

Covalent Design for Dye-Sensitized H₂-evolving Photocathodes based on a Cobalt Diimine-Dioxime Catalyst

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General methods and chemicals used. All reagents were obtained from commercially available sources and used without further purification. Solvents were dried from appropriate drying agents (calcium hydride for CH_2Cl_2 and CH_3CN , 4Å molecular sieves for DMF) and freshly distilled under argon before use. Chemical reagents were purchased from Sigma-Aldrich and used as received. $(\text{DOH})_2\text{pnN}_3$ [1], di-tert-butyl-4,4'-((4-(5-formylthiophen-2-yl)phenyl)azanediyl) dibenzoate (**I** in scheme S1) [2] and 1-cyanoacetyl-3,5-dimethyl-pyrazole [3] were synthesized as previously described. The preparation of $\text{Co}(\text{DO})(\text{DOH})\text{N}_3\text{pnBr}_2$ (**2Co**) was adapted from a reported procedure, using $(\text{DOH})_2\text{pnN}_3$ instead of $(\text{DOH})_2\text{pn}$ [4].

General characterization methods and equipments. ^1H NMR and ^{13}C NMR spectra were recorded at 298 K in 5 mm o.d. tubes either on a *Bruker AC 300* spectrometer equipped with a QNP probehead operating at 300.0 MHz for ^1H and 75.5 MHz for ^{13}C or on a *Bruker Avance III* spectrometer equipped with a *Prodigy* cryoprobe and operating at 500.0 MHz for ^1H and 126 MHz for ^{13}C . Chemical shift values are given in ppm with reference to solvent residual signals [5]. Accurate mass measurements (HRMS) were performed on a Bruker maXis mass spectrometer by the "Fédération de Recherche" ICOA/CBM (FR2708) platform and elemental analysis on a Thermofisher Scientific "Flash 2000" by the "Plateforme d'analyse pour la chimie" (GDS 3648, Strasbourg). Emission fluorescence and *UV-vis* absorption spectra of compounds were recorded on a Perkin Elmer LS50B spectrofluorimeter and on an *Agilent Technologies Cary 60 UV-Vis* spectrometer, respectively, in a 1 cm optical light path quartz cuvette. The fluorescence spectra were recorded at an excitation wavelength of 430 nm.

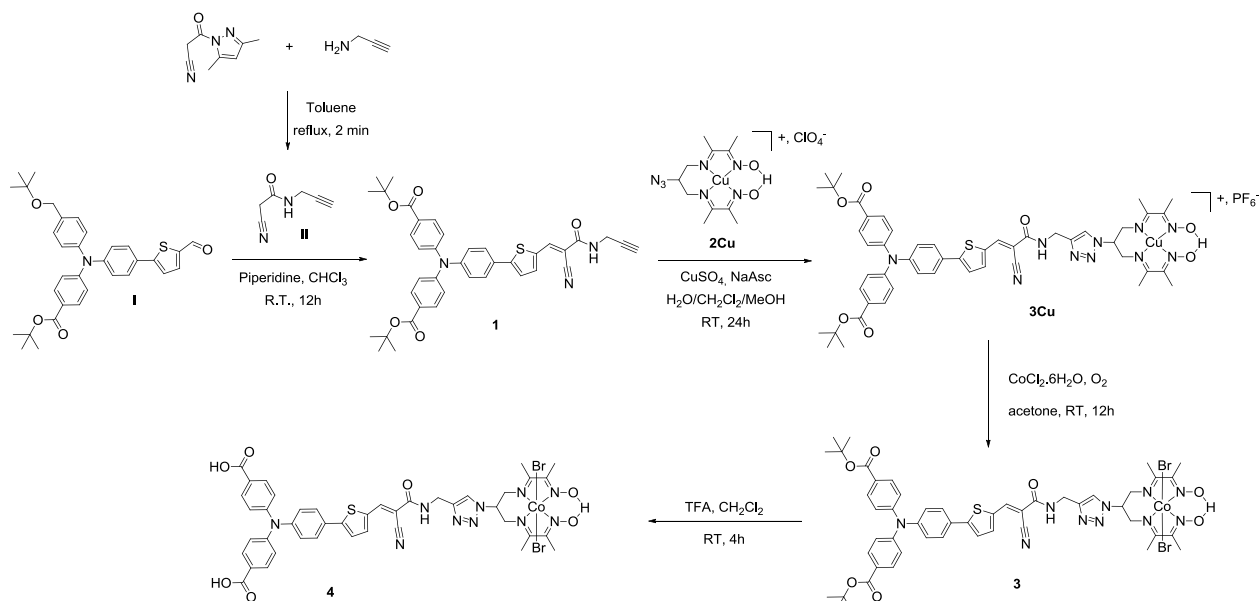
Electrochemical and photoelectrochemical measurements. Electrochemical and photoelectrochemical data were acquired with a *Biologic VSP 300* potentiostat. Electrochemical measurements were conducted in a 3-electrode cell. The working electrode was a glassy carbon electrode in the reduction potential window and a Pt one in the oxidation potential window. The reference electrode was made of a Ag/AgCl wire dipped into a KCl 3 M solution, separated from the supporting electrolyte by a Vycor® frit, and denoted below as Ag/AgCl. The counter electrode was a Pt wire. The supporting electrolyte was 0.1 M *nBu*₄NPF₆ in dry DMF. The supporting electrolyte was degassed with a flow of N₂ at least for 5 min before the measurements. The N₂ flow was removed from the solution but let in the headspace of the cell for the duration of the experiment. The concentration of the compound of interest was 1 mM. Cyclic voltammograms were typically recorded at a scan rate of 100 mV·s⁻¹. The potential of the reference electrode was

calibrated after each experiment by adding in the supporting electrolyte an internal reference (ferrocene for organic solvent, K_4FeCN_6 for aqueous solution), the potential of which was measured against the Ag/AgCl reference (0.43V for ferrocene and 0.24V for K_4FeCN_6).

Irradiation was carried out with a 300W ozone-free Xe lamp (*Newport*) operated at 280 W and mounted with a water-filled *Spectra-Physics 6123NS* liquid filter for elimination of IR ($\lambda > 800$ nm) irradiation and a *Spectra-Physics 59472* UV cut-off filter ($\lambda < 400$ nm). The power density was calibrated using a *Newport PM1918-R* power-meter. The photocurrent measurements were carried out in a specifically designed three-electrode cell, using the NiO-sensitized film as the working electrode (1.2 to 2 cm^2), Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The counter electrode compartment was separated from the cathodic one by a Vycor® frit. The supporting electrolyte was a 0.1 M 2-(N-morpholino)ethanesulfonic acid (MES)/0.1 M NaCl buffer at pH 5.5. The solution was degassed with nitrogen for 30 minutes prior to use. In a typical experiment, the volume of supporting electrolyte was 4.0 mL and the headspace was 2.4 mL. The photocathode was illuminated with a power density of 65 $mW \cdot cm^{-2}$ (ca. one sun). The amounts of evolved hydrogen were determined by sampling aliquots of the headspace in a *Perkin Elmer Clarus 580* gas chromatograph equipped with a molecular sieve 5 Å column (30m – 0.53 mm) and a TCD detector.

X-ray photoemission spectroscopy (XPS): The analyses were performed with a VersaProbe II spectrometer from Physical Electronics using a high-resolution monochromatic Al $K\alpha$ line X-ray source at 1486.7 eV. Fixed analyzer pass energy of 23 eV was used for core level scans leading to an overall energy resolution of 0.6 eV. Survey spectra were captured at pass energy of 117 eV. The photoelectron takeoff angle was 45°, which provided an integrated sampling depth of approximately 5 nm. All spectra were referenced against an internal signal, typically by adjusting the C 1s level peak at a binding energy of 284.8 eV.

Synthesis.



Scheme S1. Synthetic route to **4**.

Synthesis of propargyl cyanoacetamide (II): To a solution of 1-cyanoacetyl-3,5-dimethylpyrazole (1 equiv, 5.1 g, 31.2 mmol) in Toluene (40 mL) was added propargylamine (1 equiv, 2 mL, 31.2 mmol). The mixture was refluxed for 2 min and then stirred at room temperature. The precipitate was filtered, washed with pentane and dried to obtain a white solid as the pure product (3.16 g, 83 %). ¹H NMR (Acetone-*d*₆, 300 MHz): δ (ppm) 5.75 (s, 1H), 4.02 (d, *J* = 2.6 Hz, 2H), 3.62 (s, 2H), 2.71 (t, *J* = 2.6 Hz, 1H). ¹³C NMR (Acetone-*d*₆, 75.5 MHz): δ (ppm) 144.2, 104.21, 80.32, 72.52, 29.3, 12.06. HR-MS (ESI⁺): *m/z* calcd for C₆H₇N₂O 123.0553; found 123.0553 [M+H]⁺.

Synthesis of 1: To a solution of di-*tert*-butyl-4,4'-((4-(5-formylthiophen-2-yl)phenyl)azanediyl)dibenzoate **I** (1 equiv, 0.54 mmol, 300 mg) and propargyl cyanoacetamide (1 equiv, 0.54 mmol, 66 mg) in 20 mL of dry CHCl₃, was added piperidine (5.5 equiv, 3 mmol, 0.3 mL). The reaction mixture was stirred at room temperature for 12 hours under argon and protected from light. The mixture was diluted with CHCl₃ and washed with 1 M aqueous HCl then water. After removal of the solvent, the crude product was purified on a silica gel column using pentane / ethyl acetate (8/2) as eluent to give **1** as an orange solid (242 mg; 68 %). ¹H NMR (CD₂Cl₂, 300 MHz): δ (ppm) 8.37 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 4H), 7.72 (d, *J* = 4.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 4.1 Hz, 1H), 7.13 (m, 6H), 6.48 (t, *J* = 5.3 Hz, 1H), 4.18 (dd, *J* = 2.5 Hz, *J* =

5.3Hz, 2H), 2.34 (d, $J = 2.5$ Hz, 1H), 1.57 (s, 18H). $^{13}\text{C NMR}$ (CD_2Cl_2 , 75.5MHz): δ (ppm) 153.26, 150.56, 148.01, 145.15, 139.35, 135.38, 131.24, 129.01, 128.06, 127.56, 125.74, 124.41, 123.72, 117.45, 99.11, 81.12, 79.34, 72.10, 30.32, 28.36. **HR-MS** (ESI+): m/z calcd for $\text{C}_{39}\text{H}_{38}\text{N}_3\text{O}_5\text{S}$ 660.2527; found 660.2523 $[\text{M}+\text{H}]^+$. **E.A.:** calcd for $\text{C}_{39}\text{H}_{37}\text{N}_3\text{O}_5\text{S}$: C, 71.0; H, 5.65; N, 6.37; found: C, 70.74; H, 5.61; N, 6.31.

Synthesis of 3_{Cu} : **1** (1 equiv., 150 mg, 0.22 mmol) and **2_{Cu}** (1 equiv., 100 mg, 0.22 mmol), CH_2Cl_2 (7.3 mL) were solubilized in CH_2Cl_2 (7.3 mL) under Ar. A solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.3 equiv., 17 mg, 0.07 mmol) and sodium ascorbate (0.9 equiv., 41 mg, 0.20 mmol) in Ar-purged water (3.7 mL) was added. Then, Ar-degassed CH_3OH (12.3 mL) was added to the biphasic mixture until a single phase was obtained. The reaction mixture was stirred at R.T under Ar. After 24 h the solution was concentrated under vacuum yielding a precipitate, which was filtered and washed with water. The solid was purified by flash chromatography on silica gel using as eluent a mixture CH_3CN /aqueous KNO_3 solution at 10% of the saturating concentration. The pure product was obtained after evaporation of CH_3CN in the combined fractions and precipitation by addition of a KPF_6 -saturated aqueous solution. The precipitate was filtered, washed with water and dried under vacuum to give **3_{Cu}** as red brick solid (177 mg, 68% yield), which was directly used for the next step.

Synthesis of **3:** **3_{Cu}** (1 equiv., 160 mg, 0.14 mmol) and **$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$** (7 equiv., 234 mg, 0.98 mmol) were solubilized in acetone (24.5 mL) and stirred under air bubbling. After 12 h the solution was evaporated under vacuum and the solid was purified by flash chromatography on silica gel using as eluent a mixture of CH_3CN and aqueous KNO_3 solution at 10% of the saturating concentration, then a solution of acetone saturated in NaI to completely desorb the product from the silica gel. The desired fractions were combined and the organic solvents were evaporated under vacuum, yielding a precipitate that was filtered and washed with water. The solid was re-solubilized in acetone. To this solution is added a NaBr-saturated aqueous solution (a third of the final volume). The mixture was stirred at R.T. for three days to allow the acetone to slowly evaporate, giving a precipitate. This precipitate was filtered, washed with water and dried under vacuum to obtain the expected product **3** as a pure solid (95 mg, 59% yield). $^1\text{H NMR}$ (CD_3CN , 500 MHz): δ (ppm) 19.23 (s, 1H), 8.28 (s, 1H), 7.88 (s, 1H), 7.80 (d, $J = 8.6$ Hz, 4H), 7.68 (s, 1H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.38 (s, 1H), 7.23 (s, 1H), 7.08 (d, $J = 8.3$ Hz, 2H), 7.03 (d, $J = 8.6$ Hz, 4H), 5.71 (t, $J = 9.7$ Hz, 1H), 4.68 – 4.37 (m, 6H), 2.52 (s, 6H), 2.48 (s, 6H), 1.49 (s, 18H). $^{13}\text{C NMR}$ (CD_3CN , 126

MHz): δ (ppm) 177.32, 165.60, 161.60, 157.39, 152.73, 150.88, 148.05, 145.29, 144.76, 139.99, 135.62, 131.38, 129.32, 128.24, 127.56, 126.11, 124.87, 123.92, 123.51, 100.42, 81.25, 58.46, 55.50, 36.25, 30.83, 28.25, 18.52, 14.00. **HR-MS** (ESI+): m/z calcd for $C_{50}H_{55}BrCoN_{10}O_7S$ 1077.2486; found 1077.2487 $[M-Br]^-$. **E.A.:** calcd for $C_{50}H_{55}Br_2CoN_{10}O_7S + 0.25 NaBr$: C, 50.70; H, 4.68; N, 11.82; found: C, 50.91; H, 4.87; N, 11.53.

Synthesis of 4: 3 (1 equiv., 35 mg, 30 μ mol) was solubilized in CH_2Cl_2 (1.5 mL) and **TFA** (30 equiv., 0.15 mL, 0.88 mmol) was slowly added to this solution. The mixture was stirred at R.T. for 4 hours and then evaporated to dryness. The solid was dissolved in CH_2Cl_2 , filtered, washed successively with CH_2Cl_2 and CH_3CN and dried under vacuum to obtain **4** as a pure product (28 mg, 88% yield). **1H NMR** (Figure S1) (acetone- d_6 /DMSO- d_6 3:1, 500 MHz): δ (ppm) 19.40 (s, 1 H_{OH}), 12.58 (s, 2 H_{COOH}), 8.80 (t, $J = 5.7$ Hz, 1 H_{CONH}), 8.47 (s, 1 $H_{triazole}$), 8.40 (s, 1 H_{alkene}), 7.96 (d, $J = 8.7$ Hz, 4 H_{Ar}), 7.93 (d, $J = 4.1$ Hz, 1 H_{thio}), 7.84 (d, $J = 8.7$ Hz, 2 H_{Ar}), 7.71 (d, $J = 4.1$ Hz, 1 H_{thio}), 7.25 (d, $J = 8.7$ Hz, 2 H_{Ar}), 7.19 (d, $J = 8.7$ Hz, 4 H_{Ar}), 5.81 (t, $J = 11.4$ Hz, 1 H_{NCH}), 4.77 – 4.49 (m, 6 H_{NCH_2}), 2.74 (s, 6 H_{CH_3}), 2.57 (s, 6 H_{CH_3}). **^{13}C NMR** (acetone- d_6 /DMSO- d_6 3:1, 126 MHz): δ (ppm) 176.70, 166.75, 161.01, 156.36, 156.29, 151.24, 150.19, 147.14, 145.01, 143.42, 139.58, 134.92, 131.08, 128.81, 127.67, 125.85, 125.74, 124.54, 123.14, 122.97, 116.63, 100.86, 57.76, 54.55, 39.52, 35.43, 13.03. **HR-MS** (ESI+): m/z calcd for $C_{42}H_{39}BrCoN_{10}O_7S$ 965.1234; found 965.1235 $[M-Br]^-$. **E.A.:** calcd for $C_{42}H_{39}Br_2CoN_{10}O_7S + 0.8 NaBr$: C, 44.68; H, 3.48; N, 12.41; found: C, 44.93; H, 3.78; N, 12.06.

Photolysis experiment. Spectro-photochemical measurements were performed in an H_2O/O_2 -free glovebox. In a quartz cuvette (1 mm optical light path) a solution of **3** ($1.8 \cdot 10^{-5}$ M) in dry, degassed $CH_3CN/TEOA$ (90:10 v/v) mixture was irradiated for 1.5h at $100 \text{ mW}\cdot\text{cm}^{-2}$ (output power measured after UV and IR filters; losses through the quartz window of the glove-box and related possible de-focusing of the beam not taken into account). UV-visible spectra were recorded at time intervals with an optical fiber external-sampler connected to *UV-Vis* spectrometer.

F108-templated NiO films preparation: The precursor solution was prepared by mixing $NiCl_2$ (1 g), F108 triblock co-polymer (1 g), Milli-Q water (3 g) and ethanol (6 g) according to the literature [6]. After overnight sonication and centrifugation, the supernatant solution was spin-coated (*SPS-Europe spin150* model) for 1 min at 5000 rpm onto FTO/glass substrates (Solems, TEC 7, sheet resistance $7\Omega\cdot\text{cm}^{-1}$), followed by sintering (30 min temperature ramp from room temperature to

450°C and 30 min at 450°C) in the air in a flat oven. The process was repeated four times to increase the thickness up to 1 μm , as measured by cross-section scanning electron microscopy.

NiO films sensitization: The NiO electrodes were soaked in a CH_3CN solution of **4** (0.5 mM) with or without chenodeoxycholic acid (CDCA) (2 mM) for 24 h at room temperature on an orbital stirring table. The electrodes were rinsed with CH_3CN and dried in air.

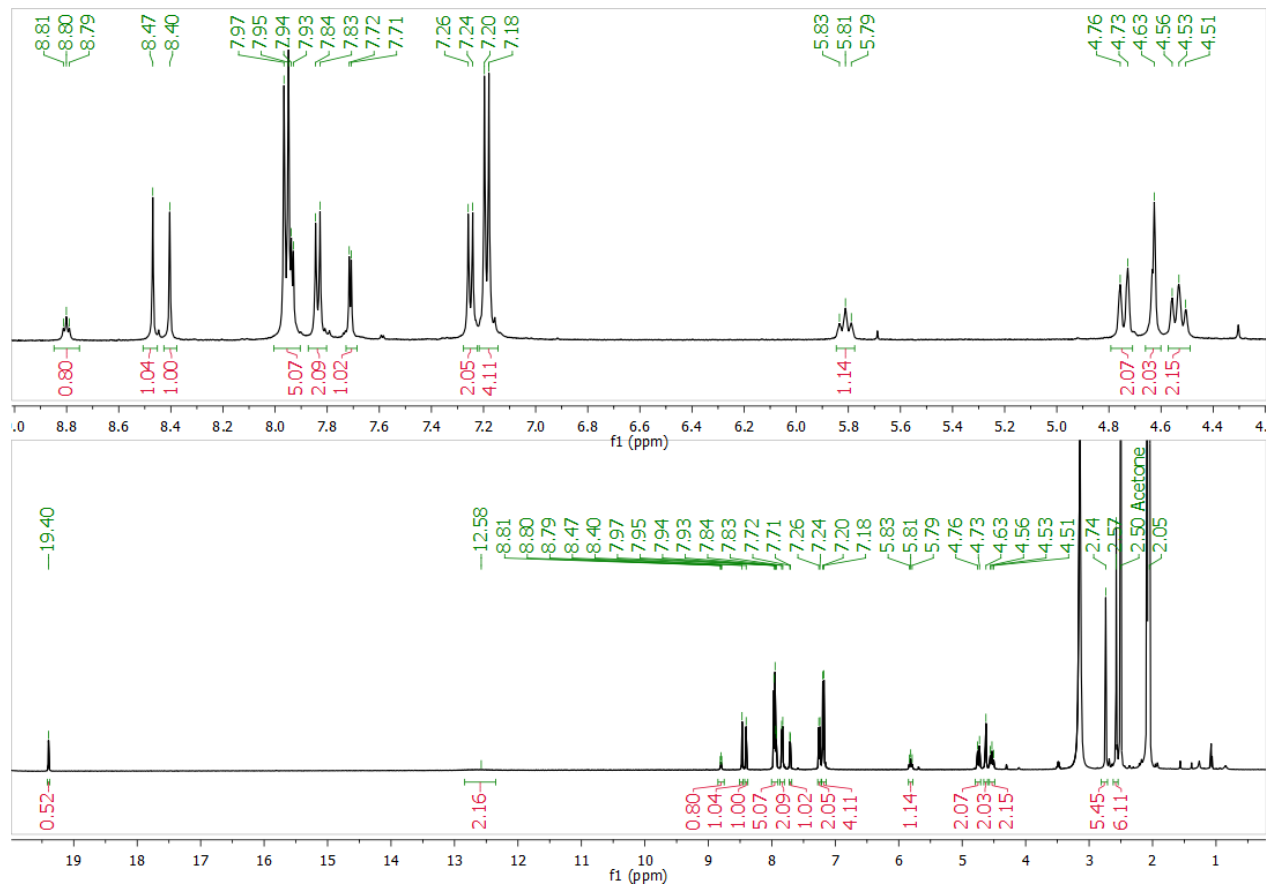


Figure S1: ^1H NMR spectrum of **4** recorded in acetone- d_6 /DMSO- d_6 (3:1).

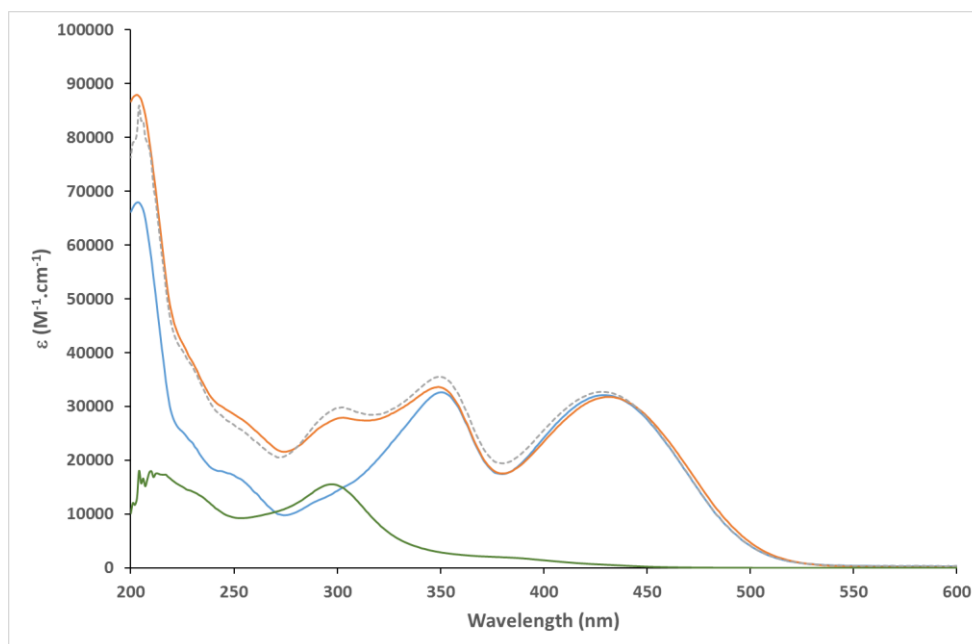


Figure S2: Absorption spectra of compounds **1** (blue line), **2c₀** (green line) and **3** (orange line) recorded in CH₃CN. The sum of the absorption of **1** and **2c₀** is represented as the dotted grey line.

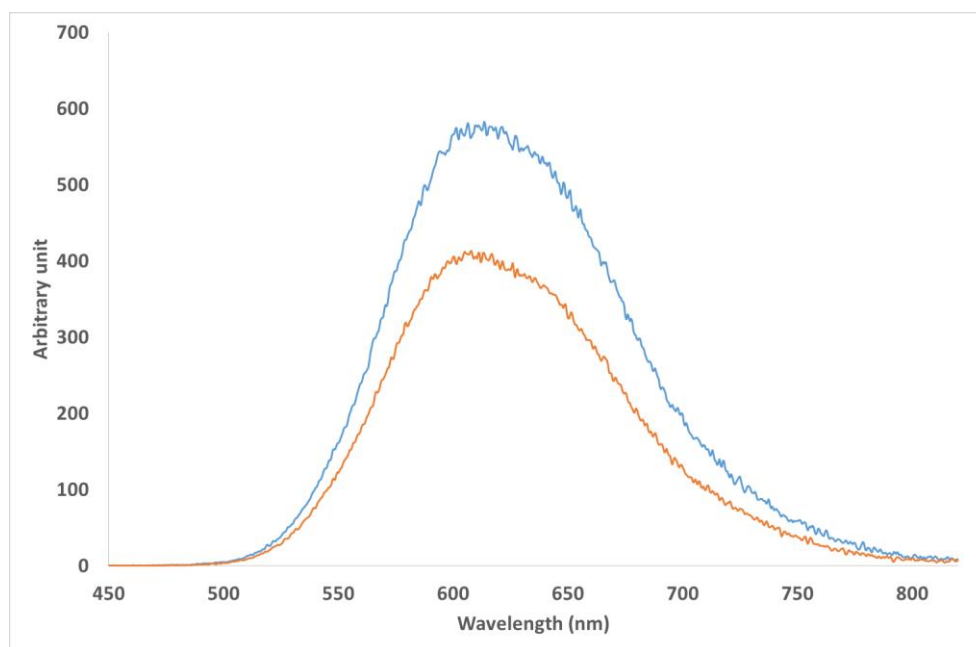


Figure S3: Emission spectra for isoabsorptive (0.1 @ $\lambda = 430$ nm) solutions of **1** (blue line) and **3** (orange line) in CH₃CN.

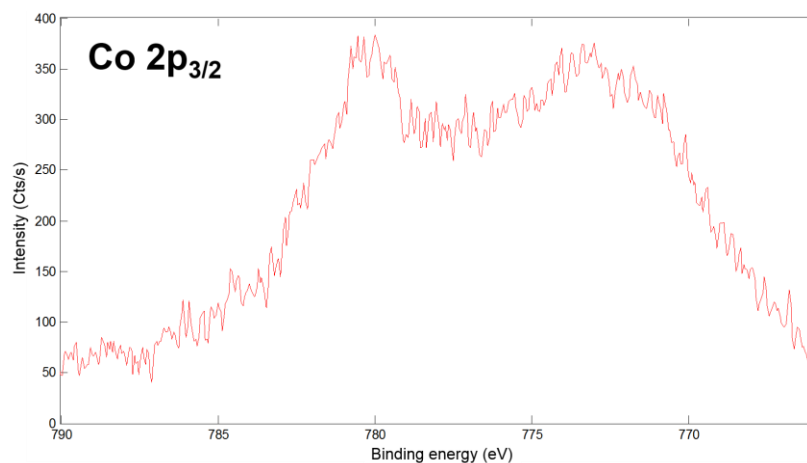


Figure S4: XPS core-level spectrum of the Co 2p_{3/2} region for a 4/CDCA-sensitized NiO electrode.

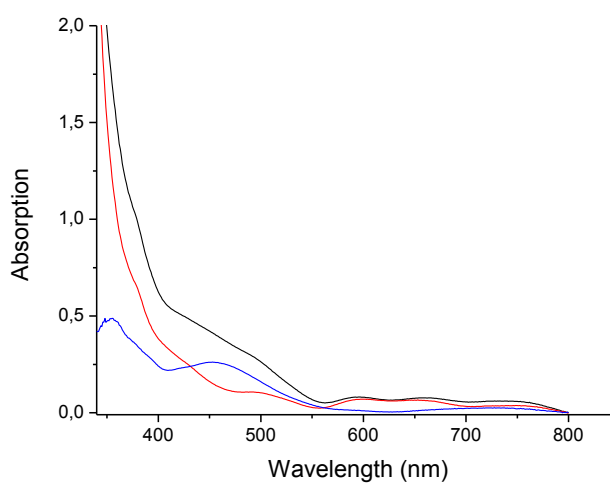
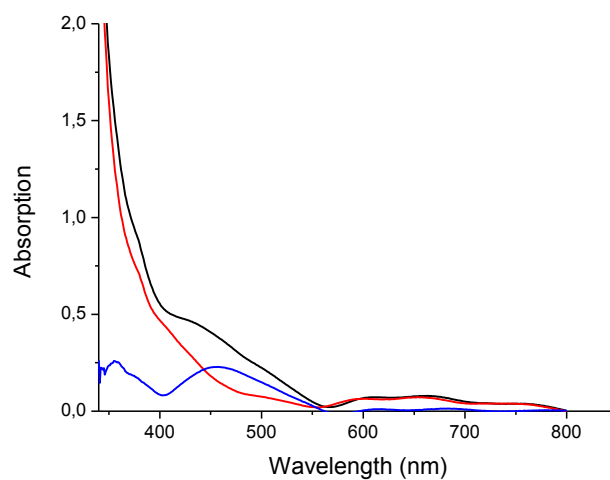


Figure S5: Absorption spectra of pristine NiO electrodes (red lines) and 4/CDCA-sensitized (top) or 4-sensitized (bottom) NiO electrodes without (black lines) or with (blue lines) subtraction of the NiO background.

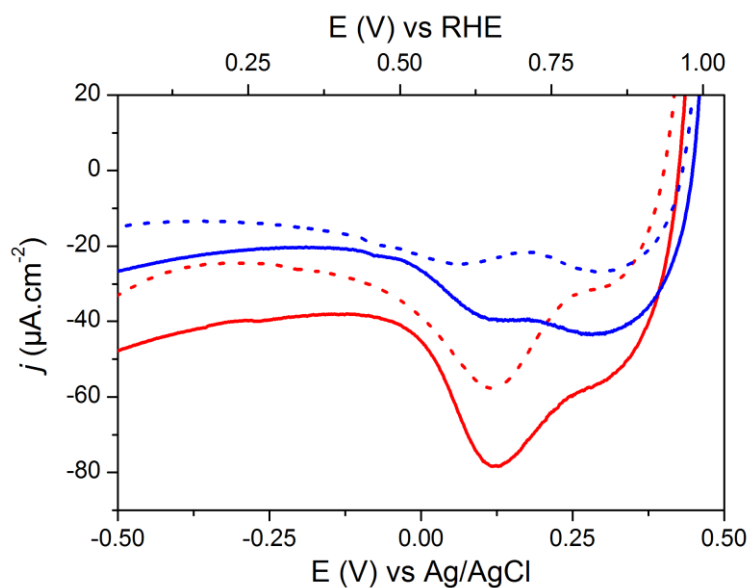


Figure S6: Linear sweep voltammograms of NiO electrodes sensitized by **4** only (blue lines) or with CDCA as co-adsorbent (red lines), recorded in a pH 5.5 MES 0.1 M/NaCl 0.1 M supporting electrolyte under irradiation (plain lines) or in the dark (dotted lines).

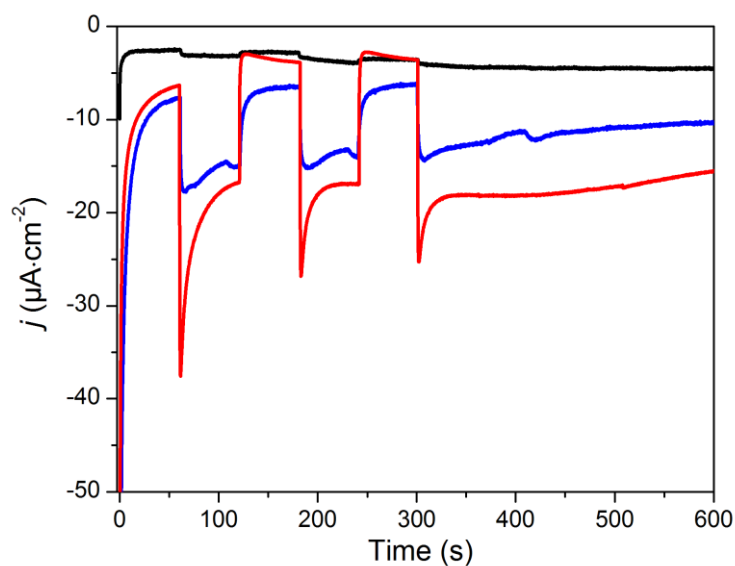


Figure S7: Steady-state photocurrents recorded in a pH 5.5 MES 0.1 M/NaCl 0.1 M supporting electrolyte, at an applied potential of 0.14 V vs RHE, at a pristine (black line), a **1**/CDCA-sensitized (blue line) and a **4**/CDCA-sensitized (red line) NiO electrodes.

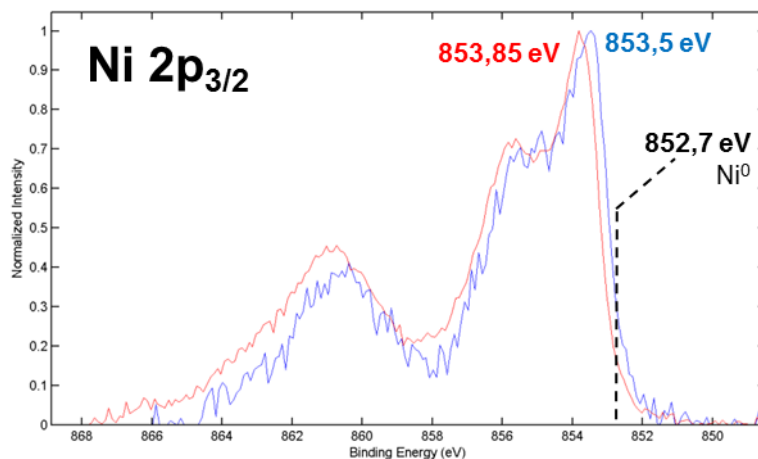


Figure S8: XPS core-level spectrum of the Ni 2p_{3/2} region for a **4**/CDCA-sensitized NiO electrode before (red) and after (blue) 2 hours of photo-electrocatalysis.

Table S1: Photocurrent densities obtained from chronoamperometric measurements at three different applied potentials, charges passed during electrolysis under irradiation at 0.14 V vs NHE and amount of hydrogen measured by GC with corresponding faradaic efficiencies.

E (V vs RHE)	0.54	0.34	0.14	Q (mC) (time/electrode surface)	H ₂ n(nmol) / F.E. (%)
	<i>j</i> (μA.cm ⁻²) ^a				
NiO	0.1	0.3	1		
1 /CDCA	7	9	8		
4	5	6	13		
4 /CDCA	6	8	15		
NiO					
1 /CDCA				61 (2h / 1.5 cm ²)	No
4				60 (2h / 1.8 cm ²)	19.1 / 6.1%
4 /CDCA				79 (2h / 1.2 cm ²)	39.0 / 9.5%
4 /CDCA				82 (2h / 1.8 cm ²)	33.9 / 7.9%
4 /CDCA				102 (3h / 1.2 cm ²)	48.9 / 9.3%
4 /CDCA				97 (3h / 1.8 cm ²)	41.4 / 8.2%

^a dark current subtracted

References:

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