

SUPPLEMENTARY INFORMATION

Table S1: CHN , ICP and TGA analysis for the **RuCo₉** salt before and after the light-driven water oxidation experiments, as compared with possible stoichiometries.

	%Ru	%Co	%W	%K	%C	%H	%N	%H ₂ O
Fresh TGA								6.1
Fresh CHN					17.8	1.9	4.0	
Fresh ICP	3.9	4.2	45.5	2.5				
[Ru(bpy) ₃] ₂ K ₁₂ [Co ₉].33H ₂ O	2.1	5.4	50.5	4.8	7.4	1.2	1.8	6.1
[Ru(bpy) ₃] ₃ K ₁₀ [Co ₉].35H ₂ O	2.9	5.1	47.8	3.8	10.5	1.4	2.6	6.1
[Ru(bpy) ₃] ₄ K ₈ [Co ₉].37H ₂ O	3.7	4.8	45.4	2.8	13.3	1.6	3.3	6.1
[Ru(bpy) ₃] _{4.5} K ₇ [Co ₉].38H ₂ O	4.1	4.7	44.3	2.4	14.6	1.7	3.6	6.1
[Ru(bpy)₃]₅K₆[Co₉].39H₂O	4.4	4.6	43.2	2.0	15.8	1.7	3.9	6.1
[Ru(bpy) ₃] ₆ K ₄ [Co ₉].41H ₂ O	5.0	4.4	41.2	1.3	18.1	1.9	4.5	6.1
[Ru(bpy) ₃] ₇ K ₂ [Co ₉].43H ₂ O	5.6	4.2	39.4	0.6	20.2	2.0	5.0	6.2
[Ru(bpy) ₃] ₈ [Co ₉].45H ₂ O	6.2	4.0	37.7	0	22.1	2.2	5.5	6.2
Used TGA								4.0
Used CHN					15.9	1.43	3.8	
Used ICP	3.5	3.5	48.3	2.8				
[Ru(bpy) ₃] ₂ K ₁₂ [Co ₉].21H ₂ O	2.1	5.5	51.7	4.9	7.6	0.9	1.9	4.0
[Ru(bpy) ₃] ₃ K ₁₀ [Co ₉].23H ₂ O	3.0	5.2	48.8	3.9	10.7	1.2	2.7	4.1
[Ru(bpy) ₃] ₄ K ₈ [Co ₉].24H ₂ O	3.8	5.0	46.4	2.9	13.6	1.4	3.4	4.0
[Ru(bpy) ₃] _{4.5} K ₇ [Co ₉].25H ₂ O	4.1	4.8	45.2	2.5	14.9	1.5	3.7	4.0
[Ru(bpy) ₃] ₅ K ₆ [Co ₉].25H ₂ O	4.5	4.7	44.2	2.1	16.2	1.5	4.0	4.1
[Ru(bpy) ₃] ₆ K ₄ [Co ₉].26H ₂ O	5.2	4.5	42.2	1.3	18.5	1.7	4.6	4.0
[Ru(bpy) ₃] ₇ K ₂ [Co ₉].27H ₂ O	5.8	4.3	40.3	0.6	20.7	1.8	5.1	4.0
[Ru(bpy) ₃] ₈ [Co ₉].28H ₂ O	6.3	4.1	38.6	0	22.6	2.0	5.6	4.0

Table S2: Crystallographic parameters for the structure of $[\text{Ru}(\text{bpy})_3]_2\text{K}_{12}[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]\cdot x\text{H}_2\text{O}$.

Crystal system	Triclinic
Space group	P-1
a (Å)	13.1889(8)
b (Å)	27.4351(7)
c (Å)	29.505(2)
α (°)	99.219(2)
β (°)	96.680(2)
γ (°)	93.043(2)
V (Å ³)	10438.7(3)
Z	2

The high disorder of the solvent molecules and counter-cations did not allow us to complete the data refinement. However, the large size of the $[\text{Ru}(\text{bpy})_3]^{2+}$ allows us to confirm the $[\text{Ru}(\text{bpy})_3]/[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3]$ stoichiometry, since there is no available space for an additional $[\text{Ru}(\text{bpy})_3]^{2+}$ in the unit cell (Figure S13). We assign a K_{12} stoichiometry because no other cations were used during synthesis.

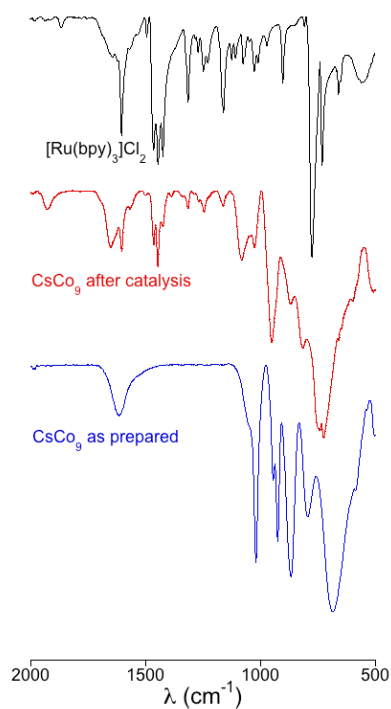


Figure S1: FT-IR spectra of the CsCo_9 salt before (blue) and after (red) light-driven water oxidation experiments vs. commercial $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (black) as a reference.

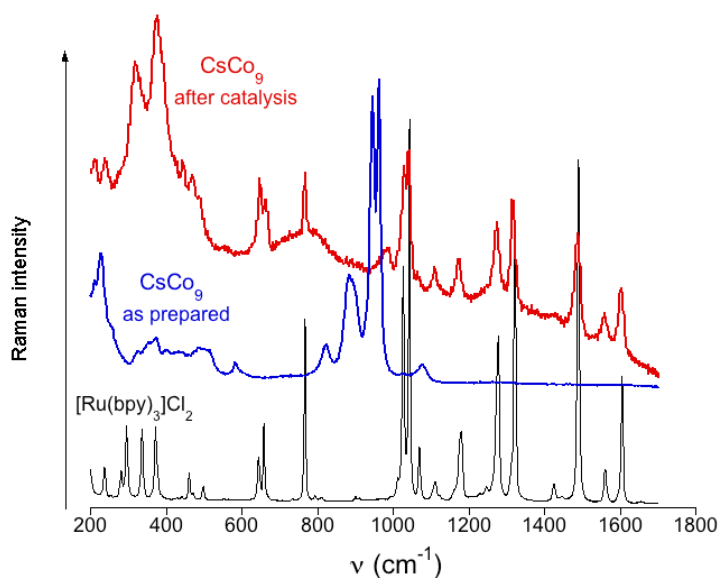


Figure S2: Raman spectra of the CsCo_9 salt before (blue) and after (red) light-driven water oxidation experiments vs. commercial $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (black) as a reference.

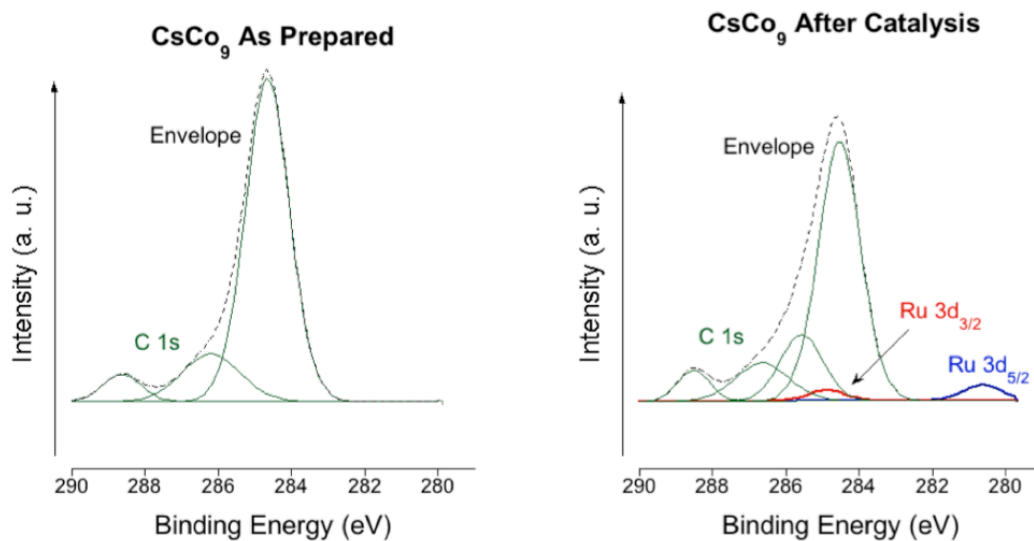


Figure S3: Ru 3d (blue and red) and C 1s (green) XPS spectra of CsCo₉ as prepared (left) and collected after the light-driven water oxidation experiments (right).

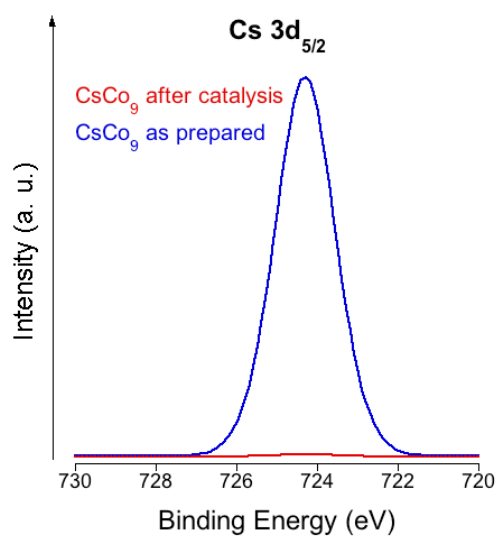


Figure S4: Cs 3d_{5/2} XPS spectra of CsCo₉ as prepared (blue) and collected after the light-driven water oxidation experiments (red).

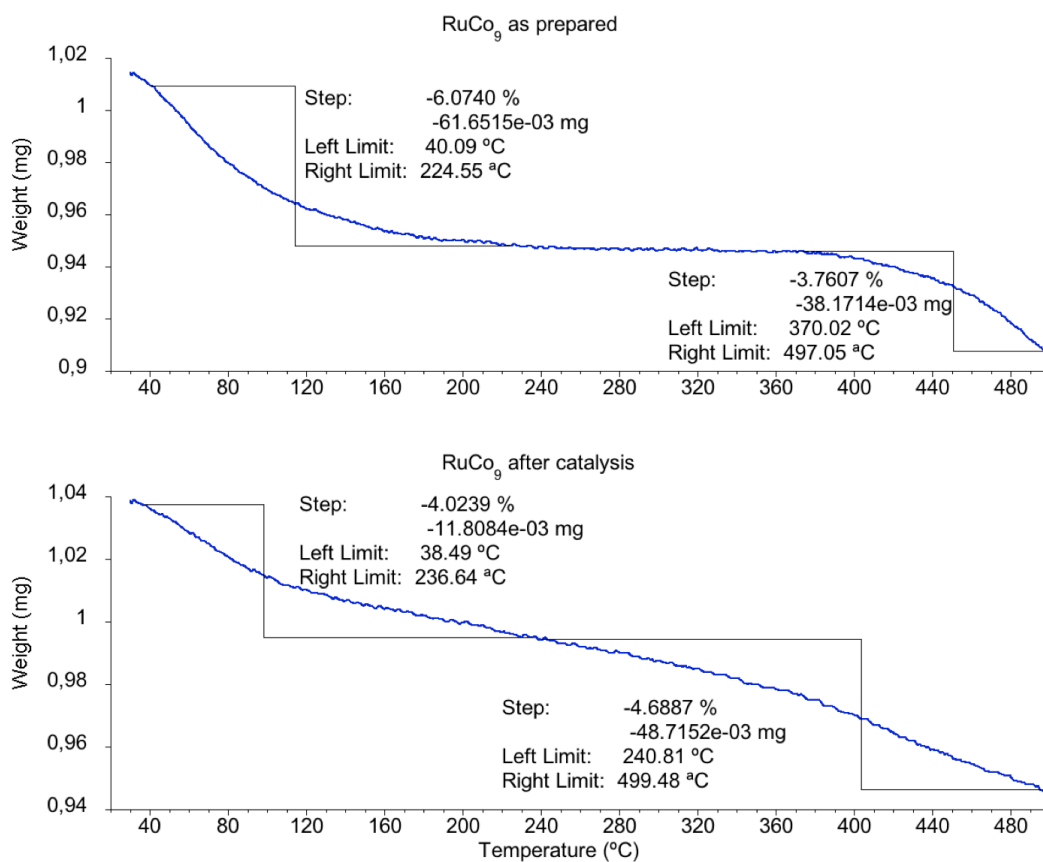


Figure S5: Thermogravimetric analysis of the **RuCo₉** salt before (top) and after (bottom) light-driven water oxidation experiments.

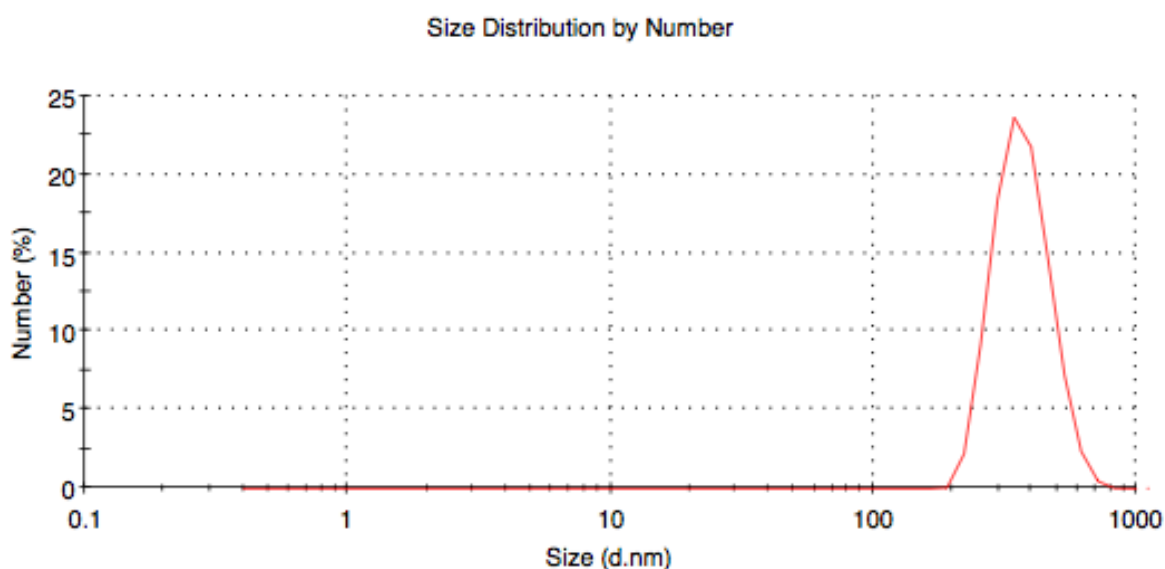


Figure S6: Dynamic light scattering measurement of as-prepared **RuCo₉** salt in suspension in water.

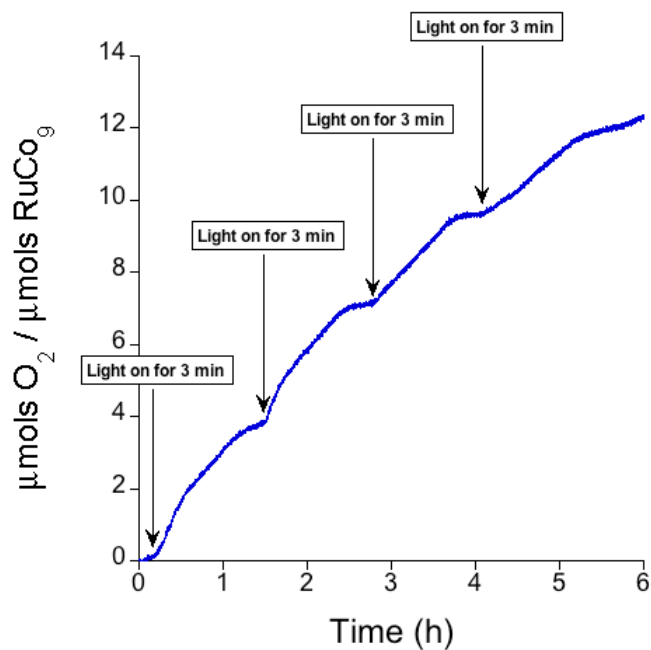


Figure S7: Measured oxygen evolution during the pulse experiments employing 10 mg of **RuCo₉** in a **KP_i** (40 mM) buffer at pH 7 with **S₂O₈²⁻** (5 mM) as sacrificial electron acceptor.

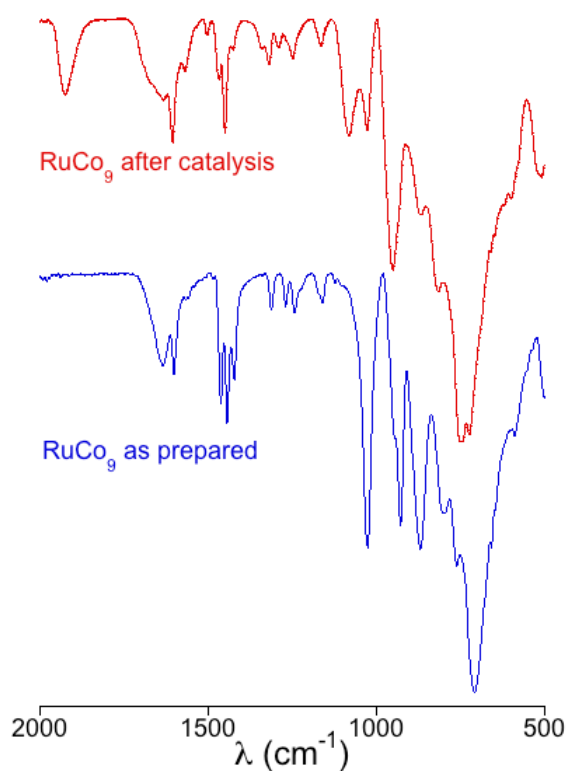


Figure S8: FT-IR spectra of the **RuCo₉** salt before (blue) and after (red) light-driven water oxidation experiments.

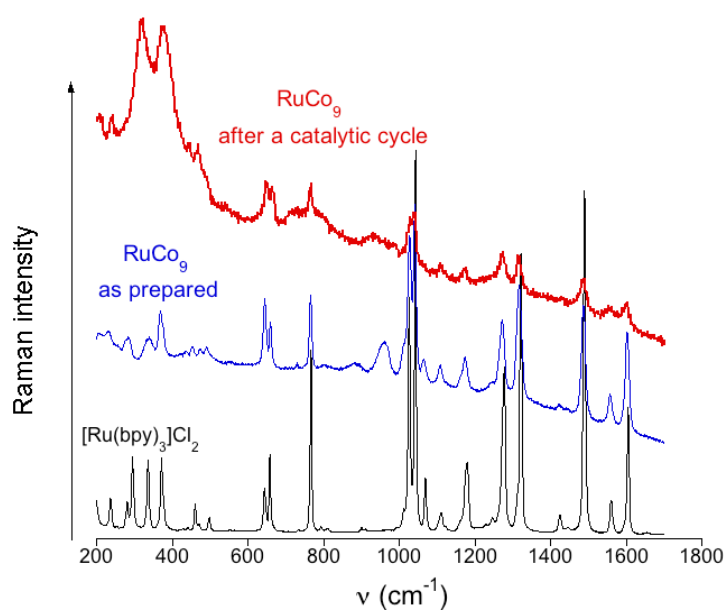


Figure S9: Raman spectra of the **RuCo₉** salt before (blue) and after (red) light-driven water oxidation experiments vs. commercial [Ru(bpy)₃]Cl₂ (black) as a reference.

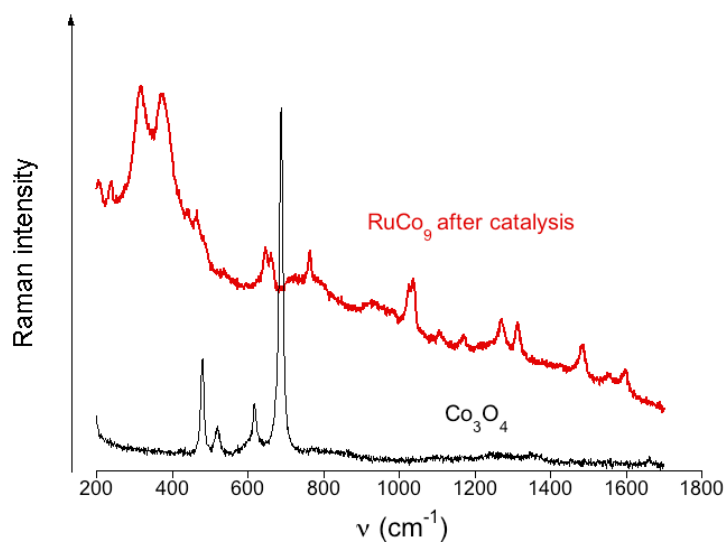


Figure S10: Raman spectra of the collected **RuCo₉** salt (red) after light-driven water oxidation experiments compared to a pristine Co₃O₄ (black) reference.

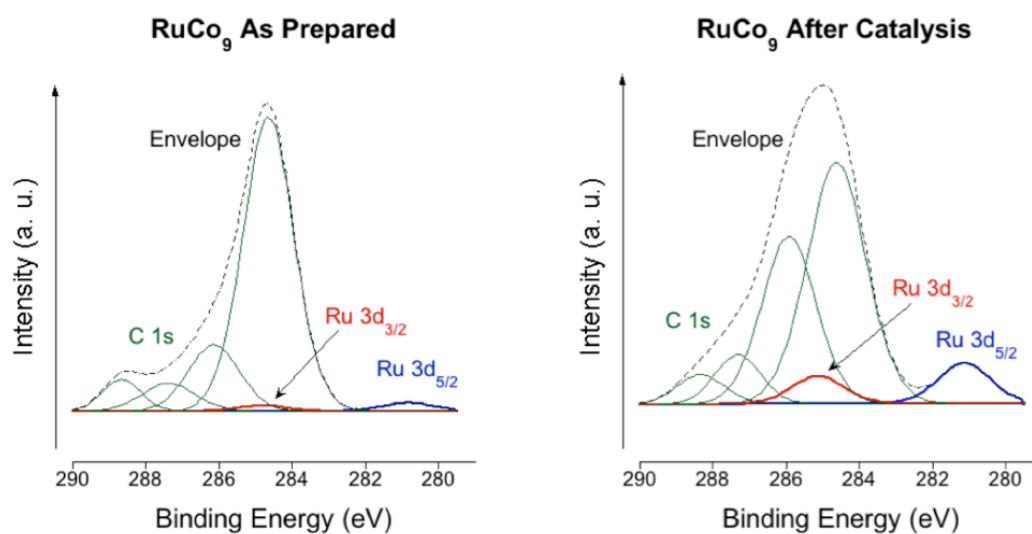


Figure S11: Ru 3d (blue and red) and C 1s (green) XPS spectra of **RuCo₉** as prepared (left) and collected after light-driven water oxidation experiments (right).

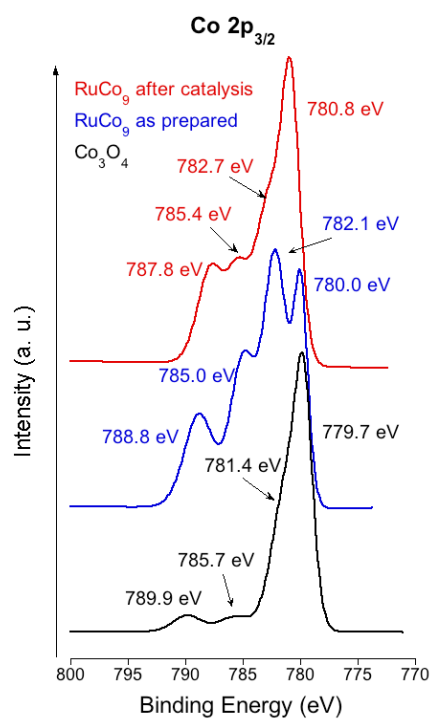


Figure S12: Co 2p_{3/2} XPS spectra of **RuCo₉** as prepared (blue) and collected after light-driven water oxidation experiments (red), compared to that obtained with pristine Co₃O₄ (black).

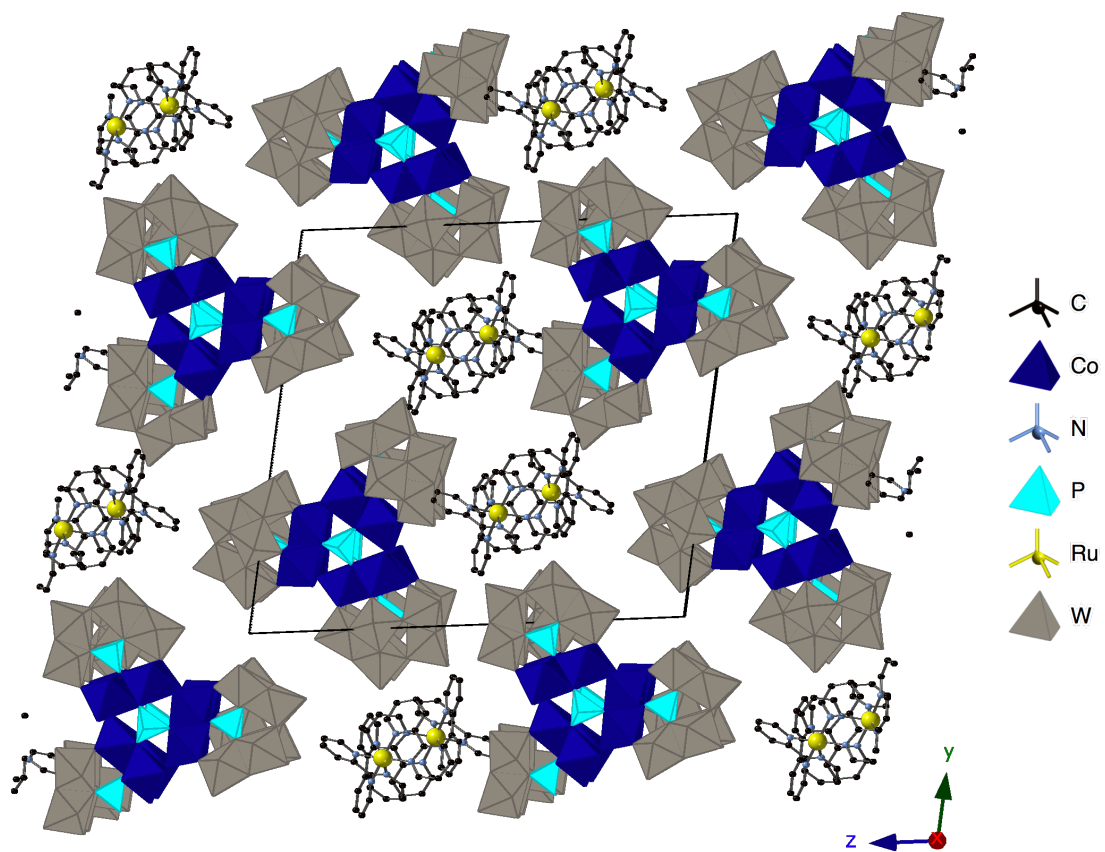


Figure S13: Representation of the unit cell for the single crystal of $[\text{Ru}(\text{bpy})_3]_2\text{K}_{12}[\text{Co}_9(\text{H}_2\text{O})_6(\text{OH})_3(\text{HPO}_4)_2(\text{PW}_9\text{O}_{34})_3] \cdot x\text{H}_2\text{O}$ (cf. Table S1).

LIGHT-DRIVEN WATER OXIDATION CATALYSIS TESTS

The number of mols of O₂ produced during the experiments were calculated from the %O₂ given by the oxygen-sensing probe employing the Dalton's law of partial pressures:

$$\%O_2 = \frac{P_{O_2}}{P_T} \times 100$$

where P_{O₂} is the partial pressure of the O₂ in the gas-space, and P_T is the total pressure and equal to 1 atm. Therefore, by substituting P_{O₂} into the ideal gas law we can calculate the number of mols of O₂ produced as:

$$n_{O_2} = \frac{\frac{\%O_2}{100} V_{gs}}{RT}$$

where n_{O₂} = number of moles of O₂; %O₂ = percentage of O₂ present in the gas-space; V_{gs} = gas-space volume (in L); R (gas constant) = 0.082 atmL/molK; and T = 298K.

The turnover number (TON) was calculated as:

$$TON = \frac{n_{O_2}}{n_{cat}}$$

where n_{O₂} = number of moles of O₂, and n_{cat} = number of moles of catalyst.

The turnover frequency (TOF, h⁻¹) was calculated by plotting n_{O₂}/n_{cat} vs. time. The slope at the beginning of the O₂ evolution follows a linear fit, and it is equal to the TOF, following the relationship:

$$TOF = \frac{n_{O_2}}{n_{cat} \cdot t} = \text{slope}$$

The chemical yield (CY, %) was calculated as:

$$CY = \frac{2 \cdot n_{O_2}}{n_{S_2O_8^{2-}}} \times 100$$

where n_{O₂} = number of moles of O₂, and n_{S₂O₈²⁻} = number of moles of Na₂S₂O₈. The number two arises because the formation of O₂ requires the removal of four electrons, but the photochemical process using the [Ru(bpy)₃]²⁺/S₂O₈²⁻ assay accepts only two electrons.