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Supporting Information

A Ru-Co hybrid material based on a molecular photosensitizer and a heterogeneous catalyst for light-driven water oxidation

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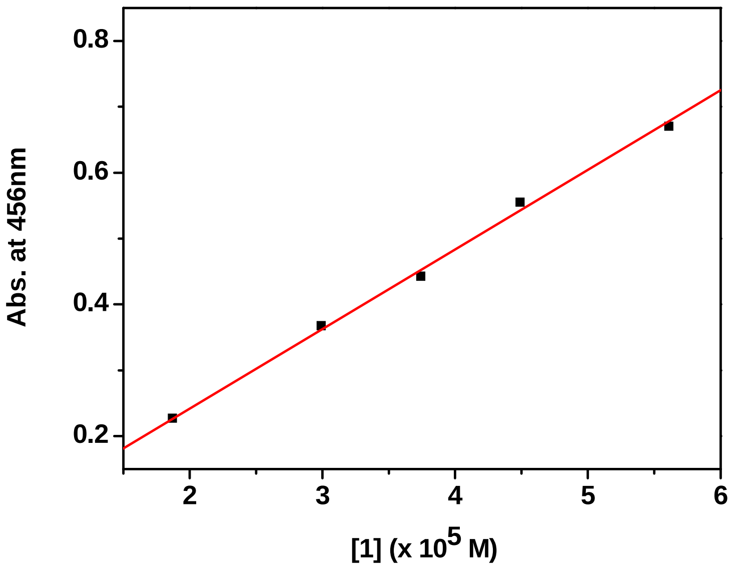

Fig. S1. Job plot of **1** in water (ε_{456nm} = 12100 $M^{-1}cm^{-1}$).

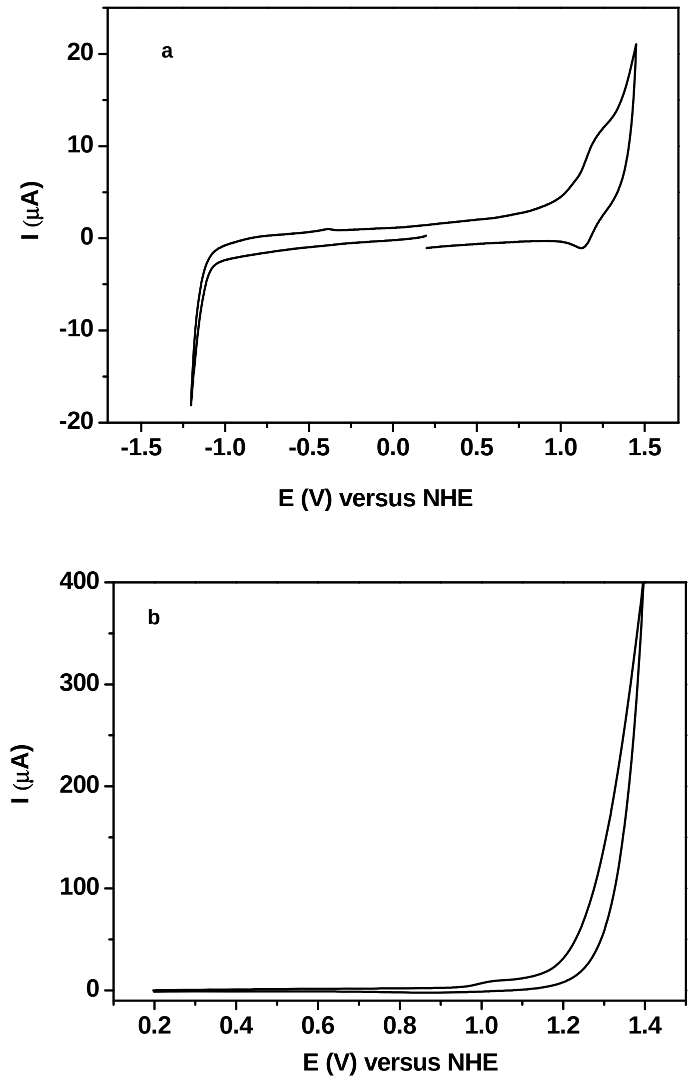

Fig. S2 Electrochemistry of (a) **1** (0.5 mM) and (b) $Co(ClO_4)_2$ (0.5 mM) in 0.1 M phosphate buffer solution with pH 8.4 at a scan rate of 100 mVs^{-1} under Ar atmosphere. In (b) $Co(ClO_4)_2$ is oxidized to Co(III) at 1.04 V vs. NHE followed by a strong feature that arises from electrocatalytic water oxidation catalyzed by the formed cobalt oxide. In (a) the potential of the Ru^{III}/Ru^{II} redox couple of **1** is 1.19 V vs. NHE, which is at the rise of the catalytic wave for water oxidation from cobalt oxide.

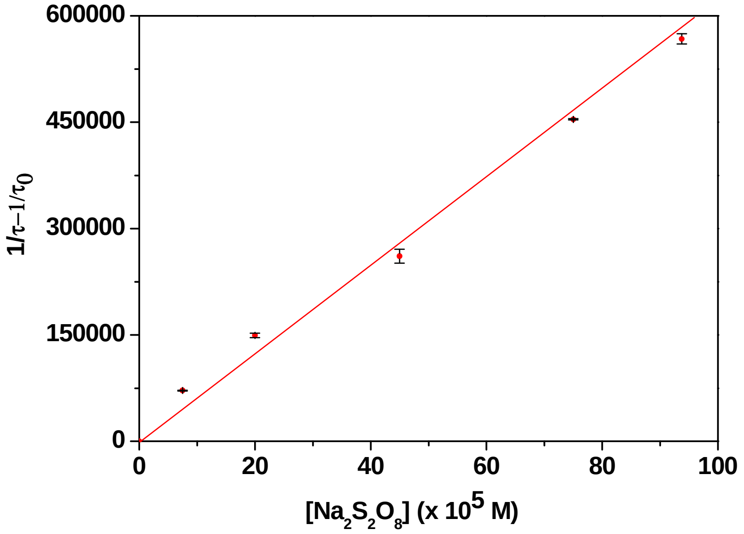

Fig. S3 Stern-Volmer plot of $1/\tau$-$1/\tau_0$ for **1** (1.5×10^{-5} M) as a function of the $Na_2S_2O_8$ concentration. The lifetimes were recorded at the emission at 626 nm, after excitation at 455 nm, in 25mM phosphate buffer (pH 8.4). In the absence of $Na_2S_2O_8$, the luminescence lifetime τ_0 was 417 ns for **1**. With the addition of 62.5 eq $Na_2S_2O_8$, the lifetime was shortened to τ_1=337 ns. Analysis of the decays suggests that the decay is monoexponential following Stern-Volmer kinetics. The shorter lifetime and luminescence quenching of **1** may be attributed to electron transfer from ***1** to the electron acceptor with the rate constant (k_{ET}) of 6.1 $\times10^8$ $M^{-1}s^{-1}$. The error bars indicate the error in the determination of the lifetimes.

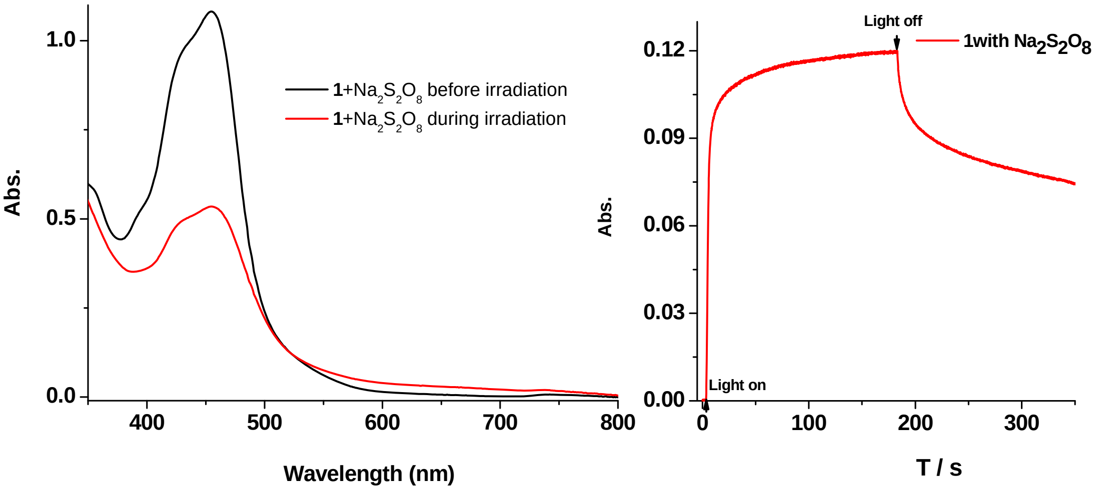

Fig. S4 (a) The absorption spectra of **1** (8×10^{-5} M) recorded in the presence of the electron acceptor $Na_2S_2O_8$ (5 mM) without irradiation (black) or during irradiation (red) in phosphate buffer (pH 8.4). (b) The absorption of **1** at 675 nm in the presence of 5mM $Na_2S_2O_8$ during illumination for 180 s by LEDs (λ = 470nm±10nm, 820 $\mu E/(m^2\cdot s)$) and after the illumination. The arrows indicate when the illumination was turned on and off.

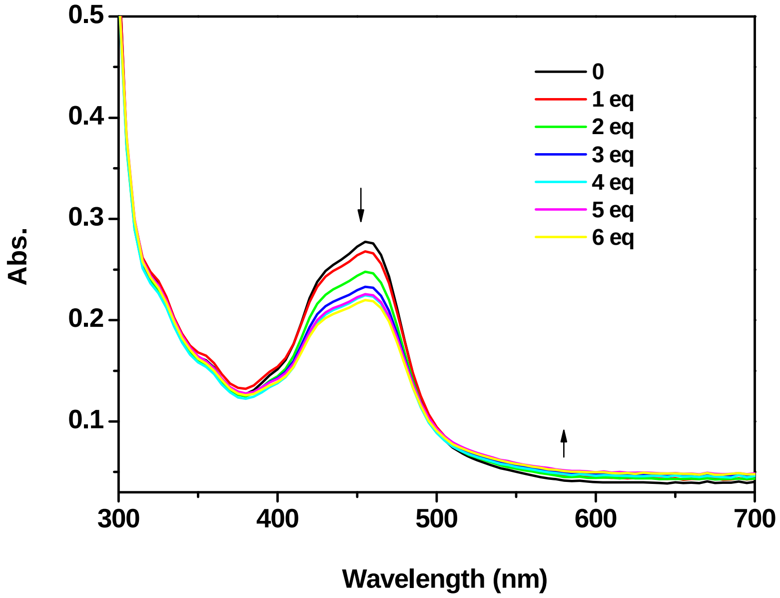

Fig. S5 Changes in the UV-visible spectrum of **1** (1.7×10^{-5} M) with the addition of $Co(ClO_4)_2$ in deionized water

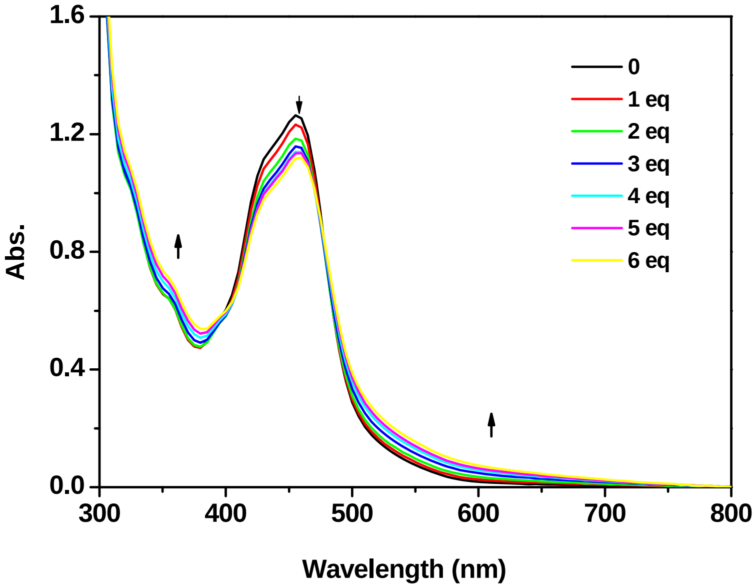

Fig. S6 Changes in the UV-visible spectrum of **1** (8×10^{-5} M) with the addition of $Co(ClO_4)_2$ in phosphate buffer (pH 8.4)

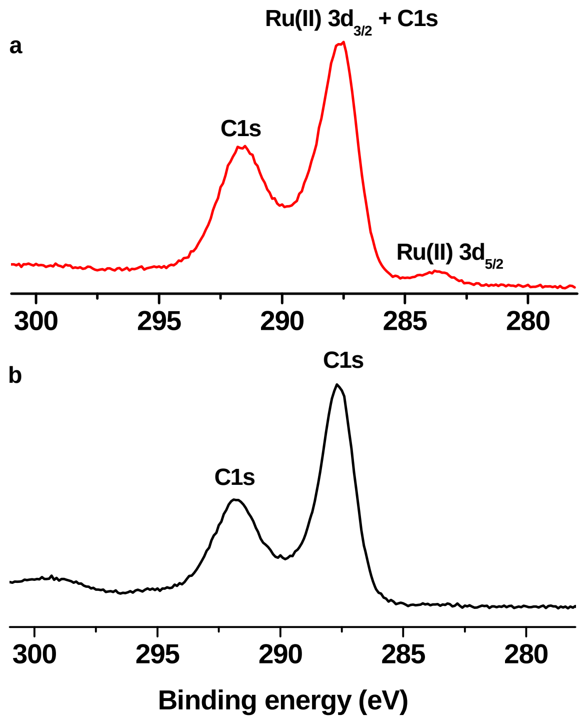

Fig. S7 XPS fine scan spectra of Ru 3d region for (a) **P1** and (b) **P2**.

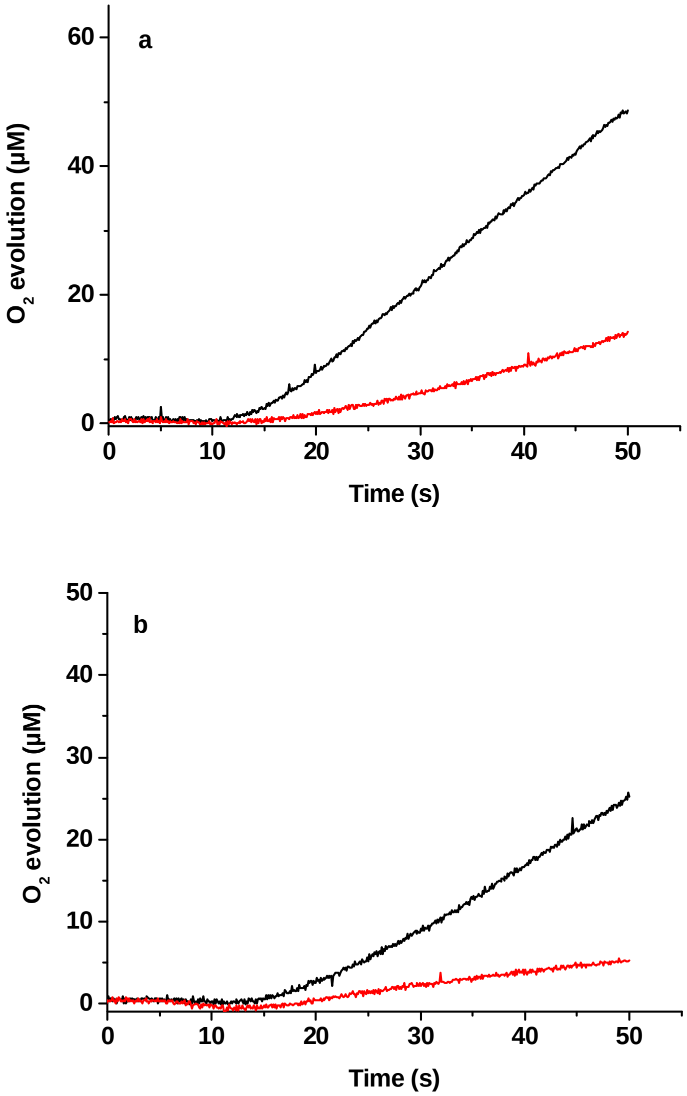

Fig. S8 (a) Light-induced water oxidation of in a mixture containing **P1** (left) and **P2** (right) (~0.13 mg, from 500 μL of a suspension of 0.65 mg material in 2.5 ml H_2O). 12 mM $Na_2S_2O_8$ in phosphate buffer (25 mM, pH 8.4). The light was applied from 0 s.

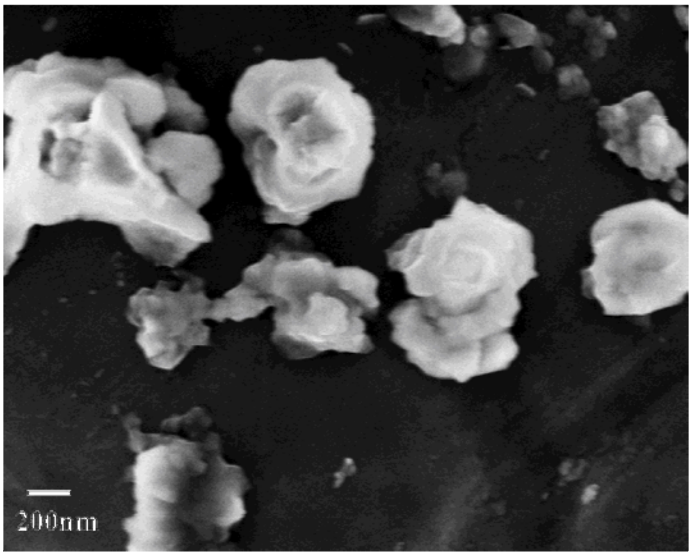

Fig. S9 SEM micrograph of **P2**.

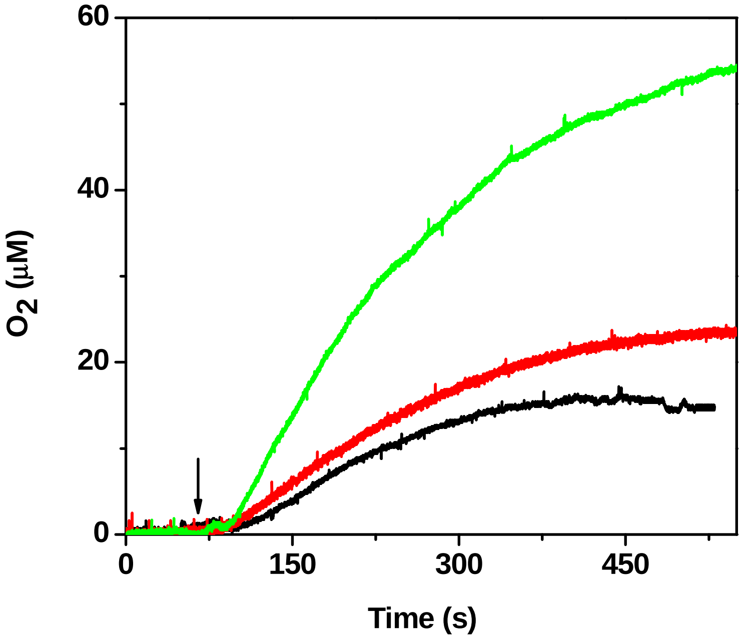

Fig. S10 Light-induced water oxidation in a mixture containing **P2** and 4 mM (black), 5 mM (red) or 6 mM (green) $Na_2S_2O_8$ in phosphate buffer (25 mM, pH 8.4). The Clark cell was kept constant at 20 °C, and the system was irradiated using LEDs ($\lambda = 470\pm10$ nm, 820 µE/($m^2\cdot s$)). The arrow indicates the start of the irradiation.

Table S1. EDX data for **P1** and **P2**.

Element	**P1**		**P2**	
	wt%[a]	molar ratio	wt%[a]	molar ratio
O	5.6	24	7.6	96
P	2.1	4.6	2.9	19
Co	1.7	1.9	2.2	7.5
Ru	1.5	1.0	0.5	1.0
N	1.3	6.3	n.d.	n.d.

n.d. = not determined. *a* The accuracy is approximately ± 0.3 wt%.