Electronic Supplementary Information

for

A Protocol for Quantifying Hydrogen Evolution by Dye-Sensitized Molecular Photocathodes and its Implementation for Evaluating a new Covalent Architecture based on an Optimized Dye-Catalyst Dyad

Christopher D. Windle, Julien Massin, Murielle Chavarot-Kerlidou and Vincent Artero*

Laboratoire de Chimie et Biologie des Métaux ; Université Grenoble Alpes ; CNRS; Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), 17 rue des Martyrs, Grenoble 38000 France

E-mail: vincent.artero@cea.fr. Tel.: +33-4-38-78-91-06

Procedure for the Clark-type microelectrode calibration: A 0.1 M solution of H_2SO_4 was bubbled with pure H_2 to saturate. The saturation concentration of H_2 in 0.1 M H_2SO_4 is 742.64 μM as calculated from the salinity and H_2 solubility table in the Unisense manual. 1 mL of the H_2 saturated H_2SO_4 solution was added to 17.5 mL of H_2SO_4 solution to give a H_2 concentration of 40 μM. The 0 μM measurement was achieved by taking a reading of pure 0.1 M H_2SO_4 solution. The measurements were taken in the thermostatted photoelectrochemical cell at 25 °C. A similar calibration was made in MES/NaCl buffer for qunatification of H_2 produced by dye-sensitized photocathode.

Procedure for the GC calibration: A 1:9 mixture of H_2 and N_2 was prepared. This was added in 10 μL increments to a gas-tight Schlenk tube, which had a certain headspace volume that resulted in each 50 μL injection to the GC containing 1.95, 3.82, 5.61, 7.32, 8.96 and 10.52 nmoles of H_2, as plotted in Figure S1 (left).

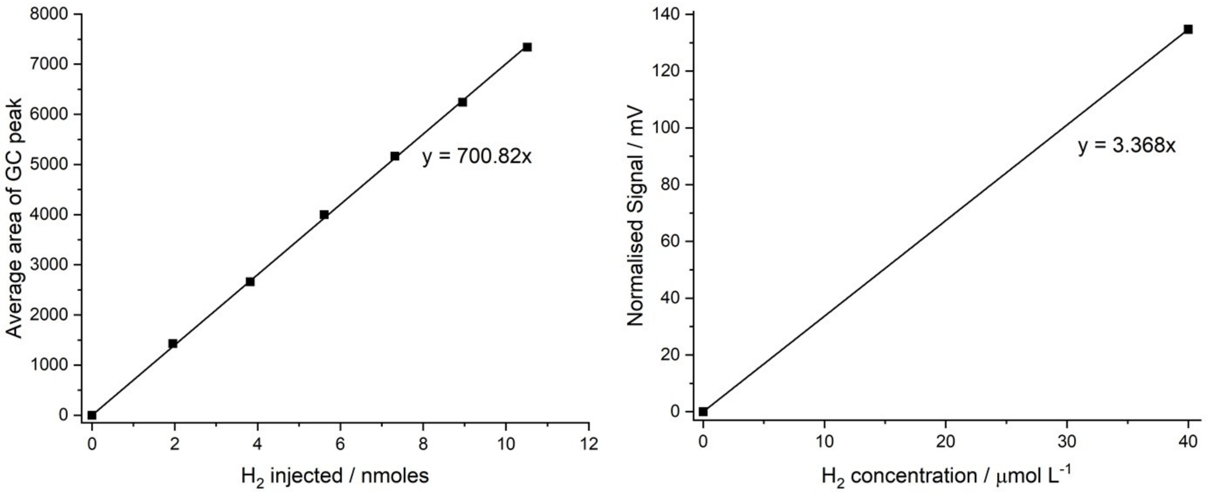
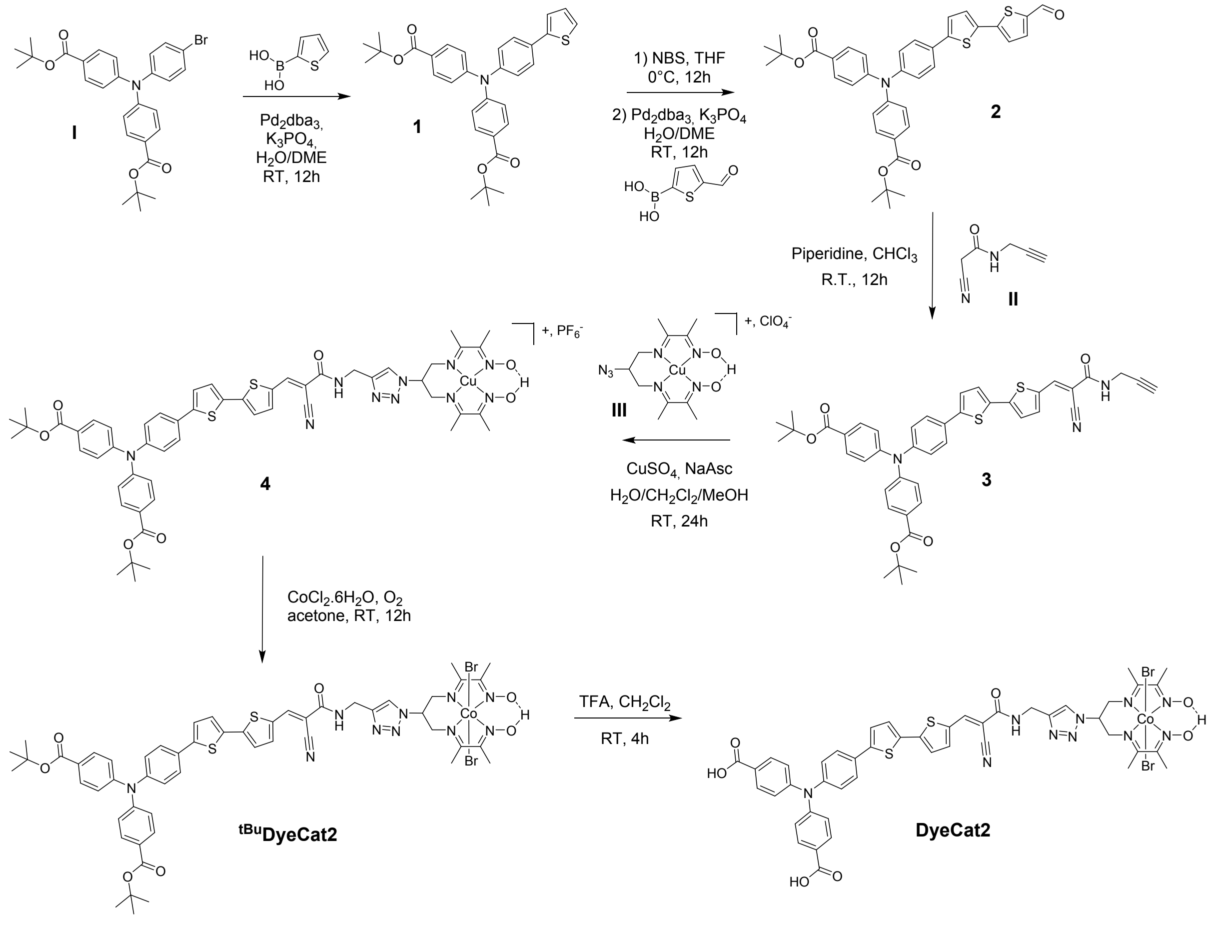


Figure S1. Example calibration curves for GC measurements in the headspace (left) and Unisense Clark-type microelectrode measurements in 0.1 M H_2SO_4 solution at 25 °C (right). Each point is the average of three measurements.



Scheme S1. Synthetic route to **DyeCat2.**

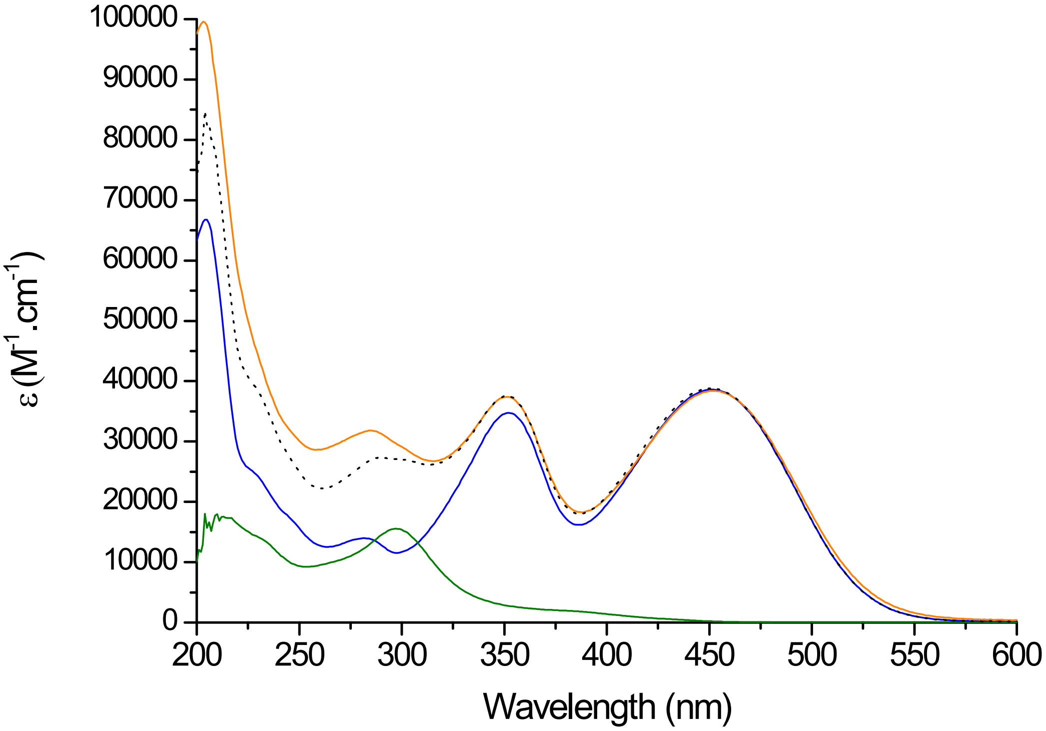


Figure S2: Absorption spectra of compounds **3** (blue line), **CoDODOH-N3** (green line) and **^{tBu}DyeCat2** (orange line) recorded in CH_3CN. The sum of the absorption of **3** and **CoDODOH-N3** is represented as the dotted grey line.

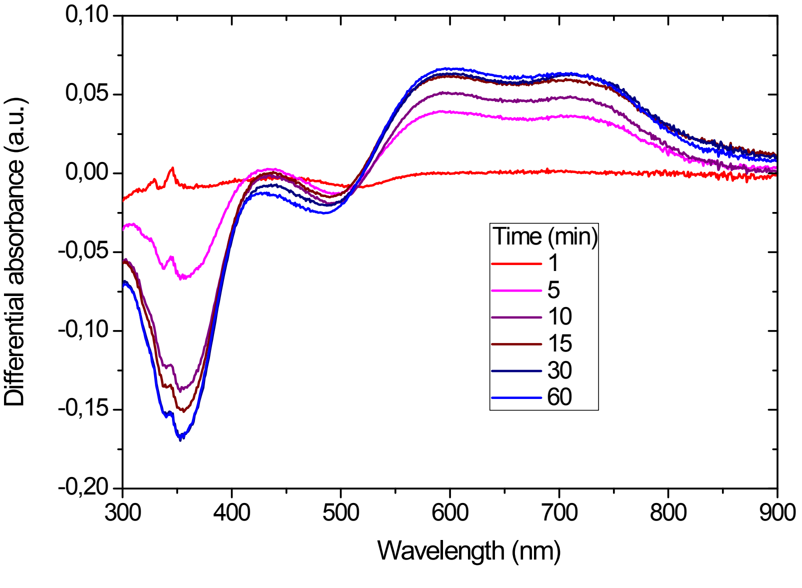


Figure S3: UV-visible monitoring (differential spectra) of the formation of the Co^I derivative of **^{tBu}DyeCat2** (2 10^{-5} M) upon visible light irradiation in CH_3CN/TEOA (90:10 v/v).

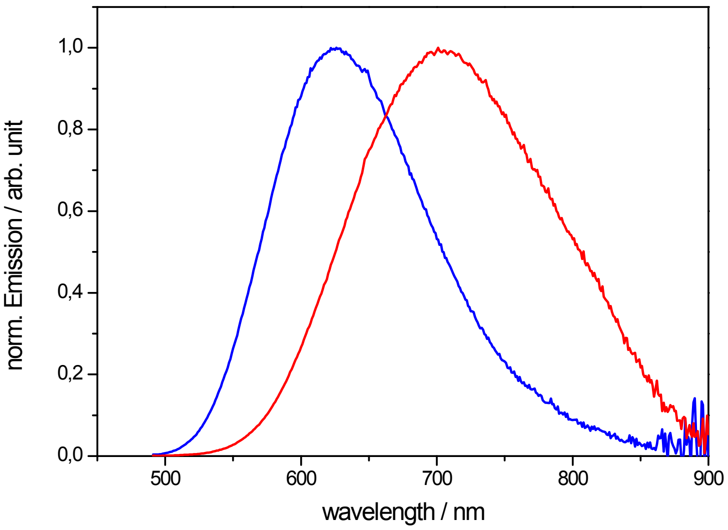


Figure S4: Normalized emission spectra (λ_{exc} = 480 nm) of **^{tBu}DyeCat1** (blue curve) and **^{tBu}DyeCat2** (red curve) in CH_3CN.

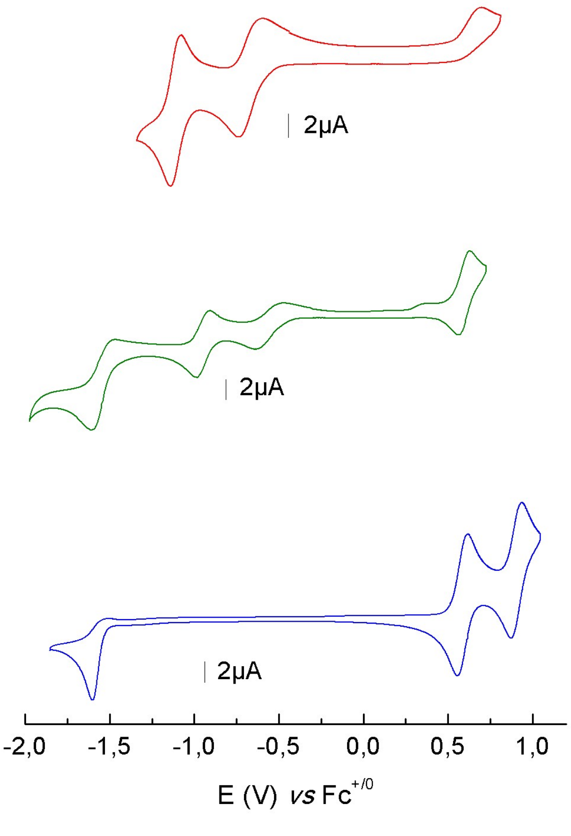


Figure S5. Cyclic voltammograms of **^{tBu}DyeCat2** (middle) compared with those of the reference catalyst **Co(DO)(DOH)pnBr$_2$** (top) and of the dye precursor **3** (bottom). Measurements were carried out at 100 mV.s^{-1} at a glassy carbon electrode in CH_3CN (1 mM in 0.1 M *n*Bu_4NPF_6).

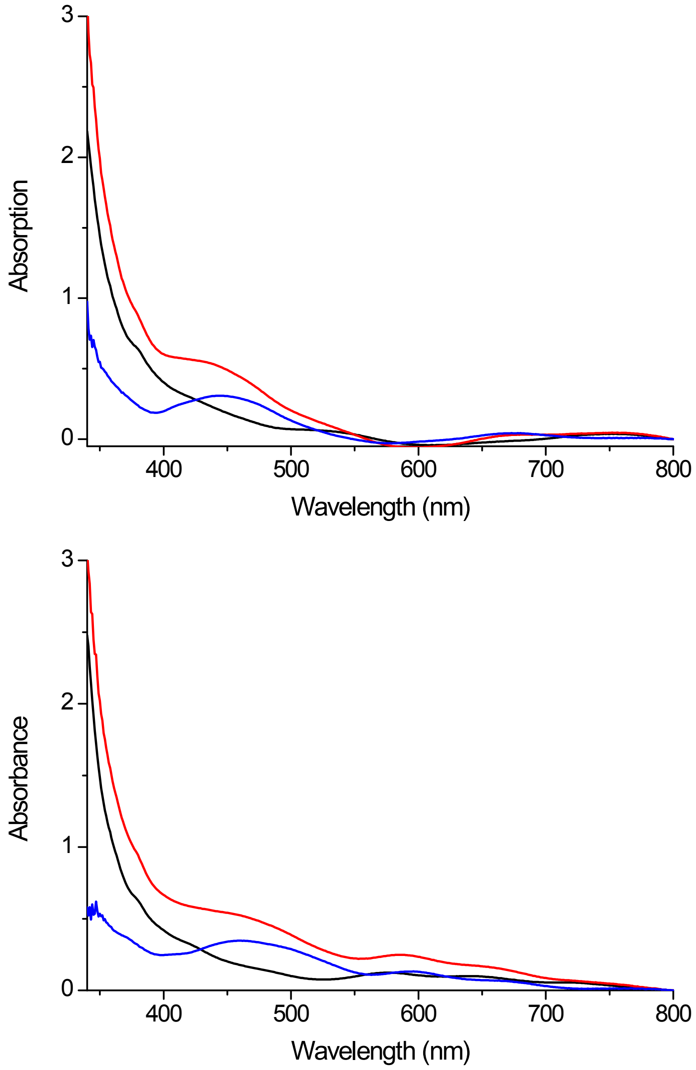


Figure S6: Absorption spectra of pristine NiO electrodes (red lines) and **DyeCat1**-sensitized (top) or **DyeCat2**-sensitized (bottom) NiO electrodes without (black lines) or with (blue lines) subtraction of the NiO background.

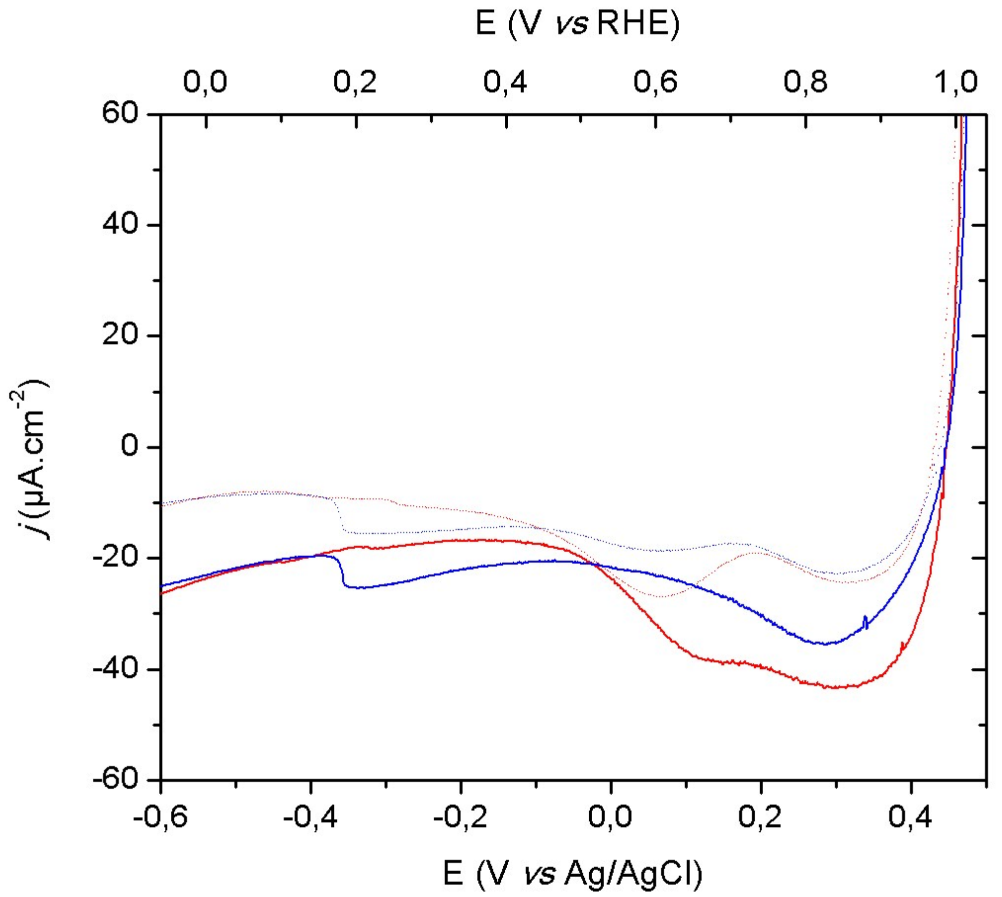


Figure S7: Linear sweep voltammograms of NiO electrodes sensitized by **DyeCat1** (red lines) or by **DyeCat2** (blue lines), recorded in a pH 5.5 MES 0.1 M/NaCl 0.1 M supporting electrolyte under irradiation (plain lines) or in the dark (dotted lines).

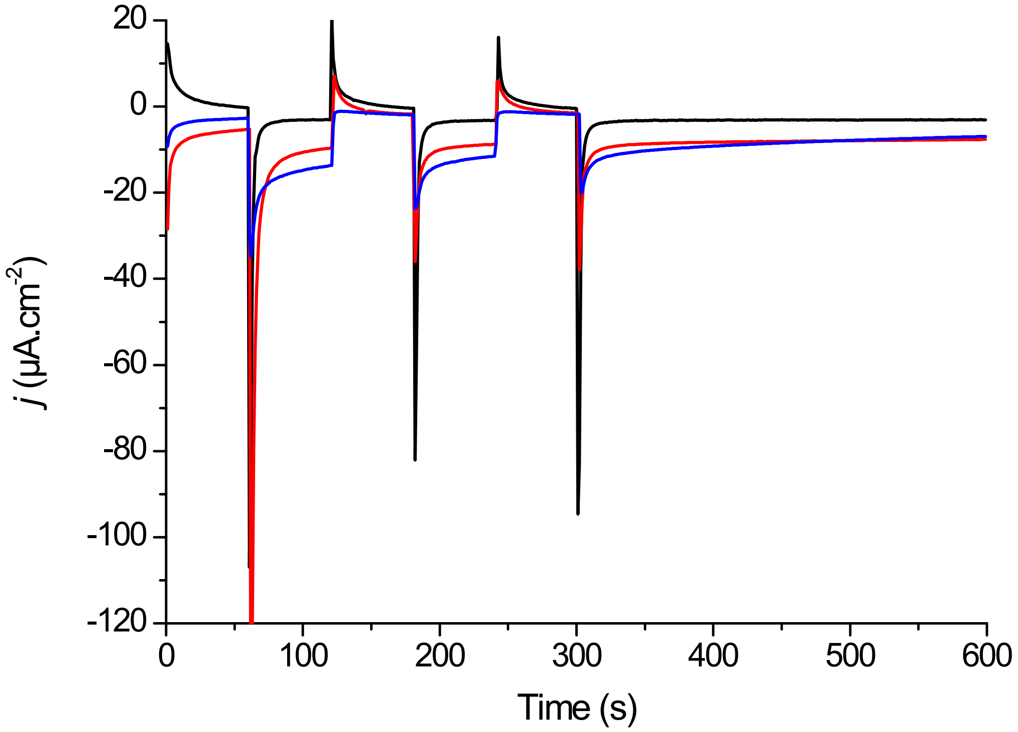


Figure S8: Steady-state photocurrents recorded in a pH 5.5 MES 0.1 M/NaCl 0.1 M supporting electrolyte, at an applied potential of 0.14 V (blue line), 0.34 V (red line) and 0.54 V (black line) vs RHE, at a **DyeCat1**-sensitized NiO electrode.

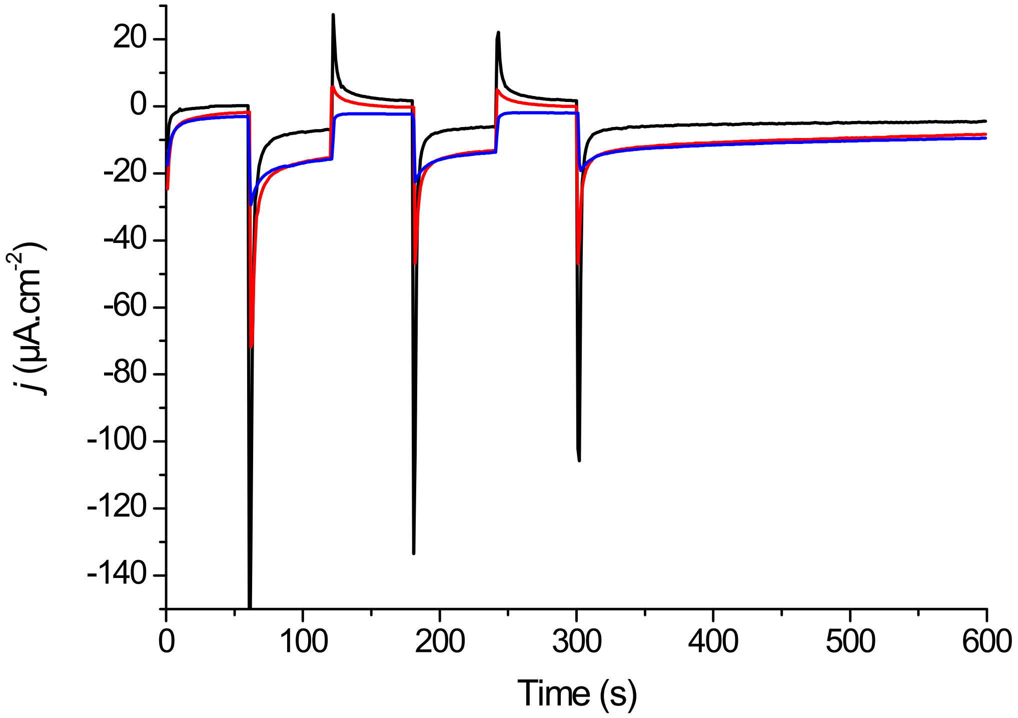


Figure S9: Steady-state photocurrents recorded in a pH 5.5 MES 0.1 M/NaCl 0.1 M supporting electrolyte, at an applied potential of 0.14 V (blue line), 0.34 V (red line) and 0.54 V (black line) vs RHE, at a **DyeCat2**-sensitized NiO electrode.

Table S1. H_2 measurements (headspace and solution) during low-current electrolysis experiments with a Pt working electrode.

Charge passed (mC)	Normalised Probe Signal (mV)	H_2 concentration (μmol L^{-1})[a]	H_2 (nmol)	FE in solution[c]	H_2 GC area	H_2 in the heasdspace[b] (nmol)	FE in the headspace[c]	Total FE
18	51	15	78	84%	190	14	15 %	99%
18	62	18	96	103%	151	10	11 %	114%
18	58	17	90	96%	105	7.0	8%	104%
36	88	26	135	73%	543	41	22%	94%
34	106	31	164	92%	444	31	18%	110%
36	109	32	168	90%	416	28	15%	104%
54	118	35	182	65%	1099	83	30%	95%
51	137	41	211	79%	897	63	24%	103%
54	146	43	225	81%	837	57	20 %	101%
72	145	43	223	60%	1755	133	36%	96%
69	149	44	230	64%	1454	103	29%	93%
72	179	53	276	74%	1402	96.0	26%	100%
90	166	49	257	55%	2400	185	40%	95%
87	169	50	261	58%	2136	153	34%	92%
90	198	59	306	66%	2065	143	31%	97%
108	187	55.4	288	51%	3264	253	45%	97%
105	247	73.3	381	70%	2856	206	38%	108%
108	223	66.2	344	62%	2868	201	36%	98%

a- H_2 concentration calculated from the calibration curve and the measured signal according to the formula: probe signal/gradient.

b- Number of moles of H_2 in the headspace, calculated from the calibration curve and the area of the H_2 signal according to the formula: (peak area/gradient) x (headspace volume/injection volume). (Injection volume: 50 μL; headspace volume: 2.05 mL).

c- Faradaic efficiency (FE) for H_2 production calculated according to the formula: moles H_2/((charge passed/Faraday constant)/2).

Table S2. Photophysical and redox properties of ^{tBu}**DyeCat1** and ^{tBu}**DyeCat2**.

	λ_{Abs}[a]	**ε ($M^{-1}.cm^{-1}$)**	λ_{Em}[a]	E_{ox}[b]	**$Ered_1$[b] ($Co^{III}/^{II}$)**	**$Ered_2$[b] ($Co^{II}/^{I}$)**	**$Ered_3$[b] (Dye/Dye^-)**	E_{0-0}[c]	ΔG_1[d]	ΔG_2[e]
^{tBu}**DyeCat1**[1,f]	431	31800	625	1.21	−0.05	−0.43	−1.08	2.37	−1.03	−0.65
^{tBu}**DyeCat2**	450	38600	703	1.14	−0.03	−0.42	−1.02	2.28	−0.99	−0.60

a- Maximum absorption and emission wavelengths in nm recorded in acetonitrile – see Figures S2 and S4.

b- In V vs NHE. ½(E_{pc}+ E_{pa}) for $Ered_1$ and $Ered_2$; E_{pc} for $Ered_3$.The redox potentials were converted from Fc^+/Fc (Figure S3) to NHE, obtained from the reduction potential considering E°(Fc^+/Fc) = 0.53 V vs. NHE.[2, 3]

c- 0–0 transition energy, $E_{0\text{–}0}$, in eV, estimated from the intercept of the normalized absorption and emission spectra in CH_3CN.

d- The Gibbs free energy in eV for the electron transfer from the reduced dye to the Co(III) catalyst was calculated according to $\Delta G_1 = e[E(Dye/Dye^-) - E(Co^{III}/Co^{II})]$

e- The Gibbs free energy in eV for the electron transfer from the reduced dye to the Co(II) catalyst was calculated according to $\Delta G_2 = e[E(Dye/Dye^-) - E(Co^{II}/Co^{I})]$

f- The emission spectrum of **^{tBu}DyeCat1** was re-recorded in this study, giving a slightly shifted maximum emission wavelength λ_{Em} value than the one previously reported in ref. 1.

Table S3. H_2 measurements at the end of photoelectrolysis experiments (2 hours; applied potential: 0.14 V vs RHE) using **DyeCat1**- and **DyeCat2**-sensitized photocathodes.

	Charge passed (mC)	Normalised Probe Signal (mV)	H_2 concentration (μmol L^{-1})[a]	H_2 (nmol)	FE in solution[c]	H_2 GC area	H_2 in the headspace[b] (nmol)	FE in the headspace[c]	Total FE
DyeCat1	53	11	3.2	13	5%	169	10	4%	9%
	57	17	5.1	23	8%	145	8.1	3%	11%
	44	7.0	2.1	9.6	4%	192	11	5%	9%
	45	8.0	2.4	11	5%	180	11	5%	10%
DyeCat2	43	14	4.2	19	9%	233	14	6%	15%
	45	14	4.0	19	8%	273	15	6%	14%
	46	7.0	2.2	10	4%	284	15	7%	11%

References.

1. N. Kaeffer, J. Massin, C. Lebrun, O. Renault, M. Chavarot-Kerlidou and V. Artero, *J. Am. Chem. Soc.*, 2016, **138**, 12308-12311.
2. J. Massin, M. Bräutigam, N. Kaeffer, N. Queyriaux, M. J. Field, F. H. Schacher, J. Popp, M. Chavarot-Kerlidou, B. Dietzek and V. Artero, *Interface Focus*, 2015, **5**, 20140083.
3. T. N. Huan, E. S. Andreiadis, J. Heidkamp, P. Simon, E. Derat, S. Cobo, G. Royal, A. Bergmann, P. Strasser, H. Dau, V. Artero and M. Fontecave, *J. Mater. Chem. A*, 2015, **3**, 3901-3907.