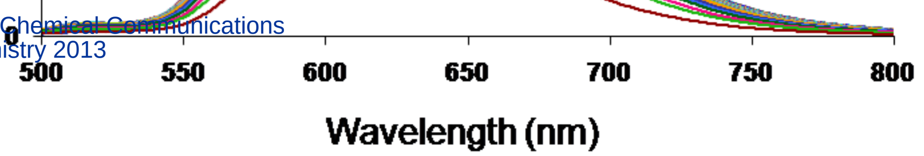

Light driven water oxidation by a single site Cobalt Salophen catalyst

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1. Materials and Methods

All solvents and reagents were purchased from Fluka, Sigma Aldrich or Carlo Erba and used as received.

Microwave synthesis: Continuous microwave irradiation was carried out in a CEM-Discover monomode microwave apparatus, with simultaneous monitoring of irradiation power, pressure and temperature. Compressed air was applied to improve the temperature control of the reaction mixtures.

ESI-MS: Mass spectra were performed with an Agilent Technologies MSD SL Trap mass spectrometer with ESI source coupled with a 1100 Series HPLC system.

FT-IR: FT-IR spectra were recorded on a Nicolet 5700 FT-IR instrument.

UV-Vis: UV-Vis spectra were collected using a Varian Cary-100 Scan spectrophotometer.

Electrochemistry: Cyclic voltammetry experiments were performed using a Cyclic voltammetry experiments were performed using a BAS EC-epsilon potentiostat. A standard three-electrode electrochemical cell was used. Glassy carbon electrode (3 mm diameter, geometric surface area = 7 mm^2) from BAS and a Pt wire were used respectively as working and auxiliary electrode. Potentials were referred to an Ag/AgCl/3 M NaCl reference electrode.

Laser flash photolysis: Nanosecond transient absorption measurements were performed with an Applied Photophysics laser flash photolysis apparatus, using a frequency-tripled (355 nm, 160 mJ) Surelite Continuum II Nd/YAG laser (half-width 6-8 ns) as excitation source. Transient detection was obtained using a photomultiplier-oscilloscope combination (Hamamatsu R928, LeCroy 9360).Kinetics of bleach recovery were collected in the following experimental conditions: Excitation wavelength = 355 nm; analysis wavelength = 450 nm; $[Ru(bpy)_3]^{2+}$ = $1.0\cdot10^{-4}$ M; $[Na_2S_2O_8]$ = $5.0\cdot10^{-3}$ M; [**CoSlp**] = $0\text{-}50\cdot10^{-6}$ M in 20 mM phosphate buffer, pH 7. **CoSlp** was added into the cuvette by diluting a $5\cdot10^{-3}$ M solution in 50 : 50 acetonitrile : water.

Light driven water oxidation: In a typical experiment, 15 mL of a 20 mM phosphate buffer (pH = 7.1) containing $[Ru(bpy)_3]Cl_2\cdot6H_2O$ (1 mM), $Na_2S_2O_8$ (5 mM) and **CoSlp** (25-100 μM) were introduced in a glass reactor (internal diameter 18 mm, total internal volume of 24 mL), deoxygenated with nitrogen and allowed to equilibrate at 25 °C under exclusion of light. Irradiation of the solution was then conducted with one monochromatic LED emitting at 450 nm (LED450-06 from Roithner Lasertechnik GmbH); oxygen evolution was monitored with a FOXY-R-AF probe, inserted in the reaction headspace and interfaced with a Neofox Real-Time software for data collection; dissolved oxygen was assumed to be negligible. Quantum Yield for oxygen production (Φ_{O_2}) was determined by the following equation:

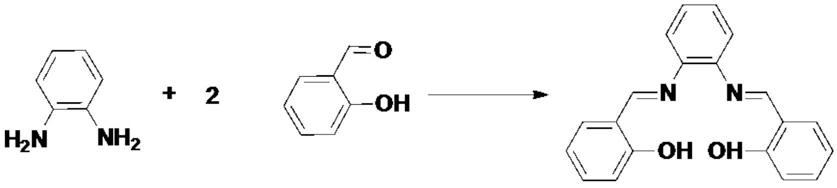
$$\Phi_{O_2} = \frac{\text{rate of } O_2 \text{ production } (\text{mol}\cdot\text{s}^{-1})}{\text{absorbed photons per unit of time } (\text{einstein}\cdot\text{s}^{-1})}$$

The rate of oxygen production was taken from the maximum slope of the kinetic curves shown in figure 1, between 10 and 20 minutes of irradiation. Reactions were run in duplicates; it was confirmed that the concomitant presence of **CoSlp**, $Ru(bpy)_3^{2+}$, $S_2O_8^{2-}$ and light was necessary to achieve oxygen production. The number of absorbed photons was assumed to be equivalent to the number of incident photons, given the high Optical Density of the solution and the negligible loss of photons by reflection events. The incident photons on the reactor were obtained by measuring the power emitted from one LED (7 mW), corresponding to 1.58×10^{16} photons/s (2.63×10^{-8} einstein/s) at 450 nm. The power of light was measured by means of a Newport 1835-C Multi-Function Optical Power Meter equipped with a model 818-UV calibrated silicon detector.

Electron Paramagnetic Resonance: X-band continuous-wave EPR spectra were recorded on a Bruker ELEXSYS E580 spectrometer equipped with a ER4102ST cavity working at 9.38 GHz. Cryogenic temperatures were achieved using a liquid helium flow cryostat (Oxford Instruments ESR-900) driven by a temperature controller (Oxford Instruments ITC503). The experimental conditions were the following: T=10 K, non-saturating microwave power=2 mW, modulation amplitude=10 G, conversion time=81.92 ms and time constant=163.84 ms, number of scans=3. Simulation of the CW-EPR spectra, to obtain the g-tensor principal components, were performed using Easyspin routine in Matlab®; g values were estimated by calibration with a strong-pitch sample (S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42-55).

2. Synthesis of Co-salophen

2.1 Synthesis of N,N’-disalicylal-1,2-phenylenediamine: Salophen (Slp) ligand



Slp

In a 100 mL round-bottom flask was solved 1.00 g (9.25 mmol) of 1,2-benzenediamine in 15 mL of ethanol by using vigorous magnetic stirring. To this solution, 1.97 mL (18.50 mmol) of salicyaldehyde was dropped. The mixture was refluxed by applying continuous MW irradiation (40W, 78ºC) for 10 min and the crude was cooled to 0ºC observing the presence of a precipitate. This solid was filtered and washed with ethanol to obtain the desired **Slp** ligand as a microcrystalline yellowish orange solid (2.90 g, 84% yield). All characterization data was in agreement with literature (D.A. Safin, K. Robeyns, Y. Garcia *RSC Advances*, **2012**, *2*, 11379–11388).

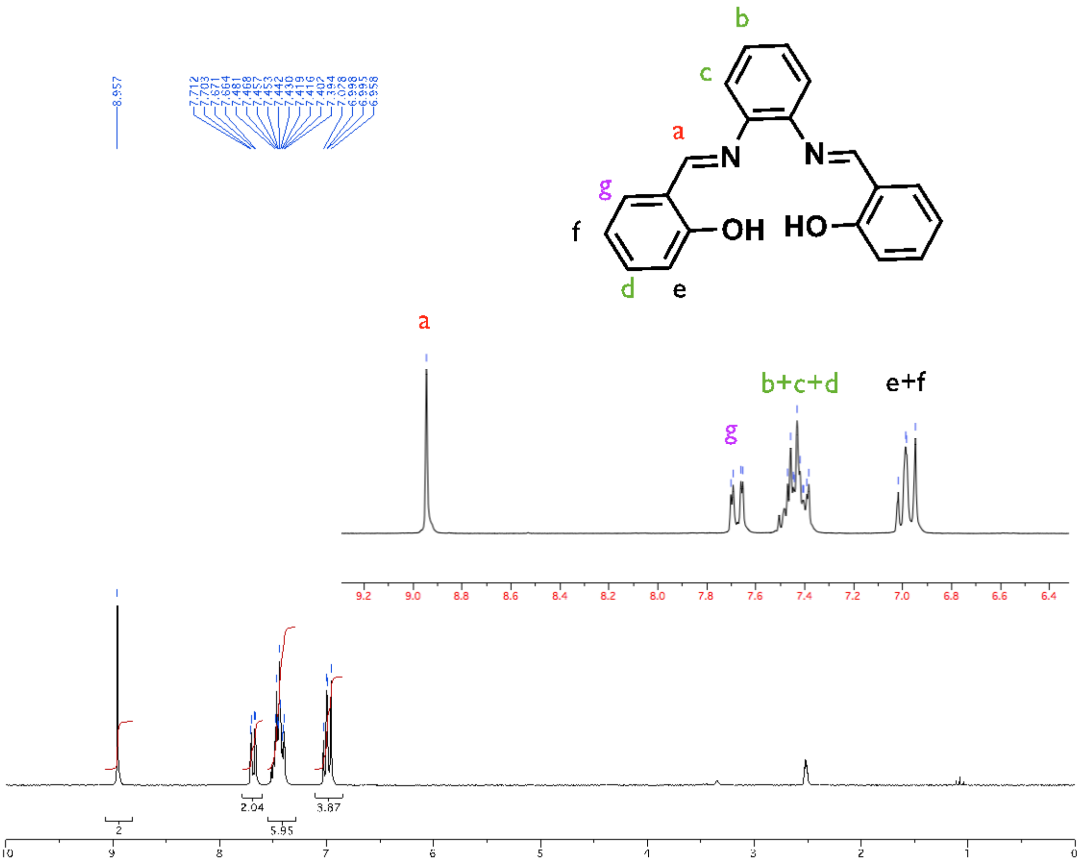
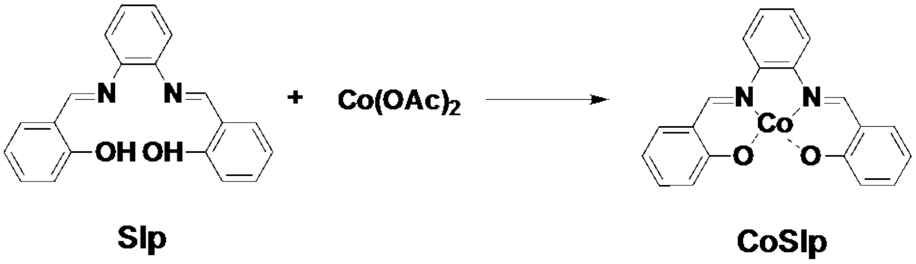


Figure S1. ^{1}H-NMR (200 MHz) spectra of **Slp** in d^6-DMSO.

2.2 Synthesis of Co-Salophen (CoSlp)



Synthesis of **CoSlp** was performed by a slight modification of literature procedures ((a) R. H. Bailes, M. Calvin, *J. Am. Chem. Soc.* **1947**, *69*,1886-1893 (b) R. Deiasi, S. L. Holt, B. Post, *Inorg. Chem.* **1971**, *10*,1498-1500).

In a 100 mL round-bottom flask 397 mg (1.256 mmol) of **Slp** were dissolved in 30 mL of methanol. To this solution, 313 mg (1.260 mmol) of $Co(OAc)_2{\cdot}4\ H_2O$ were added and an immediate colour change in the solution from pale orange to dark brown was observed. The mixture was stirred for 3 hours at room temperature, when diethyl ether (20 mL) were added to induce the formation of a precipitate; this was filtered and washed with diethyl ether and recrystallized from chloroform to obtain a brownish orange solid (75% yield).

ESI-MS (H_2O, *m/z*): 373 $[\{Co(C_{20}H_{14}N_2O_2)\}H]^+$.

FT-IR (KBr, cm^{-1}): 1603 (m), 1544 (m), 1465 (m), 1308 (m), 1193 (m), 753 (s), 573 (w), 474 (w).

UV-Vis (phosphate buffer 20 mM at pH 7): λ_{max} = 451 nm (ε_{max} = 3300 L mol^{-1} cm^{-1}).

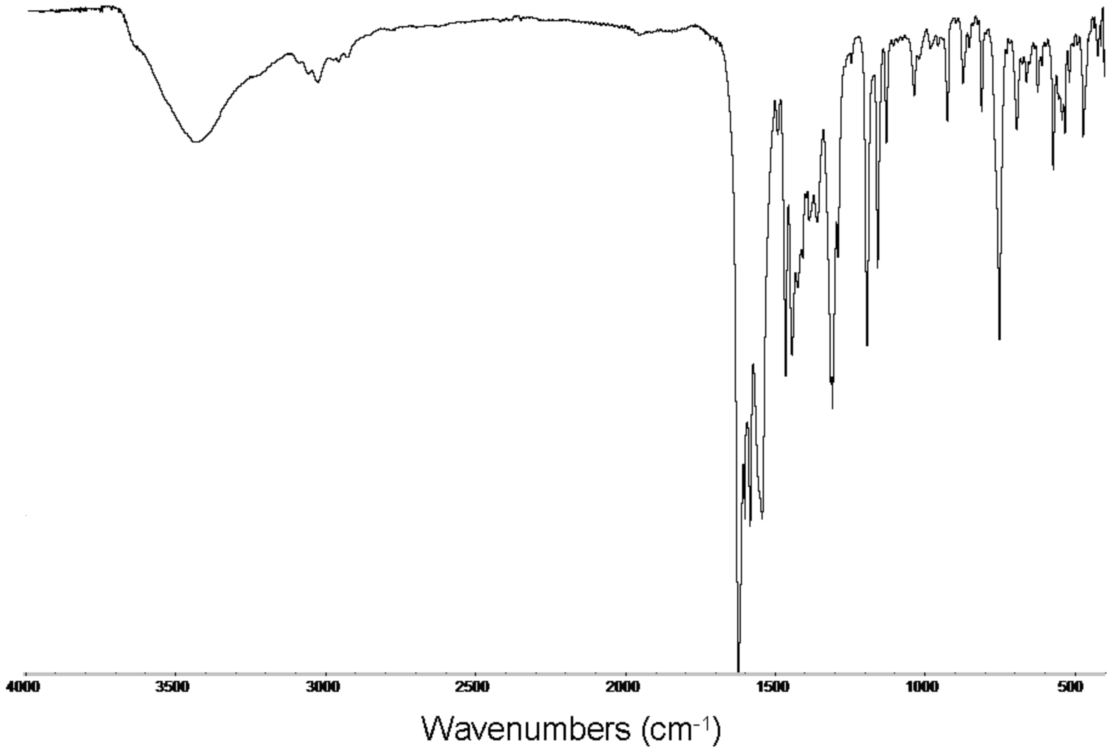


Figure S2. FT-IR of **CoSlp** (2% in KBr pellet).

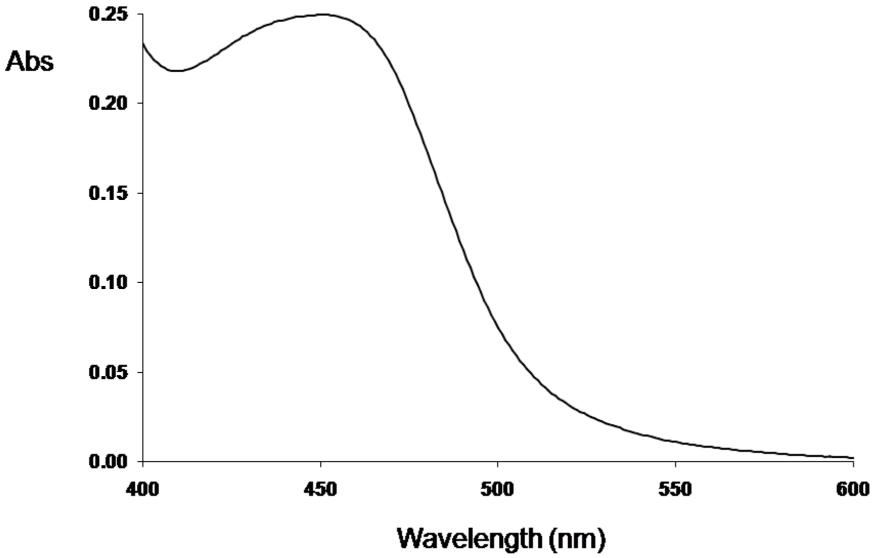


Figure S3. UV-Vis spectra of a fresh 0.1 mM **CoSlp** solution in buffer phosphate 20 mM (pH 7).

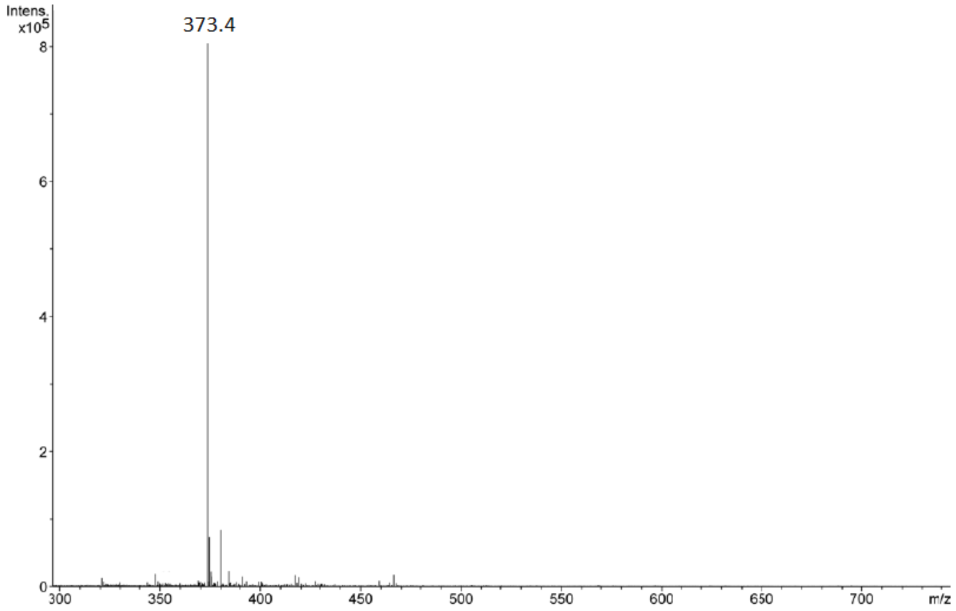
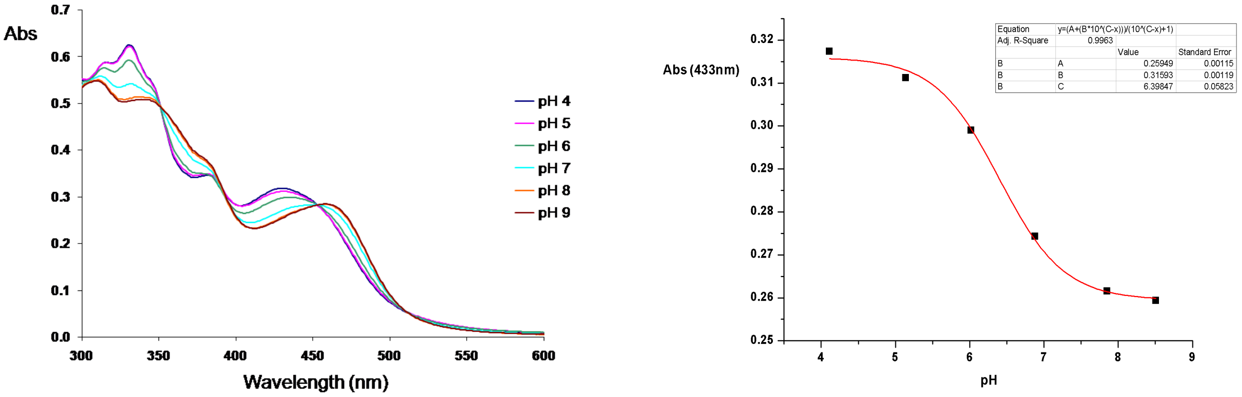
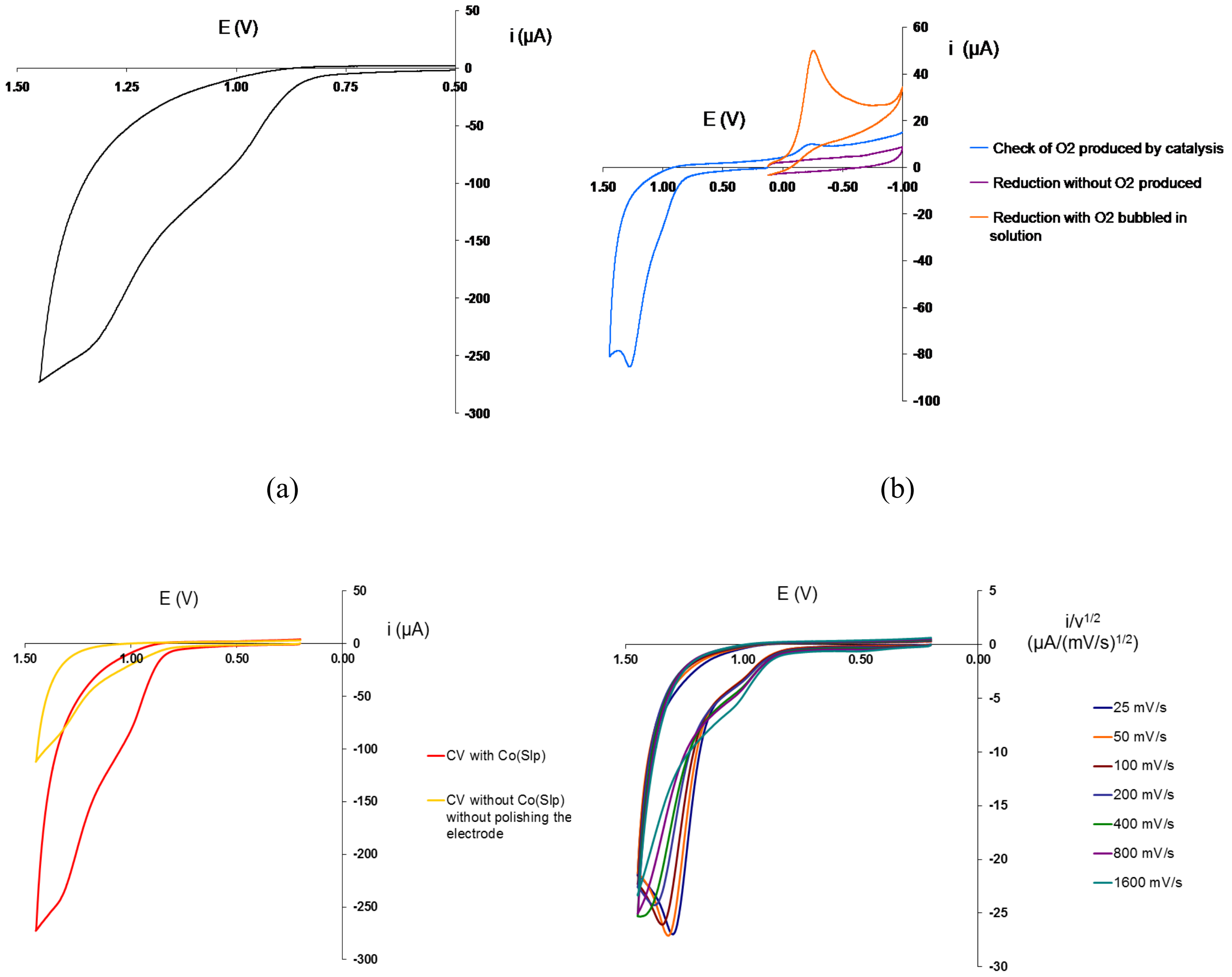


Figure S4. ESI-MS spectra of a 10^{-5} M solution in H_2O of **CoSlp.**



(a) (b)

Figure S5. (a) UV-vis spectra variations of a 10^{-4} M **CoSlp** solution in aqueous buffers at different pH values; (b) Determination of pK_a value by fitting the absorbance values at 433 nm. Spectra were recorded under air atmosphere.



(a)

(b)

(c)

(d)

Figure S6. (a) CV scan of a 0.5 mM **CoSlp** solution in 0.2 M phosphate buffer (pH 7.1); (b) CV scans of a 0.2 mM **CoSlp** solution in 0.2 M phosphate buffer, evidencing the cathodic wave at -230 mV due to Oxygen reduction, appearing only after former application of the anodic scan. (c) CV scans of a 0.5 mM **CoSlp** solution in 0.2 M phosphate buffer (pH=7.1) (red line) and a blank buffer solution (without **CoSlp)** with no polishing of the electrode (orange line). (d) CV scan of a 0.4 mM **CoSlp** solution in 0.2 M phosphate buffer (pH 7.1) at different scan rates.

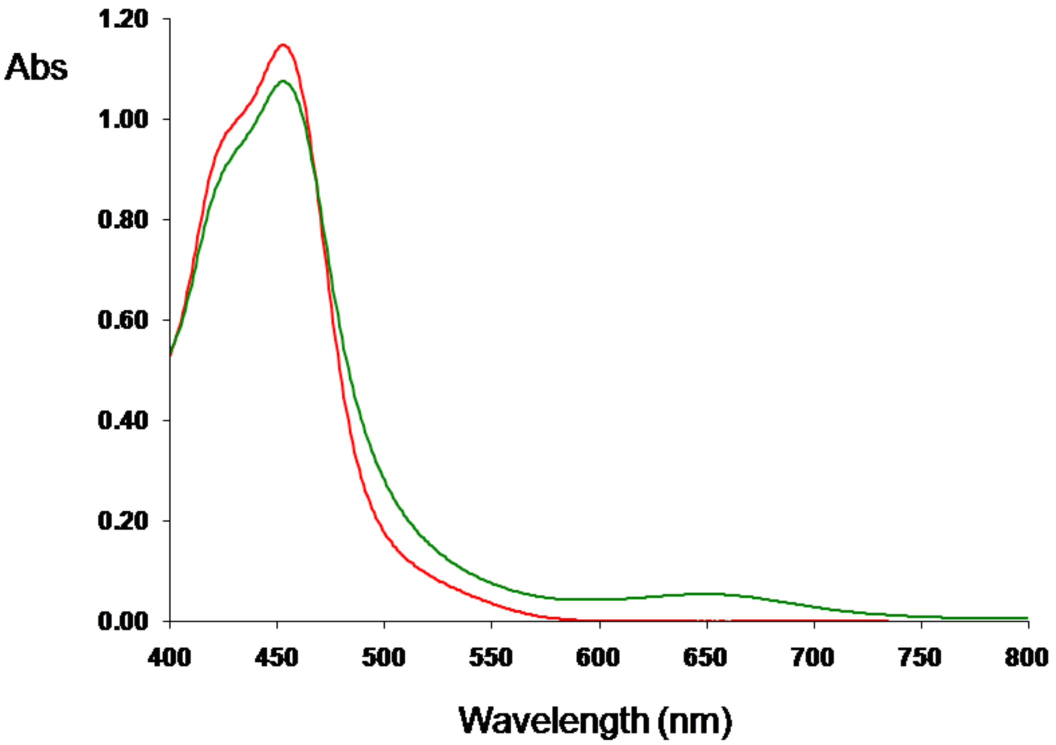


Figure S7. UV-vis spectra of a 10^{-4} M $Ru(bpy)_3^{2+}$ solution in 20 mM phosphate buffer recorded before (red line) and after photocatalysis (green line).

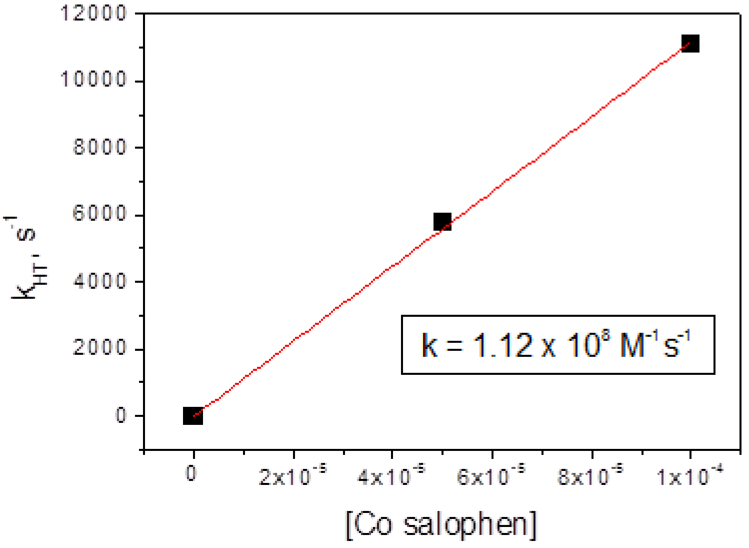


Figure S8. Plot of the pseudo-first order rate constant versus **CoSlp** concentration (the slope of the linear fitting is the bimolecular rate constant for primary hole scavenging). Laser flash photolysis experiments (λexc = 355 nm) conducted in aqueous phosphate buffer (pH 7) containing 5 mM $S_2O_8^{2-}$ and: (a) 50 μM $Ru(bpy)_3^{2+}$, 0, 50 and 100 μM **CoSlp**.

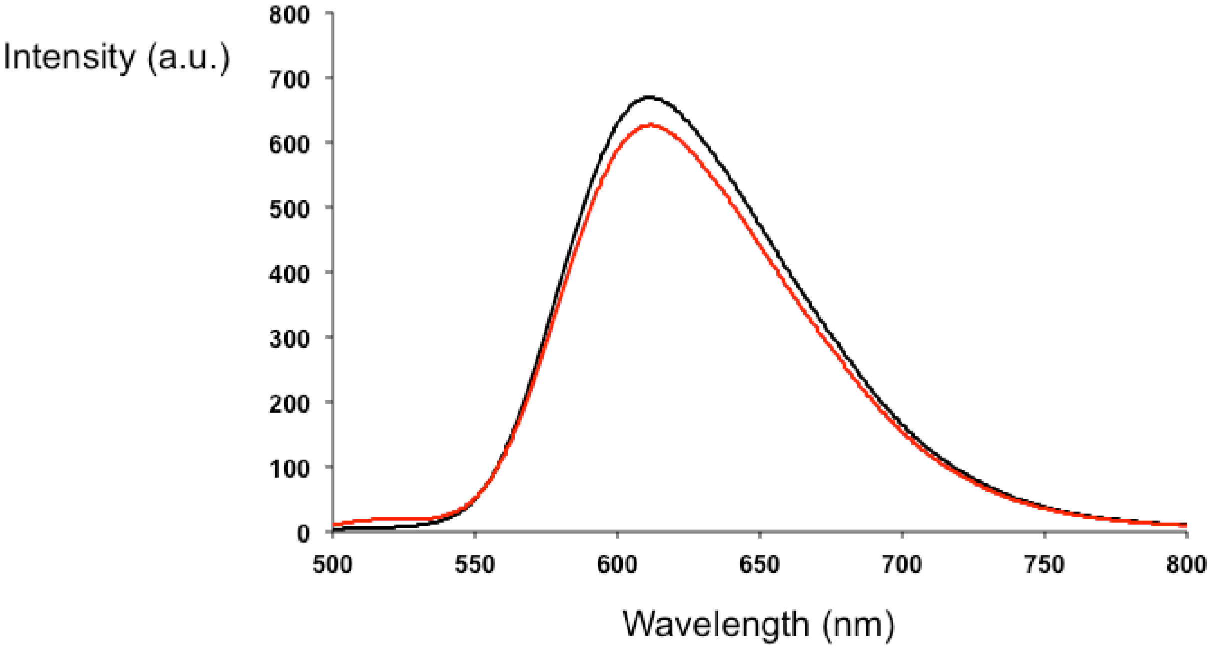


Figure S9. Emission spectra after excitation at 450 nm of a 10^{-5} M $Ru(bpy)_3^{2+}$ solution in phosphate buffer before (black line) and after (red line) addition of 1 equivalent of **CoSlp.**

Table S1. Catalytic parameters of **CoSlp** in oxygen evolving experiments. [**CoSlp**] = 15-125 μM, $[Ru(bpy)_3^{2+}]$ = 1 mM, $[S_2O_8^{2-}]$ = 5 mM in 20 mM phosphate buffer, pH = 7; illumination by LED emitting at 450 nm.

#	**CoSlp**, μM	Total O_2 amount, μmol (turnovers)	O_2 evolution rate, $\mu mol\cdot s^{-1}$ (turnover frequency, s^{-1})	Quantum Yield
1	15	2.73 (12.1)	$1.26\cdot10^{-3}$ ($5.58\cdot10^{-3}$)	0.048
2	25	6.51 (17.3)	$1.54\cdot10^{-3}$ ($4.10\cdot10^{-3}$)	0.058
3	37.5	8.58 (15.0)	$1.88\cdot10^{-3}$ ($3.30\cdot10^{-3}$)	0.071
4	50	8.38 (11.2)	$1.96\cdot10^{-3}$ ($2.61\cdot10^{-3}$)	0.074
5	75	8.86 (7.87)	$2.08\cdot10^{-3}$ ($1.86\cdot10^{-3}$)	0.079
6	100	8.24 (5.49)	$2.05\cdot10^{-3}$ ($1.36\cdot10^{-3}$)	0.077
7	125	6.39 (3.41)	$1.40\cdot10^{-3}$ ($0.75\cdot10^{-3}$)	0.053