.15, 0.07 and 0.04 were obtained at 452 nm with an ε value of 14 600 M^{-1} cm^{-1} in water for **Rubpy** for the respective concentrations of 100, 50 and 25 µM, and absorbances of 0.29, 0.15 and 0.07 were obtained at 462 nm with an ε value of 29 300 M^{-1} cm^{-1} in water for **RuSPhphen** for the respective concentrations of 100, 50 and 25 µM.

The solutions of **Ru** and **Co** (5 mL) were then transferred in a homemade glass tube with a diameter of 2 cm fused with a round bottom flask (total volume of 204 mL, which corresponds to a head space volume of 199 mL considering that a solution of 5 mL is introduced) containing a magnetic stirrer (volume < 0.1 mL). The glass tube was sealed with a rubber septum and the solution was degassed for about 30 minutes by argon bubbling. Then sodium ascorbate (NaHA)

(545 mg, 0.55 M) and ascorbic acid (H_2A) (484.3 mg, 0.55 M) were quickly added as solids to the solution (after the septum removal) to give a total concentration of 1.1 M, and the septum was quickly repositioned on the glass reactor. The latter was covered with a sheet of aluminum foil to protect the solution from light, and the solution was further degassed for 15 minutes before irradiation.

For experiments conducted in 1.0 M acetate buffer at pH 4.5, with 0.1 M NaHA/H_2A, a similar procedure was followed to prepare photocatalytic solution, except that the aqueous solution (Milli-Q water) was buffered with acetate. The 1.0 M acetate buffer solution at pH 4.5 was prepared by mixing AcOH (0.183 mL, 0.64 M) and NaOAc (0.148 g, 0.36 M) in Milli-Q water. The pH was adjusted to 4.5 by adding suitable amounts of NaOH or HCl. In addition, NaHA (0.075 g, 76 mM) and H_2A (0.021 g, 24 mM) were added as solids to the solution of **Ru** and **Co** to give a total concentration of 0.1 M in NaHA/H_2A.

Irradiation conditions. Continuous irradiation was performed at 298 K under stirring with a xenon lamp (150 W, Hamamatsu L8253, type LC8-03) equipped with a 400 – 700 nm large band filter which was placed 4 cm from the sample. The irradiation power received by the sample (P = 86.5 ± 2.5 mW.cm^{-2}) was measured with a calibrated Avantes spectrometer AvaSpec-ULS2048CL-EVORS-UA, with a slit of 20 µM, equipped with a fiber cable FC-UVIR400-1 and a Cosine corrector CC-UV/VIS/NIR-8MM.

Quantification of H_2. The amount of hydrogen evolved during photocatalysis was quantified from an analysis of the gas mixture in the headspace of the glass tube (sampling of 100 µL of gas) by gas chromatography (Perkin Elmer Autosystem XL Gas Chromatograph equipped with a 5 Å molecular sieve column (oven temperature = 303 K) and a thermal conductivity detector (TCD)), which uses argon as a carrier gas. Prior to each experiment, GC/TCD calibration was carried out by using two samples of the reference gas (1.045 % and 4.967 % H_2 in N_2).

The turnover number (TON) and turnover frequency (TOF) for H_2 production were determined as previously described.[1, 7]

Table S2. Wavelengths of the absorption maxima in the visible region (λ_{max}^{Abs}), the emission maxima (λ^{Em}_{max}) and the emission lifetimes (τ) for $[Ru(bpy)_3]Cl_2$ (**Rubpy**) and $(Na)_4[Ru((SO_3Ph)_2phen)_3]$ (**RuSPhphen**) PSs.

Complex^{Ref}	Solvent	λ_{abs}^{max}/nm (ε, M^{-1} cm^{-1})	λ_{em}^{max}/nm	τ^0/µs^a
Rubpy[2, 8]	H_2O	452 (14 600^b)	630 (590^c)	0.61
	DMF	452 (14 000)	635	
RuSPhphen[2]	H_2O	462 (29300)	632 (615^d)	3.80
	DMF	462 (32800)	637	

^{a} deaerated solutions; ^{b} from reference[9]; ^{c} from reference[5]; ^{d} measured in this work in deaerated aqueous solution (Figure S6).

Table S3. Photocatalytic activities towards hydrogen evolution of all systems studied in terms of TON_{Cat}, TOF_{Cat}, n_{H_2} and v_{H_2}. Experiments were carried out at 22° C in the presence of the $[Co^{III}(CR14)Cl_2]Cl$ (**Co**) catalyst (Cat) and a photosensitizer $[Ru(bpy)_3]Cl_2$ (**Rubpy**) or $(Na)_4[Ru((SO_3Ph)_2phen)_3]$ (**RuSPhphen**) at various concentrations in an aqueous buffer of 1.1 M $NaHA/H_2A$ at pH 4.0 (5 mL) or in 1 M acetate buffer (5 mL) with 0.1 M $NaHA/H_2A$, under visible-light irradiation (λ = 400 -700 nm).

PS [μM]	Cat [μM]	$NaHA/H_2A$ [M] pH	PS/Cat	TON_{Cat}^a (TON_{Cat}*)^b	TOF_{Cat}^a	$^a v_{H_2}$ mL (v_{H_2*})^b	$n_{H_2}^a$ μmol (n_{H_2*})^b	Irrad. time^c h
0	**Co** (100)	0.55/0.55 4.0	-	0	0	0	0	21
Rubpy (100)	0	0.55/0.55 4.0	-	-	-	0.0103	0.42	22
	$CoCl_2•6H_2O$ (100)		1/1	1	-	0.012	0.48	22
	Co (5)		20/1	1632 (1615)	1680	1.00 (0.99)	40.80 (40.38)	25.3
	Co (10)		10/1	1384 (1375)	518	1.70 (1.69)	69.19 (68.77)	26.5
	Co (50)		2/1	816 (814)	38	5.00 (4.99)	204 (203.58)	23.5
	Co (100)		1/1	470 (470)		5.76 (5.75)	235.2 (234.81)	25
RuSPhphen (100)	0	0.55/0.55 4.0	-	-	-	0.026	1.06	20.5
	$CoCl_2•6H_2O$ (100)		1/1	2	-	0.024	0.96	22
	Co (5)		20/1	3173 (3131)	765	1.94 (1.91)	79.33 (78.27)	21.5
	Co (10)		10/1	2607 (2586)	503	3.19 (3.16)	130.35 (129.29)	22
	Co (50)		2/1	874 (870)	30	5.35 (5.33)	218.52 (217.46)	27
	Co (100)		1/1	412 (410)	3	5.04 (5.02)	205.86 (204.80)	28
+ Hg	**Co** (10)		10/1	2543 (2522)	496	3.12 (3.09)	127.15 (126.09)	22
Rubpy (50)	**Co** (10)	0.55/0.55 4.0	5/1	701	411	0.86	35.06	23
Rubpy (25)	**Co** (10)		2.5/1	310	117	0.38	15.49	22
RuSPhphen (50)	**Co** (10)	0.55/0.55 4.0	5/1	1482	226	1.82	74.08	21
RuSPhphen (25)	**Co** (10)		2.5/1	708	255	0.87	35.42	21
0	**Co** (100)	0.03/0.07 4.5	-	0	0	0	0	21
Rubpy (100)	0	0.03/0.07 4.5	-	-	-	0.087	3.54	22.8
	$CoCl_2•6H_2O$ (100)		1/1	2	-	0.024	0.96	21.8
	Co (5)		20/1	3897 (3755)	1348	2.39 (2.30)	97.42 (93.88)	22
	Co (10)		10/1	3009 (2938)	582	3.69 (3.60)	150.44 (146.90)	22
	Co (50)		2/1	948 (934)	32	5.81 (5.72)	236.94 (233.40)	28
	Co (100)		1/1	150 (143)	1	1.84 (1.75)	74.92 (71.38)	28
RuSPhphen (100)	0	0.03/0.07 4.5	-	-	-	0.019	0.71	22
	$CoCl_2•6H_2O$ (100)		1/1	1	-	0.012	0.48	20
	Co (5)		20/1	4772 (4744)	1095	2.92 (2.90)	119.3 (118.59)	23
	Co (10)		10/1	3214 (3200)	249	3.94 (3.92)	160.69 (159.98)	21
	Co (50)		2/1	1312 (1309)	13	8.04 (8.02)	327.99 (327.28)	29
	Co (100)		1/1	373 (372)	1	4.57 (4.55)	186.62 (185.91)	28.5

^{a}TON_{Cat} and TOF_{Cat} are respectively the maximum turnover number and the initial turnover frequency (TOF_{Cat} = TON_{Cat} h^{-1}) per catalyst exhibited by the system, n_{H_2} and v_{H_2} the total mole number and volume of H_2 produced for a specific irradiation time. ^{b}TON_{Cat}*, n_{H_2*} and v_{H_2*} are the corrected values of TON_{Cat}, n_{H_2} and v_{H_2}, respectively, obtained by subtracting the production of H_2 stemming from **Rubpy** or **RuSPhphen** without catalyst. ^{c}Irrad. time: time of irradiation for the last H_2 measurement.

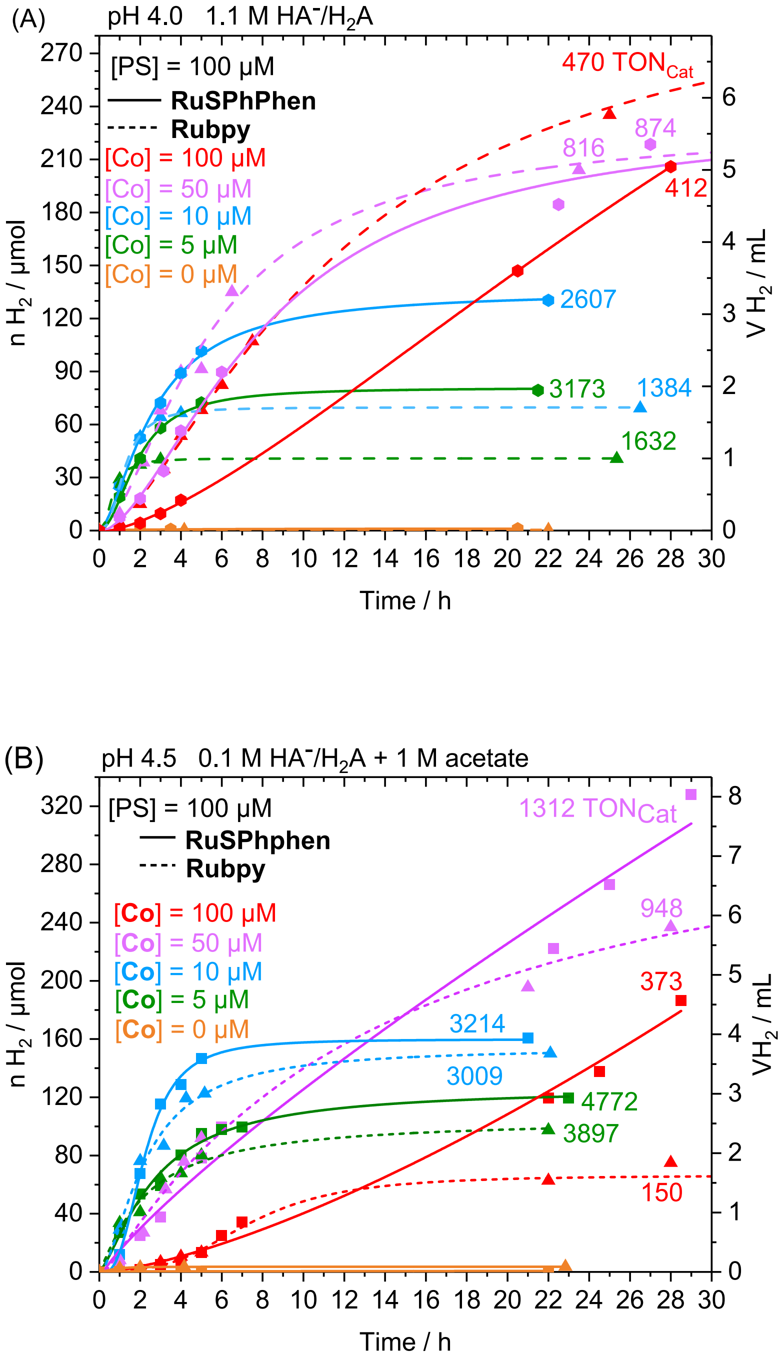

Fig. S4. Photocatalytic hydrogen production under visible light irradiation (400 – 700 nm) as a function of time in n_{H_2} and v_{H_2} from a deaerated aqueous solution (5 mL) of (A) NaHA (0.55 M) and H_2A (0.55 M) at pH 4.0 and (B) NaHA (0.0714 M), H_2A (0.0286 M) and acetate buffer (1 M) at pH 4.5, in presence of a PS (100 µM **RuSPhphen** or **Rubpy**) and the **Co** catalyst at various concentrations (5, 10, 50, 100 µM).

Mercury poisoning test for photocatalytic experiments. Colloidal cobalt can act as a catalyst for the reduction of protons into hydrogen.[10] To exclude the formation of such particles that could result from the decomposition of the cobalt molecular catalyst, **Co**, in the course of the photocatalysis, a mercury poisoning test was performed. Mercury is known to form amalgam with colloidal metal or to adsorb to nanoparticle of metal catalysts[11] and mercury poisoning has been reported for cobalt colloids.[12] A drop of mercury was added to the 5 mL aqueous solution containing **RuSPhphen** (100 µM) and **Co** (10 µM). This mixture was stirred and degassed by argon bubbling during 30 min in a septum sealed glass reactor. Then, the septum was quickly removed and NaHA/H_2A (1.1 M) was then added, and the septum was quickly repositioned on the glass reactor. The latter was covered with a sheet of aluminum foil to protect the solution from light, and the solution was further degassed for 15 minutes before irradiation.

The solution was then irradiated under vigorous stirring and the H_2 production was analyzed under the same conditions as the classical photocatalytic experiment (Figure S4).

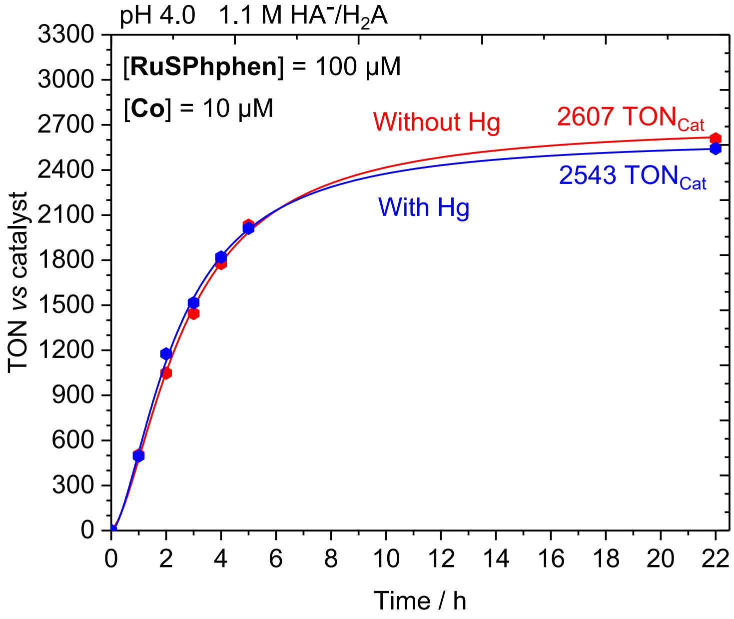

Fig. S5. Photocatalytic hydrogen production (TON_{Cat}) as a function of time from a deaerated aqueous solution (5 mL) of NaHA (0.55 M) and H_2A (0.55 M) at pH 4.0 under visible light irradiation (400 – 700 nm) in presence of **RuSPhphen** (100 µM) and **Co** (10 µM) with (blue) and without mercury (red).

5. Photophysics

Emission spectroscopy. The emission spectrum was recorded on Fluoromax-4 spectrofluorimeter (Horiba Scientific) at room temperature with a quartz cuvette of 1 cm (entry and exit slits of 2 nm, integration time 0.1 s).

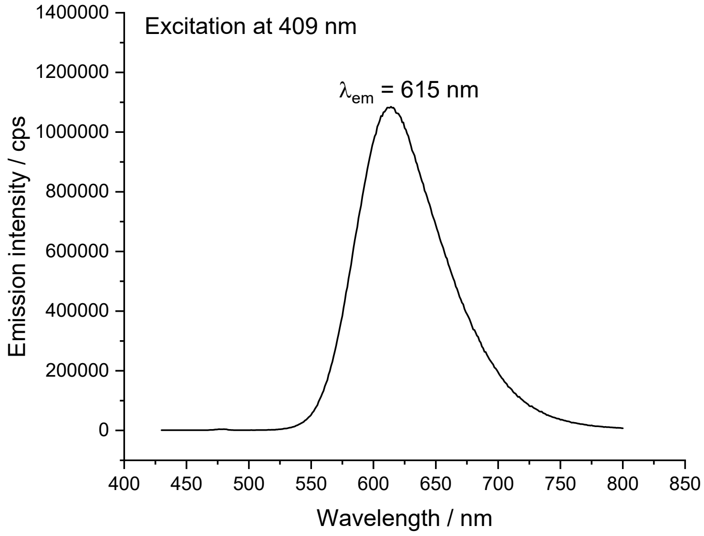

Fig. S6. Emission spectra performed in deaerated aqueous solution at pH 4.5 (0.1 M acetate buffer) containing 3.4 µM **RuSPhphen**, with an excitation at 409 nm; optical path = 1 cm.

Stern-Volmer plot. Stern-Volmer experiments were carried out with several degassed aqueous solutions (1 M acetate buffer at pH 4.5 and pH 4.0) containing **Rubpy** (10 µM) or **RuSPhphen** (3.4 µM), respectively, in the presence of $[Co^{II}(CR14)(H_2O)_2]^{2+}$ at different concentrations (0 ; 0.06; 0.08; 0.1; 0.15 mM) for oxidative quenching of PS, and in the presence of DS NaHA/H_2A at different concentrations (0; 3.3; 7.7; 15.4 and 19.8 mM) for reductive quenching. All these solutions were prepared in a glovebox under argon atmosphere inside quartz cells (optical path = 1 × 1 cm^2). Stern-Volmer experiments were carried out with $[Co^{II}(CR14)(H_2O)_2]^{2+}$ as our previous studies have shown that during photocatalysis, this species is immediately generated following the reduction of $[Co^{III}(CR14)Cl_2]^+$ by ascorbate HA^- as well as through the exchange of chloride ligands with the solvent.[1] $[Co^{II}(CR14)(H_2O)_2]^{2+}$ solutions were prepared from an aqueous solution of $[Co^{III}(CR14)Cl_2]^+$ (0.5 mM) containing 0.1 M $NaClO_4$ (pH 4.5), which underwent an exhaustive electrochemical reduction at -0.20 V *vs* Ag/AgCl.

For Stern-Volmer plots obtained from I_0/I values, emission spectra of PSs were recorded after excitation at 462 nm for **RuSPhphen** and 450 nm for **Rubpy**, and the intensity of emission band at 614 nm for **RuSPhphen** and 610 nm for **Rubpy** in the absence (I_0) and presence of catalyst or SD (I) were used to calculate the I_0/I values to trace the Stern-Volmer plots. The emission spectra of PSs were recorded on Fluoromax-4 spectrofluorimeter (Horiba Scientific) at room temperature (entry and exit slits of 2 nm, integration time 0.1 s).

For Stern-Volmer plots obtained from τ_0/τ values, emission decays (τ) of the excited state of PSs (*PSs) were recorded at room temperature after excitation at 409 nm with a picosecond pulsed laser diode (PDL 800D PicoQuant, laser diode: LDH-P-C-405, entry and exit slits of 1 mm) and using time-correlated single photon counting detection (picoHarp 300). The lifetimes of *PSs in the absence (τ_0) and presence of catalyst or SD (τ), estimated from the luminescence decay correlation curve of ***Rubpy** at 610 nm and ***RuSPhphen** at 614 nm, were used to calculate the τ_0/τ value to trace the Stern-Volmer plots. The correlation curves are multi-exponential functions of the type $I_{em}(t) = \sum_{i=1}^{n} A_i e^{-\frac{t}{\tau_i}}$ (where n = 1 or 2 or 3) where $I_{em}(t)$ is the emission intensity over time of the solution containing PS and Cat (or PS and SD) and τ_i is the lifetime of the luminescence decay with A_i, its percentage contribution.

The lifetimes of ***Rubpy** and ***RuSPhphen** alone (τ_0) were determined in degassed water at 595 ns and 4.0 µs, respectively. The global oxidative quenching kinetic constants ($k_{ox} = k_S + k_D$) of ***Rubpy** and ***RuSPhphen** by $[Co^{II}(CR14)(H_2O)_2]^{2+}$ were estimated, at pH 4.5, at 7.07×10^9 and 1.34×10^{10} M^{-1} s^{-1}, respectively, and at pH 4.0 with ***RuSPhphen** at 9.22×10^9 M^{-1} s^{-1}. The kinetic constant for reductive quenching of ***RuSPhphen** by HA^- was determined to be 9.41×10^7 and 5.04×10^7 M^{-1} s^{-1} at pH 4.5 and 4.0, respectively.

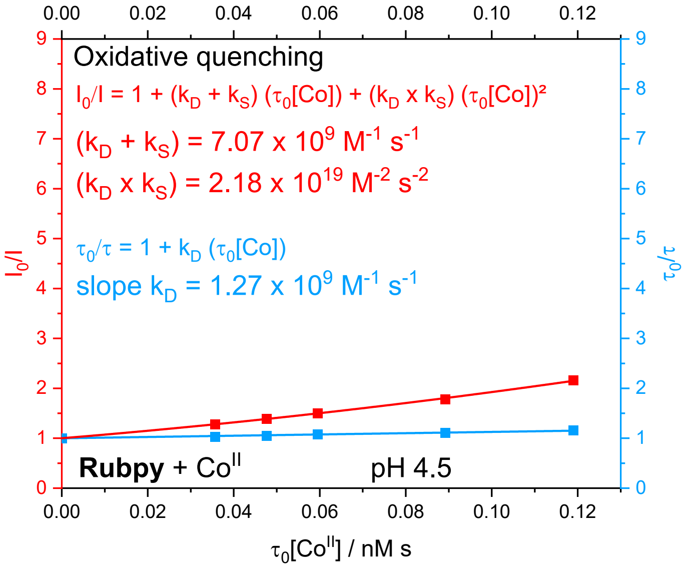

Fig. S7. Stern-Volmer plot performed by stationary (I_0/I, red trace) and time-resolved (τ_0/τ, blue trace) luminescence spectroscopies in deaerated aqueous solution at pH 4.5 (0.1 M acetate buffer) for the oxidative quenching of **Rubpy** (10 µM) at the excited state by **Co^{II}** by varying its concentration (0, 0.08, 0.10, 0.15 and 0.20 mM). I and I_0 are respectively the emission intensities of ***Rubpy** registered at 608 nm with an excitation at 450 nm, with or without **Co^{II}**. τ and τ_0 are respectively the lifetimes of ***Rubpy Rubpy** registered at 610 nm with an excitation at 409 nm, with or without **Co^{II}**. Lifetime of ***Rubpy** without catalyst (τ_0) was determined to be 595 ns.

Nanosecond transient absorption spectroscopy. The photocatalytic mechanism was investigated by photolysis experiments with nanosecond laser flashes, which were performed by exciting degassed aqueous solutions at 455 nm: (i) with acetate buffer (1 M) at pH 4.5 containing **RuSPhphen** (50 µM) and NaHA/H_2A mixture (0,1 M), in the presence or absence of $[Co(CR14)Cl_2]Cl$ (**Co**) (200 µM), and (ii) at pH 4.0 containing **RuSPhphen** (50 µM) and NaHA/H_2A mixture (1.1 M), in the presence or absence of **Co** (200 µM). Samples were prepared in a glovebox under an argon atmosphere inside a quartz cell (optical path = 1 × 1 cm²). Transient absorption spectra were recorded using an Edinburgh Instruments LP 920K system. Excitation at 455 nm was performed using the third harmonic of a Brilliant-Quantel Nd:YAG laser at 6 Hz, equipped with an OPO (Rainbow). A Xe900 pulsed Xenon lamp was used as the probe source. Photons were scattered using a monochromator, transcribed by a R928 photomultiplier (Hamamatsu) and recorded on a TDS3012C oscilloscope (Tektronix). Analysis of individual wavelengths and a global analysis of transient absorption data were performed using Origin software.

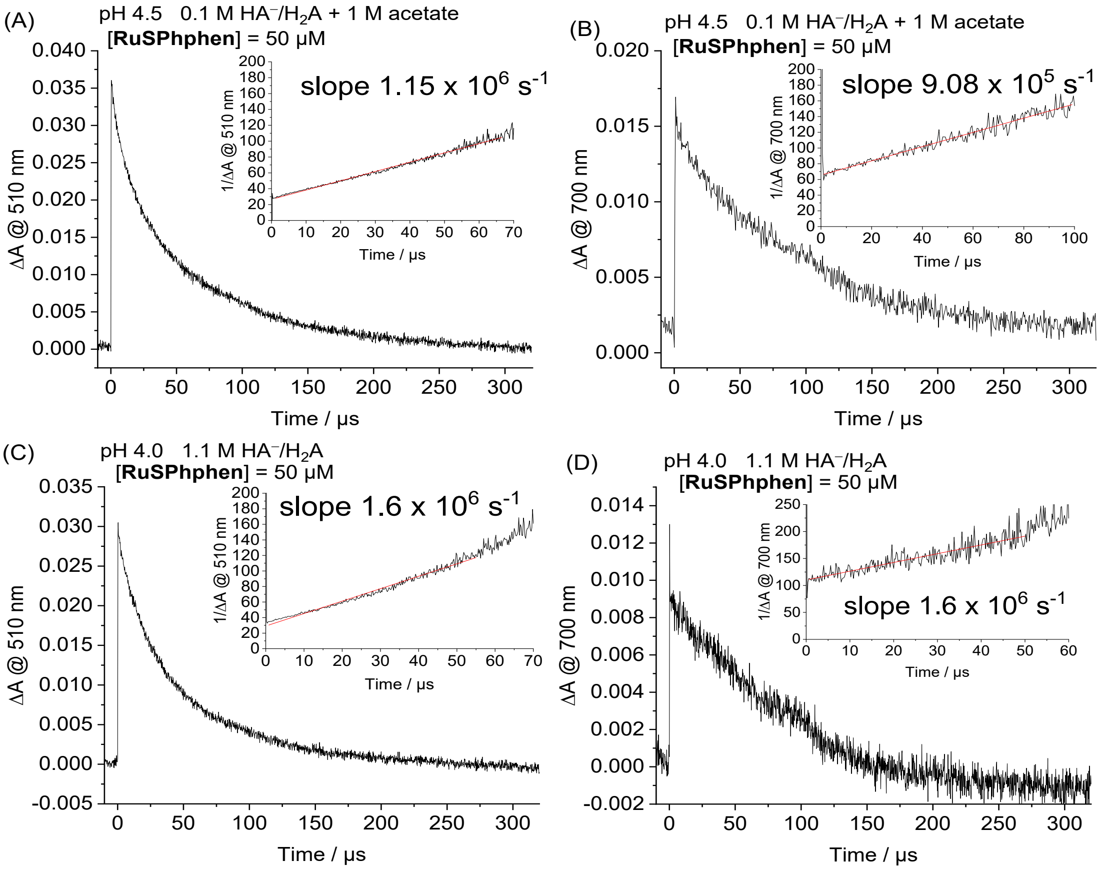

Fig. S8. Transient absorption traces on the microsecond time scale recorded at 510 (A and C) and 700 nm (B and D) after laser excitation ($\lambda = 462$ nm) of (A-B) a deaerated aqueous solution of 1 M acetate buffer and NaHA/H_2A (0.1 M) at pH 4.5 containing **RuSPhphen** (50 µM) and (C-D) a deaerated 1.1 M NaHA/H_2A aqueous solution at pH 4.0 containing **RuSPhphen** (50 µM)); optical pathlength = 1 cm. Insets: second order kinetics analysis of the decay at 510 (A and C) and 700 nm (B and D). The slopes give a second order kinetics ($k_{obs} = k_{BET}/\Delta\varepsilon$) of 1.15×10^6 s^{-1} (A) and 9.08×10^5 s^{-1} (B) respectively with the decays at 510 and 700 nm at pH 4.5, and 1.6×10^6 s^{-1} (C-D) with the decays at 510 and 700 nm at pH 4.0.

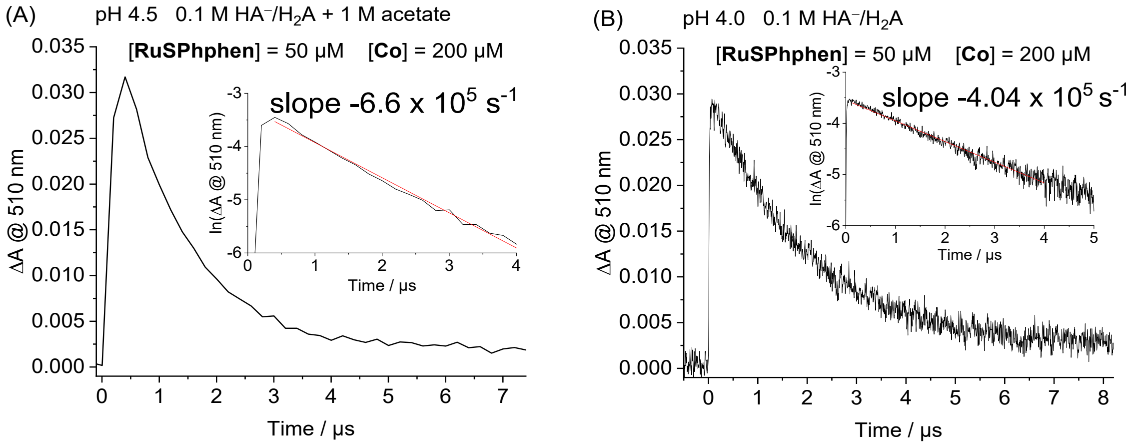

Fig. S9. Transient absorption traces recorded at 510 nm after laser excitation (λ = 462 nm) of (A) a deaerated aqueous solution of 1 M acetate buffer and NaHA/H_2A (0.1 M) at pH 4.5 containing **RuSPhphen** (50 µM) and **Co** (200 µM) within the time ranges 0-7 µs, and (B) a deaerated 1.1 M NaHA/H_2A aqueous solution at pH 4.0 containing **RuSPhphen** (50 µM), **Co** (200 µM) and within the time ranges 0-8 µs; optical pathlength = 1 cm. Insets (A and B): pseudo order kinetics analysis of the decay at 510 nm. The slopes for the decays at 510 nm give a second order kinetics (k_{obs}) of 6.6 × 10^5 s^{-1} (A) at pH 4.5 and 4.04 × 10^5 s^{-1} (B) at pH 4.0.

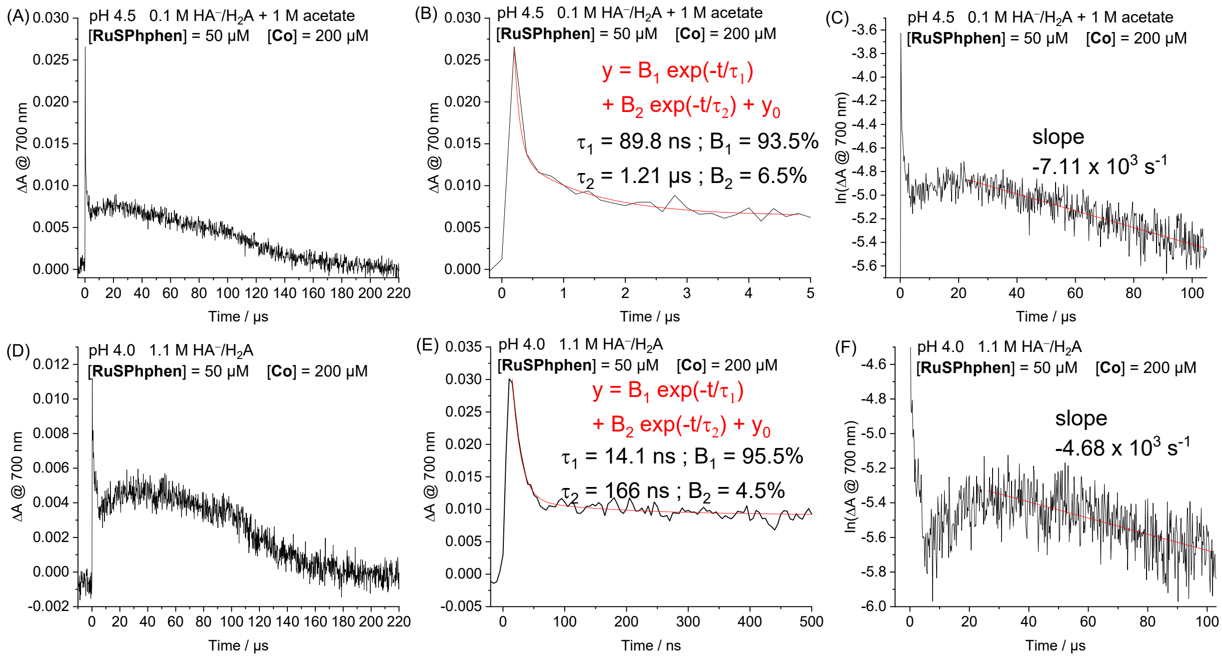

Fig. S10. Transient absorption traces recorded at 700 nm after laser excitation (λ = 462 nm) of (A-B) a deaerated aqueous solution of 1 M acetate buffer at pH 4.5 and NaHA/H_2A (0.1 M) containing **RuSPhphen** (50 µM), **Co** (200 µM) within the time ranges 0-220 µs (A) and 0-5 µs (B), and (D-E) a deaerated 1.1 M NaHA/H_2A aqueous solution at pH 4.0 containing **RuSPhphen** (50 µM) and **Co** (200 µM) within the time ranges 0-220 µs (D) and 0-500 ns (E) ; optical pathlength = 1 cm. Pseudo-first order kinetics analyses of the decay at 700 nm in the time range 0 – 100 µs (C and F).

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