

# Electronic Supplementary Information

## Push-pull organic dyes and dye-catalyst assembly featuring a benzothiadiazole unit for photoelectrochemical hydrogen production

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**General methods and chemicals used.** All reagents were obtained from commercially available sources (Sigma-Aldrich, Fluorochem and Alfa-Aesar) and used without further purification. Solvents were dried from appropriate drying agents (sodium and benzophenone for THF) and freshly distilled under argon before use. Compounds IDT (**I**)<sup>1</sup>, TPA (**II**)<sup>2</sup>, BTD (**III**)<sup>3</sup>, CN-Alc (**IV**)<sup>4</sup>, [Cu(DO)(DOH)N<sub>3</sub>pn(OH<sub>2</sub>)](ClO<sub>4</sub>) (**Cu-N<sub>3</sub>**)<sup>5</sup>. Batches of **Co** (Co(DO)(DOH)pnBr<sub>2</sub>), <sup>t</sup>Bu**T1** and <sup>t</sup>Bu**T2R** synthesized and characterized during the course of our previous studies<sup>6,7</sup> were employed to record UV-Vis absorption spectra in dichloromethane.

**General characterization methods and equipments.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 298 K on a Bruker Avance 400 MHz spectrometer and the resulting spectra are referenced to the residual solvent peak and reported in relative to tetramethylsilane reference ( $\delta = 0$  ppm). Emission fluorescence and UV-Vis absorption spectra of compounds were recorded on Perkin Elmer LS50B spectrofluorimeter and on an Agilent Cary 60 UV-Vis spectrometer, respectively, in a 1 cm optical light path quartz cuvette at 25 °C.

**Electronic conductivity measurements.** The electronic conductivity of NiO mesoporous films was measured with an Ossila Four-Point Probe System and the corresponding Ossila software. This measurement uses four probes arrayed in a line, with equal spacing between each probe. A current is passed between the outer two probes, causing a reduction in voltage between the inner two probes. By measuring this change in voltage, the electronic conductivity can then be calculated.

**MALDI-ToF mass spectrometry.** The mass spectra were acquired in positive ion mode on a Bruker Microflex LRF mass spectrometer equipped with a 337 nm nitrogen laser and pulse delay extraction. The resolution was increased by using the reflector mode, which allows obtaining the isotopic profile. The matrix was prepared as saturated solution of  $\alpha$ -cyano-4-hydroxycinnamic acid (HCCA) in 7:3 acetonitrile/water (v/v). Sample (1  $\mu$ L) was added to 1  $\mu$ L of the matrix solution and spotted on a polished stainless target plate using the dried droplet method. Mass spectra were calibrated using reference peptides mixture of known masses.

**Electrochemistry in solution.** Electrochemical analysis was performed with a BioLogic SP300 potentiostat controlled via EC-Lab V10 software. Electrochemical measurements were recorded in a three-electrode cell combining a glassy-carbon working electrode, a platinum wire counter electrode and a custom-made Ag/AgCl reference electrode. Typical measurements were carried out in argon-purged dichloromethane or N-dimethylformamide solution (0.1 M *n*-Bu<sub>4</sub>NBF<sub>4</sub> as supporting electrolyte) for oxidation or reduction respectively. Ferrocene was added at the end of each measurement as an internal reference; hence, every value is referenced versus the Fc<sup>+0</sup> redox couple.

**Photoelectrochemical measurements.** For a typical photoelectrocatalytic experiment, irradiation was carried out with a Newport 300W ozone-free Xe lamp operated at 280 W, equipped with a water-filled filter (Spectra-Physics 6123NS) to eliminate IR irradiation ( $\lambda > 800$  nm) and a UV cut-off filter (Spectra-Physics 59472,  $\lambda > 400$  nm). The power density was measured with a Newport PM1918-R power-meter and calibrated to 0.65 sun (corresponding to the 400-800 nm range of the full spectrum) using a 60% neutral density filter. The experiments were performed in a three-electrode cell, using the NiO-sensitized film as working electrode (2.5 to 3.5 cm<sup>2</sup>, measured for each experiment), Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The supporting electrolyte was 0.1 M 2-(*N*-morpholino)ethanesulfonic acid (MES) / 0.1 M NaCl buffer at pH 5.5. The volume of supporting electrolyte (around 4 mL) and the headspace volume (around 2.5 mL) were accurately measured for each single experiment. The different compartments of the cell and the electrolyte were degassed for 30 minutes before the PEC experiments. The amount of evolved hydrogen was determined after two hours by sampling 50  $\mu$ L of the headspace in Perkin Elmer Clarus 580 gas chromatograph equipped with a molecular sieve 5 A column (30m – 0.53 mm).

**Density Functional Theory (DFT).** Prior to any synthesis, the energy level and the localization of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of target molecules were calculated a computational method. The calculations were made using the ADF 2016 package.<sup>8,9</sup> Geometry optimizations were carried out with the revPBE functional where dispersion was taken into account based on the Grimme's D3 correction<sup>10</sup>, followed by a single-point with B3LYP and modelling the solvent using the COSMO model for water. The TZ2P basis sets<sup>11</sup> were used for optimizations and single points.

**Time-Dependent Density Functional Theory (TD-DFT).** Time-Dependent DFT calculations were performed with ADF to estimate the electronic excitations on the molecules <sup>t</sup>BuAM1-alkyne and <sup>t</sup>BuAM1-w/oBTD-alkyne. Only singlet allowed transitions were chosen, and ten roots were evaluated. PBE hybrid functional was investigated together with TZ2P basis sets. The solvent (dichloromethane) was taken into account as a polarisable model (COSMO). The spectra were displayed using the ADF Graphical User Interface.

### **F108-templated NiO films and Li-doped F108-templated NiO films preparation and characterization.**

*NiO films:* NiO films were prepared according to our previously reported procedure.<sup>12</sup> The precursor solution was prepared by mixing NiCl<sub>2</sub> (2 g), F108 triblock co-polymer (2 g), Milli-Q water (6 g) and ethanol (12 g). After overnight sonication and centrifugation, the supernatant solution was filtered through a 0.45  $\mu$ m pore size polyethersulfone syringe filter. FTO-coated glass substrates (2.2 mm thick, 7 ohm/sq from Solaronix) were cleaned by sonication in Gigapur solution, water then ethanol for 10 min each. A 15 min ozone treatment was performed to remove any impurities from the surface of the substrate. The F108 precursor solution was then spin-coated on the substrates (5000 rpm, 60 s), followed by sintering (30 min temperature ramp from 25°C to 450 °C and 30 min at 450°C) in the air in a flat oven. The spin-coating process was repeated four times to end up with a film thickness comprised between 700 nm and 1  $\mu$ m, as measured by cross-section scanning electron microscopy.

*Li-doped NiO films:* Similar precursor solution was prepared as well as a highly concentrated (8 M) solution of LiCl (340 mg) in deionized water (1 mL). Then, addition of this solution in the precursor solution was done to obtain a range of Li-containing precursor solution (1.5, 3 and 6 molar%). The Li-doped NiO films were then made similarly to NiO films. Unfortunately, the 6% Li-doped NiO electrodes peeled off during the calcination of the 2<sup>nd</sup> layer and were, then, non-studied.

**NiO film sensitization.** The F108-templated NiO films were soaked for 24 hours in a 0.5 mM solution of **AM1-OMe** or **AM1-Co** in CHCl<sub>3</sub>/EtOH (1/1) at room temperature on an orbital stirring table. The electrodes were then rinsed with CHCl<sub>3</sub> and EtOH, then dried in air.

**Determination of the dyad (or dye) loading.** Every film was cut in half after sensitization. The first half was used to determine the dyad (dye) loading while the second half was used for the photoelectrochemical tests. The freshly grafted half of the film was dipped for 4 hours in a 0.1 M solution of phenylphosphonic acid in THF in order to desorb the dyad from the surface, according to previously reported procedures.<sup>13,14</sup> The desorption solution was then washed with water and extracted with dichloromethane. Organic layers were gathered and the solvent evaporated. The residual solid was dissolved in 400  $\mu$ L of dichloromethane and the absorption spectrum of the solution was recorded. This allows to determine the amount of dye/dyad loaded on the NiO film which is used to calculate turn-over numbers (TON).

**Synthesis of 1:** Compound **I** (1.0 g, 0.98 mmol, 1 eq) was dissolved in freshly distilled THF and cooled down to -78 °C. A commercial solution of *n*-butyl lithium 2.5 M in hexane (0.41 mL, 1.03 mmol, 1.05 eq) was added dropwise. The reaction mixture was stirred at -78 °C for one hour. Isopropoxy boropinacolic ester (0.22 mL, 1.08 mmol, 1.1 eq) was added dropwise. The reaction mixture was stirred at -78 °C for 20 min then overnight at room temperature. The reaction mixture was poured in 1M NH<sub>4</sub>Cl solution and extracted with dichloromethane. Organic layers were washed with water, brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude material was dissolved in a solution THF/water (20/5mL) with compound **II** (0.35 g, 1.06 mmol, 1.1 eq) and potassium phosphate (0.55 g, 2.6 mmol, 2.7 eq). The mixture was argon-flushed for 20 minutes. Pd<sub>2</sub>dba<sub>3</sub> (17.4 mg, 0.019 mmol, 0.02 eq) and HPtBu<sub>3</sub>BF<sub>4</sub> (22 mg, 0.077 mmol, 0.08 eq) were added and the mixture was heated up to 40°C for 16h. The mixture was poured into brine and extracted with dichloromethane. Organic layers were washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated. Product **1** was purified by silica gel column chromatography using hexane/DCM (9/1) as eluent. (orange powder, 613 mg, 0.50 mmol, 50% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 10.10 (s, 1H) ; 8.15 (q, *J* = 8.3 Hz, 2H) ; 8.09 (s, 1H) ; 8.04 (d, *J* = 8.3 Hz, 2H) ; 7.94 (d, *J* = 7.6 Hz, 1H) ; 7.78 (d, *J* = 7.7 Hz, 1H) ; 7.53 (s, 1H) ; 7.46 (s, 1H) ; 7.27 (d, *J* = 5.0 Hz, 1H) ; 7.25 (d, *J* = 8.2 Hz, 4H) ; 7.17 (d, *J* = 8.2 Hz, 4H) ; 7.08 (m, 8H) ; 7.02 (d, *J* = 5.0 Hz, 1H) ; 2.56 (m, 8H) ; 1.59 (m, 8H) ; 1.28 (m, 40 H) ; 0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  (ppm) = 191.7, 156.8, 156.4, 154.0, 153.9, 153.6, 152.4, 143.9, 143.1, 142.1, 142.0, 141.7, 141.6, 141.3, 136.1, 135.7, 135.0, 130.2, 130.0, 129.7, 128.9, 128.6, 128.5, 128.1, 128.0, 124.3, 124.1, 123.3, 118.1, 117.6, 63.4, 62.9, 35.7, 32.0, 31.5, 29.6, 29.4, 22.8, 14.3

**Synthesis of 2:** Compound **1** (613 mg, 0.49 mmol, 1 eq) was dissolved in THF (15 mL), cooled down to 0 °C and protected from light. A solution of NBS (91 mg, 0.51 mmol, 1.05 eq) in DMF (10 mL) was added dropwise. Let stir for 16h at 25°C. The mixture was poured into brine and extracted with ethyl acetate. Organic layers were washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated. Product **2** was purified by silica gel column chromatography using hexane/DCM (8/2) as eluent. (red wax, 613 mg, 0.46 mmol, 94% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) = 10.09 (s, 1H) ; 8.16 (q, *J* = 7.9 Hz, 2H) ; 8.16 (s, 1H) ; 8.01 (d, *J* = 8.3 Hz, 2H) ; 7.88 (d, *J* = 7.5 Hz, 1H) ; 7.73 (d, *J* = 7.5 Hz, 1H) ; 7.63 (s, 1H) ; 7.51 (s, 1H) ; 7.30 (d, *J* = 8.0 Hz, 1H) ; 7.20 (d, *J* = 8.2 Hz, 4H) ; 7.14 (m, 8H) ; 7.09 (s, 1H) ; 2.59 (t, *J* = 6.4 Hz, 8H) ; 1.61 (m, 8H) ; 1.31 (m, 40 H) ; 0.90 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  (ppm) = 191.9, 157.5, 155.6, 154.5, 154.0, 153.3, 152.7, 143.7, 143.3, 142.6, 142.5, 142.4, 142.1, 141.9, 141.8, 136.2, 135.9,

135.7, 130.9, 130.1, 129.2, 129.0, 128.4, 128.2, 126.7, 124.9, 124.3, 118.3, 117.9, 114.6, 64.1, 63.7, 36.0, 32.4, 32.0, 30.0, 29.7, 23.2, 14.4.

**Synthesis of 3:** Compounds **2** (613 mg, 0.46 mmol, 1 eq), **III** (289 mg, 0.5 mmol, 1.1 eq) and potassium phosphate (263 mg, 1.24 mmol, 2.7 eq) were dissolved in THF (12 mL) and water (3 mL). The mixture was argon-flushed for 20 minutes then Pd<sub>2</sub>dba<sub>3</sub> (8.2 mg, 9 μmol, 0.02 eq) and HPtBu<sub>3</sub>BF<sub>4</sub> (10.7 mg, 37 μmol, 0.08 eq) were added. Reaction mixture was stirred at 40°C for 16h. The mixture was poured into ammonium chloride (1M) and extracted with dichloromethane. Organic layers were washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated. Product **3** was purified by silica gel column chromatography using hexane/DCM (5/5) as eluent. (Purple wax, 724 mg, 0.43 mmol, 93% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) = 10.09 (s, 1H) ; 8.18 (q, *J* = 8.3 Hz, 2H) ; 8.16 (s, 1H) ; 8.02 (d, *J* = 8.3 Hz, 2H) ; 7.98 (d, *J* = 7.5 Hz, 1H) ; 7.86 (d, *J* = 8.8 Hz, 4H) ; 7.82 (d, *J* = 7.6 Hz, 1H) ; 7.58 (s, 1H) ; 7.56 (d, *J* = 8.6 Hz, 2H) ; 7.50 (s, 1H) ; 7.24 (m, 8H) ; 7.10 (m, 15H) ; 2.57 (m, 8H) ; 1.57 (m, 26H) ; 1.28 (m, 40 H) ; 0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ (ppm) = 191.6, 165.1, 157.2, 156.8, 154.0, 153.7, 153.5, 152.4, 150.4, 146.9, 145.7, 143.5, 143.1, 142.0, 141.9, 141.8, 141.7, 140.1, 135.9, 135.8, 134.9, 131.2, 130.7, 130.5, 129.7, 129.6, 128.9, 128.5, 127.9, 127.8, 126.6, 126.5, 126.1, 124.5, 123.8, 122.7, 118.9, 117.8, 117.3, 80.6, 63.3, 35.5, 31.9, 31.5, 29.5, 29.3, 28.0, 22.7, 13.9. **E.A.:** calculated for C<sub>113</sub>H<sub>125</sub>N<sub>3</sub>O<sub>5</sub>S<sub>3</sub> : C, 79.77; H, 7.41; N, 2.47; S, 5.65; found: C, 79.60; H, 7.29; N, 2.02; S, 5.50.

**Synthesis of <sup>t</sup>BuAM1-OMe:** Compound **3** (190 mg, 0.11 mmol, 1 eq), methyl cyanoacetate (0.29 mL, 0.33 mmol, 3 eq) and ammonium acetate (170 mg, 2.2 mmol, 20 eq) were dissolved in toluene (15 mL). Reaction mixture was heated up to 90°C for 3 days. Reaction mixture was poured in water then extracted with ethyl acetate. Organic layers were washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated. The crude product was purified by silica gel column chromatography using hexane/DCM (6/4) as eluent. Purple wax was recovered and rinsed with methanol for 3h. (purple wax, **90 mg, 0.05 mmol, 46%**). <sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz): δ (ppm) = 8.33 (s, 1H) ; 8.16 (s, 4H) ; 8.10 (s, 1H) ; 7.95 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 4H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.46 (s, 1H) ; 7.27 (d, *J* = 8.3 Hz, 4H) ; 7.21 (d, *J* = 7.2 Hz, 4H) ; 7.10 (m, 15H) ; 3.96 (s, 3H) ; 2.57 (m, 8H) ; 1.59 (m, 26H) ; 1.26 (m, 40 H) ; 0.87 (m, 12H). <sup>13</sup>C NMR (THF-d<sub>8</sub>, 100 MHz): δ (ppm) = 165.5, 163.2, 157.3, 156.8, 154.6, 153.9, 153.8, 153.5, 152.6, 150.5, 146.6, 145.6, 144.3, 142.3, 141.9, 141.7, 141.6, 140.5, 136.1, 135.0, 131.7, 131.6, 131.1, 131.0, 130.2, 129.9, 129.0, 128.6, 128.1, 128.0, 126.7, 126.5, 126.2, 124.5, 124.1, 122.8, 119.2, 117.9, 117.5, 115.8, 102.5, 80.9, 63.3, 63.2, 35.7, 32.0, 31.5, 29.6, 29.4, 28.4, 22.8, 14.2. **HR-MS** (ESI+): *m/z* calculated for C<sub>117</sub>H<sub>128</sub>N<sub>4</sub>O<sub>6</sub>S<sub>3</sub> 1780.899, found 1780.898 [M+H]<sup>+</sup>.

**Synthesis of AM1-OMe:** Compound <sup>t</sup>BuAM1-OMe (20 mg, 11 μmol, 1 eq) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and trifluoroacetic acid (42 μL, 550 μmol, 50 eq) was added to the solution. The mixture was stirred at 25 °C for 6 hours then evaporated to dryness. The solid was dissolved in tetrahydrofuran and washed with water. Organic layers were dried under vacuum to obtain **AM1-OMe** as pure product (purple solid, **18.2 mg, 10.5 μmol, 95%**). <sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz): δ (ppm) = 8.37 (s, 1H) ; 8.31 (d, *J* = 7.9 Hz, 2H) ; 8.27 (s, 1H) ; 8.23 (d, *J* = 8.2 Hz, 2H) ; 8.10 (d, *J* = 7.6 Hz, 1H) ; 7.98 (d, *J* = 7.7 Hz, 1H) ; 7.88 (m, 4H) ; 7.68 (s, 1H) ; 7.63 (m, 3H) ; 7.45 (s, 1H) ; 7.26 (m, 8H) ; 7.10 (m, 14H) ; 3.89 (s, 3H) ; 2.56 (t, *J* = 7.2 Hz, 8H) ; 1.58 (m, 8H) ; 1.31 (m, 40H) ; 0.92 (m, 12H). **HR-MS** (ESI+): *m/z* calculated for C<sub>109</sub>H<sub>112</sub>N<sub>4</sub>O<sub>6</sub>S<sub>3</sub> 1668.77, found 1668.78 [M+H]<sup>+</sup>.

**Synthesis of <sup>t</sup>BuAM1-alkyne:** Compound **3** (160 mg, 0.09 mmol, 1 eq), propargylic cyanoacetamide **IV** (23 mg, 0.19 mmol, 2 eq) and ammonium acetate (145 mg, 1.9 mmol, 20 eq) were dissolved in toluene (15 mL). Reaction mixture was heated up to 90 °C for 3 days. Reaction mixture was poured in water then extracted with ethyl acetate. Organic layers were washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated. Product <sup>t</sup>BuAM1-alkyne was purified by silica gel column chromatography using hexane/ethyl acetate (90/10) as eluent. Purple wax was recovered and rinsed with methanol for 3h. (Purple wax, 113 mg, 0.063 mmol, 70% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) = 8.42 (s, 1H) ; 8.13 (q, J = 8.8 Hz, 4H) ; 8.10 (s, 1H) ; 7.93 (d, J = 7.6 Hz, 1H) ; 7.89 (d, J = 8.8 Hz, 4H) ; 7.78 (d, J = 7.6 Hz, 1H) ; 7.53 (s, 1H) ; 7.52 (d, J = 8.5 Hz, 2H) ; 7.46 (s, 1H) ; 7.27 (d, J = 8.2 Hz, 4H) ; 7.21 (d, J = 7.0 Hz, 4H) ; 7.10 (m, 15H) ; 6.60 (t, J = 5.3 Hz, 1H) ; 4.25 (dd, J = 2.5 Hz, J = 5.2 Hz, 2H) ; 2.62 – 2.51 (m, 8H) ; 2.33 (t, J = 2.5 Hz, 1H) ; 1.59 (s, 26H) ; 1.26 (s, 40H) ; 0.87 (d, J = 2.6 Hz, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ (ppm) = 165.5, 160.2, 157.3, 156.8, 153.9, 153.8, 153.5, 153.0, 152.6, 150.5, 146.5, 145.6, 144.2, 141.9, 141.7, 141.6, 140.5, 136.1, 135.0, 131.6, 131.3, 131.2, 131.0, 130.3, 129.9, 128.9, 128.5, 128.4, 128.1, 128.0, 126.7, 126.5, 126.2, 124.5, 122.8, 119.2, 117.9, 117.5, 117.0, 103.2, 80.9, 78.5, 74.6, 72.7, 69.3, 63.3, 63.2, 62.4, 62.1, 35.7, 34.3, 32.0, 31.9, 31.5, 30.4, 29.6, 29.4, 28.4, 25.4, 22.8, 14.2. **HR-MS** (ESI+): *m/z* calculated for C<sub>119</sub>H<sub>129</sub>N<sub>5</sub>O<sub>5</sub>S<sub>3</sub> 1803.915, found 1803.912 [M+H]<sup>+</sup>.

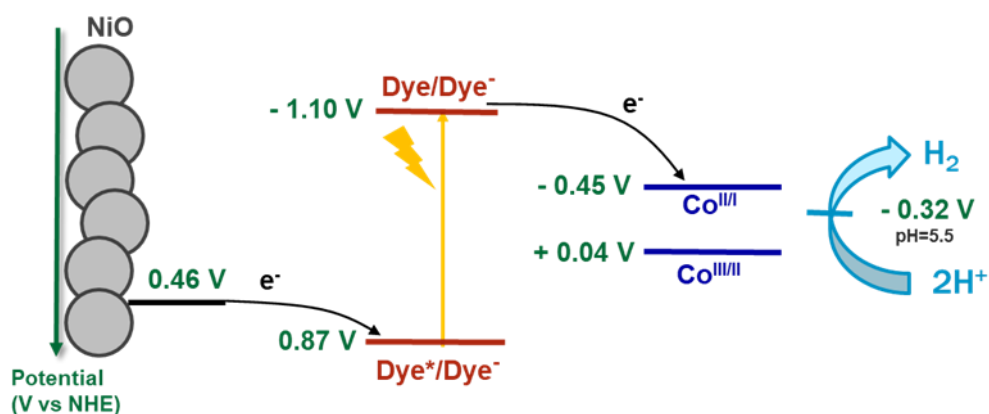
**Synthesis of <sup>t</sup>BuAM1-Cu:** Compound <sup>t</sup>BuAM1-alkyne (100 mg, 55 μmol, 1 eq) and [Cu(DO)(DOH)N<sub>3</sub>pn(OH<sub>2</sub>)](ClO<sub>4</sub>) (28 mg, 61 μmol, 1.1 eq) were dissolved in dichloromethane (3mL). A solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (4 mg, 15 μmol, 0.3 eq) and sodium ascorbate (10 mg, 46 μmol, 0.9 eq) in water was added. Methanol was added to obtain a homogeneous solution. Reaction mixture was stirred at 25°C for a 24h. Solvent was removed *in vacuo* and crude was dissolved in dichloromethane. Organic phase was washed with 1M ammonium chloride solution, water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated *in vacuo*. **HR-MS** (ESI+): *m/z* calculated for C<sub>130</sub>H<sub>147</sub>N<sub>12</sub>O<sub>7</sub>S<sub>3</sub>Cu 2146.997, found 2146.997 [M – ClO<sub>4</sub> - H<sub>2</sub>O]<sup>+</sup>.

**Synthesis of <sup>t</sup>BuAM1-Co:** Compound <sup>t</sup>BuAM1-Cu (100 mg, 46 μmol, 1 eq) was dissolved in 3 mL of DCM. A solution of CoBr<sub>2</sub>·2H<sub>2</sub>O (97 mg, 370 μmol, 8 eq) in 3 mL of acetone was added and the reaction mixture was stirred at 25 °C in open air for 2 days. The mixture was extracted with dichloromethane, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> then concentrated *in vacuo*. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz): δ (ppm) = 19.36 (s, 1H) ; 8.44 – 7.37 (m, 18H) ; 7.30 – 7.06 (m, 22H) ; 5.78 (s, 1H) ; 4.65 (m, 1H) ; 4.51 (m, 4H) ; 3.55 (m, 12H) ; 2.56 (m, 8H) ; 1.56 (m, 26H) ; 1.29 (m, 40H) ; 0.87 (m, 12H). **HR-MS** (MALDI-TOF): *m/z* calculated for C<sub>130</sub>H<sub>147</sub>N<sub>12</sub>O<sub>7</sub>S<sub>3</sub>CoBr<sub>2</sub> 2300.845, found 2300.841 [M+H]<sup>+</sup>.

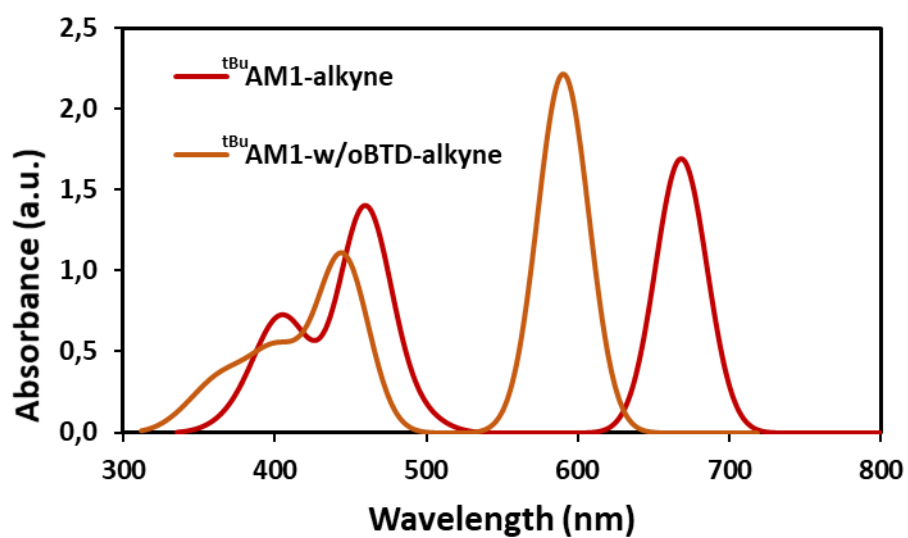
The <sup>1</sup>H NMR performed in THF-d<sub>8</sub> of the compound <sup>t</sup>BuAM1-Co in Figure S5 shows the characteristic signal of the hydrogen atom present on the bridge of the diamine-dioxime complex at 19.36 ppm.<sup>12</sup> The signal from 8.44 to 7.37 ppm corresponds to one part of the aromatics protons, the other part, from 7.30 to 7.06 corresponds to the 16 protons of the penyl of the IDT unit and the 6 protons closest to the nitrogen atom of the TPA. The signals at 4.65 and 4.51 ppm should correspond to the sp<sup>3</sup> carbons between the triazole ring and the diimine functions.

**Synthesis of AM1-Co:** Compound <sup>tbu</sup>AM1-Co (25 mg, 11 μmol, 1 eq) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) and trifluoroacetic acid (42 μL, 55 μmol, 50 eq) was added to the solution. The mixture was stirred at 25 °C for 6 hours then evaporated to dryness. The solid was dissolved in tetrahydrofuran and washed with water. Organic layers were dried under vacuum to obtain **AM1-Co** as pure product (purple solid, **21 mg, 9.6 μmol, 89%**). <sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz): δ (ppm) = 19.45 (s, 1H) ; 8.40 (s, 1H) ; 8.34 (d, J = 8.7 Hz, 2H) ; 8.31 (s, 1H) ; 8.20 (d, J = 8.7 Hz, 1H) ; 8.16 (d, J = 5.6 Hz, 1H) ; 8.13 (s, 1H) ; 8.01 (d, J = 7.6 Hz, 1H) ; 7.95 (d, J = 8.6 Hz, 4H) ; 7.72 (s, 1H) ; 7.68 (m, 3H) ; 7.49 (s, 1H) ; 7.35 – 7.25 (m, 8H) ; 7.21 – 7.06 (m, 15H) ; 5.91 (t, J = 11.5 Hz, 1H) ; 4.69 (m, 4H) ; 4.58 (m, 1H) ; (4.06 (t, J = 11.5, 2H) ; 3.68 – 3.55 (m, 12H) ; 2.57 (m, 8H) ; 1.62 (m, 8H) ; 1.33 (m, 40H) ; 0.91 (m, 12H). **MS** (MALDI-TOF): *m/z* calculated for C<sub>122</sub>H<sub>131</sub>N<sub>12</sub>O<sub>7</sub>S<sub>3</sub>CoBr<sub>2</sub> 2189.720, found 2030.5 [M-2Br]<sup>+</sup>, *m/z* calculated for C<sub>122</sub>H<sub>131</sub>N<sub>12</sub>O<sub>7</sub>S<sub>3</sub>Co 2030.8. (Note: The two bromide atoms are removed and the singly-charge molecule is observed during the measurements. This was previously observed in the literature for ruthenium complexes with the same cobalt catalyst<sup>14</sup>).

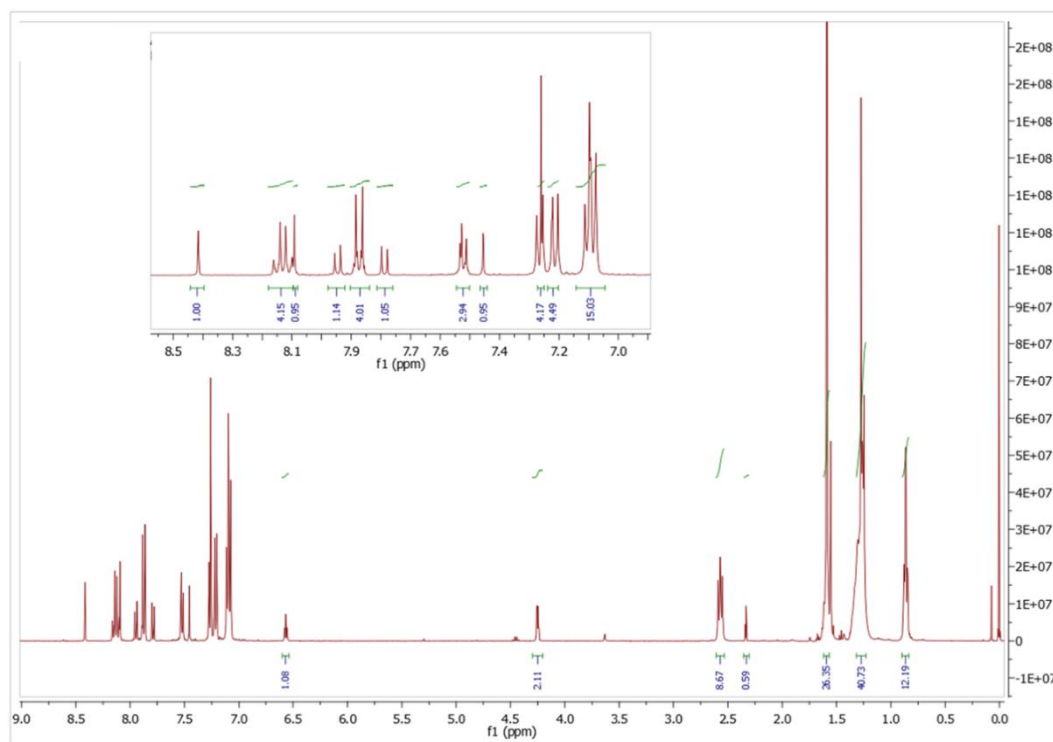
The <sup>1</sup>H NMR performed in THF-d<sub>8</sub> of the compound **AM1-Co** in figure S7 shows the characteristic signal of the hydrogen atom present on the bridge of the diamine-dioxime complex at 19.36 ppm.<sup>12</sup> Besides, comparing the signals at 2.55 ppm, 1.59 ppm and 0.90 ppm with the ones of <sup>tbu</sup>AM1-alkyne (figure S3), it appears that the signal at 1.59 ppm integrates only for 8 protons instead of 26 in the <sup>tbu</sup>AM1-alkyne spectrum. This 18 protons difference comes from the two *tert*-butylester hydrolysis giving the proof that the carboxylic acids were obtained.



**Figure S1:** Energy diagram of the **AM1-Co**-sensitized NiO photocathode at pH 5.5. The NiO valence band edge potential was estimated from the 0.37 V vs NHE value previously reported at pH 7.<sup>15</sup> The values of the potentials were calculated by cyclic voltammetry (See Figures S9 and S10 and Table 1).

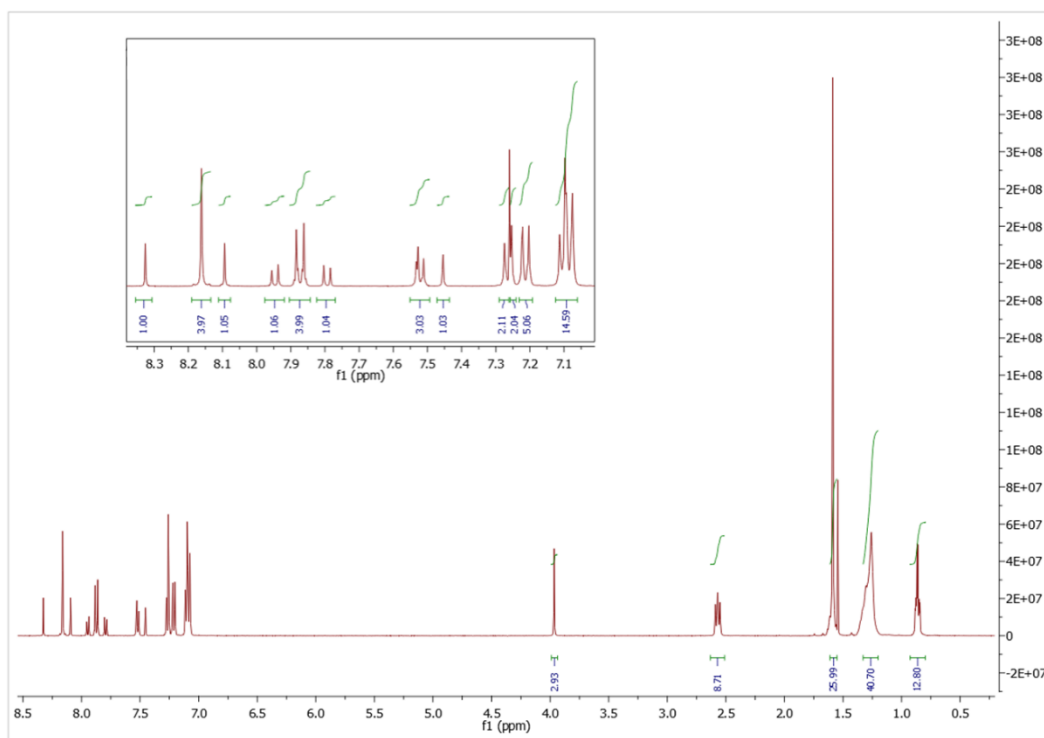


**Figure S2:** Simulated absorption spectra of BTD-Based and BTD-free dyes from the PBE0 single-points after geometry optimisation with RevPBE functional

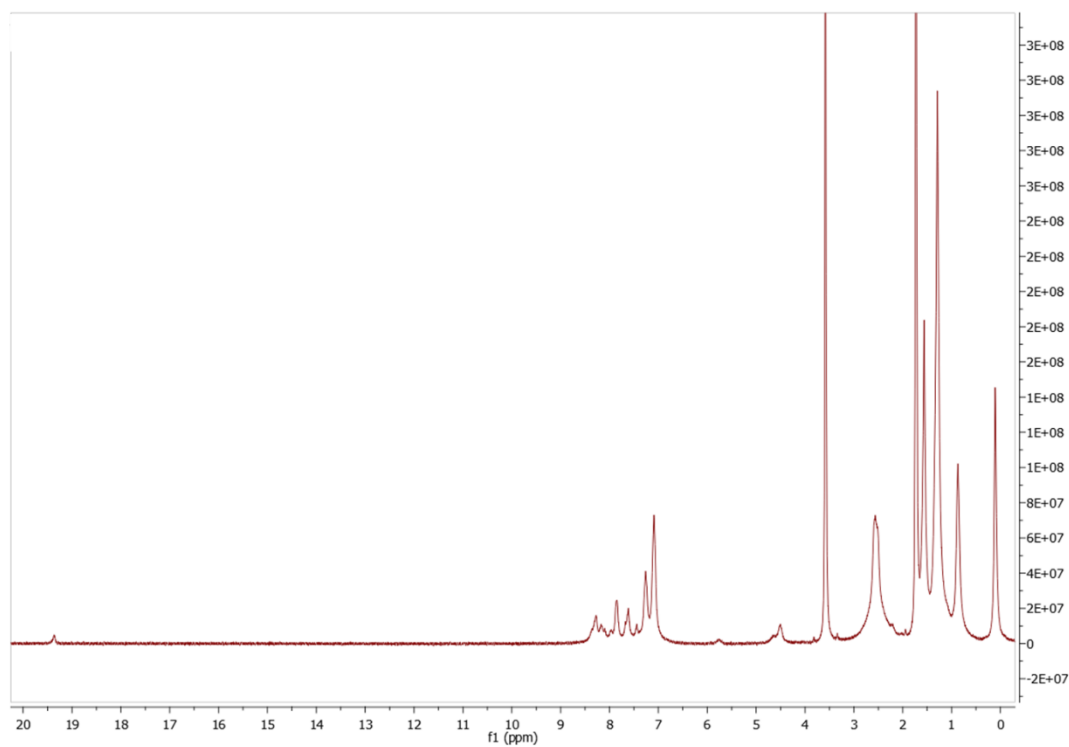


**Figure S3:**  $^1\text{H}$  NMR (400 MHz) spectrum of compound  $^{\text{tBu}}\text{AM1-alkyne}$  recorded in  $\text{CDCl}_3$  at  $25^\circ\text{C}$

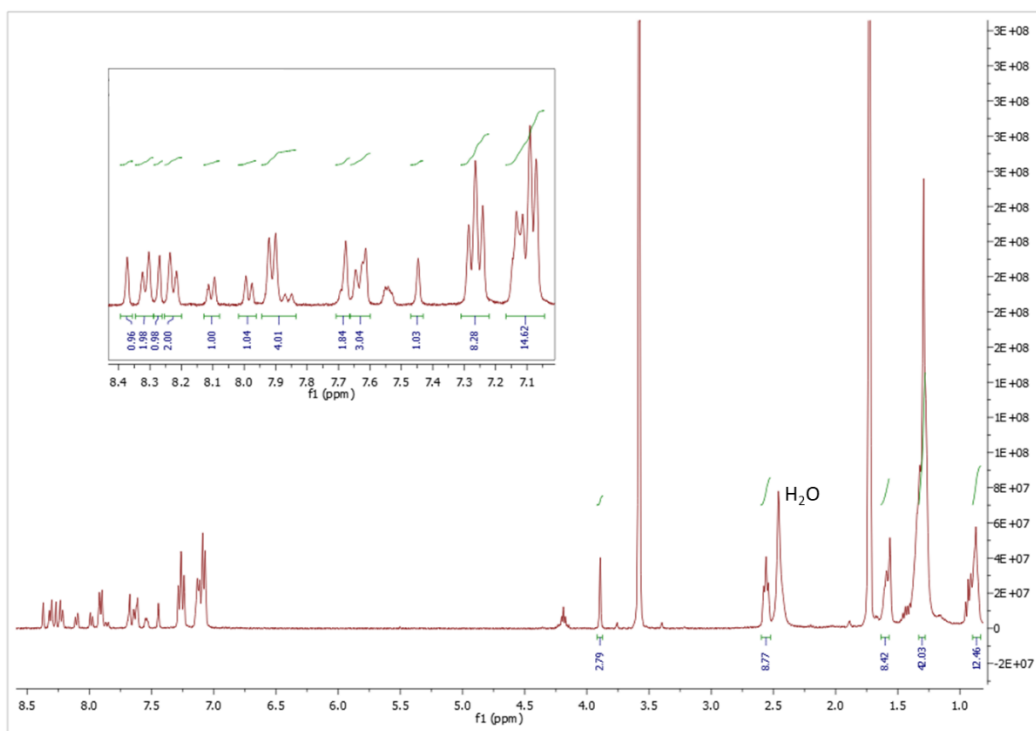




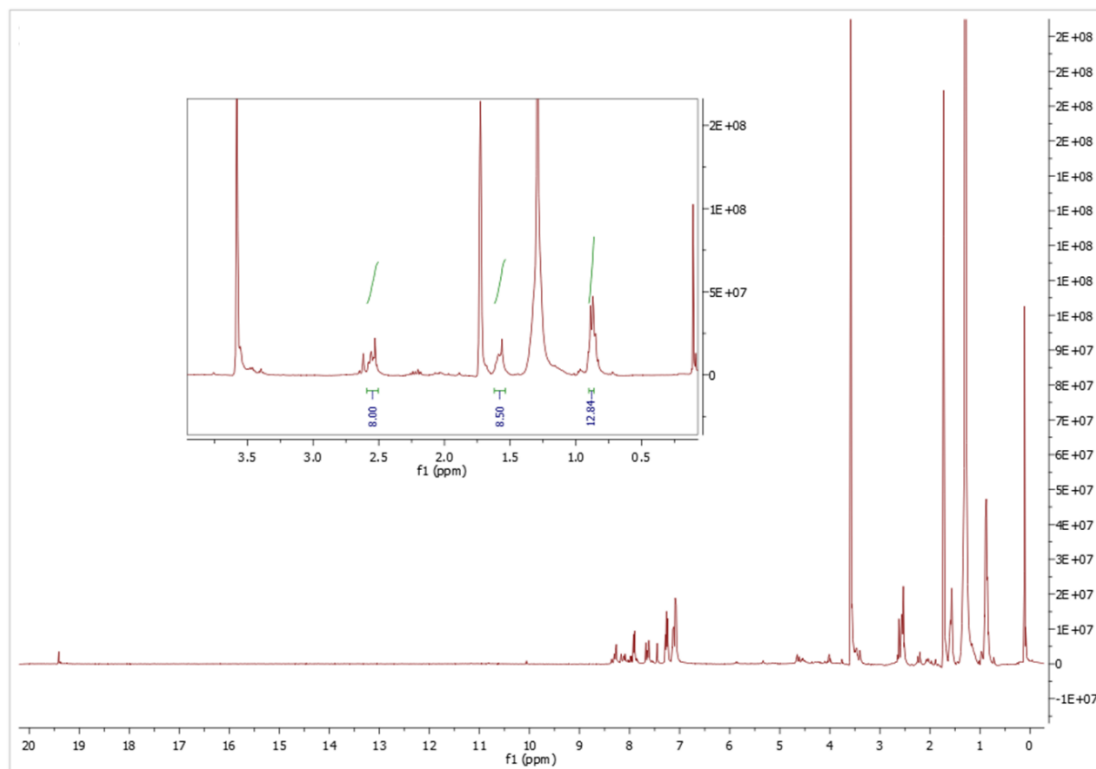
**Figure S4:**  $^1\text{H}$  NMR (400 MHz) spectrum of compound  $^t\text{BuAM1-OMe}$  recorded in  $\text{CDCl}_3$  at  $25^\circ\text{C}$



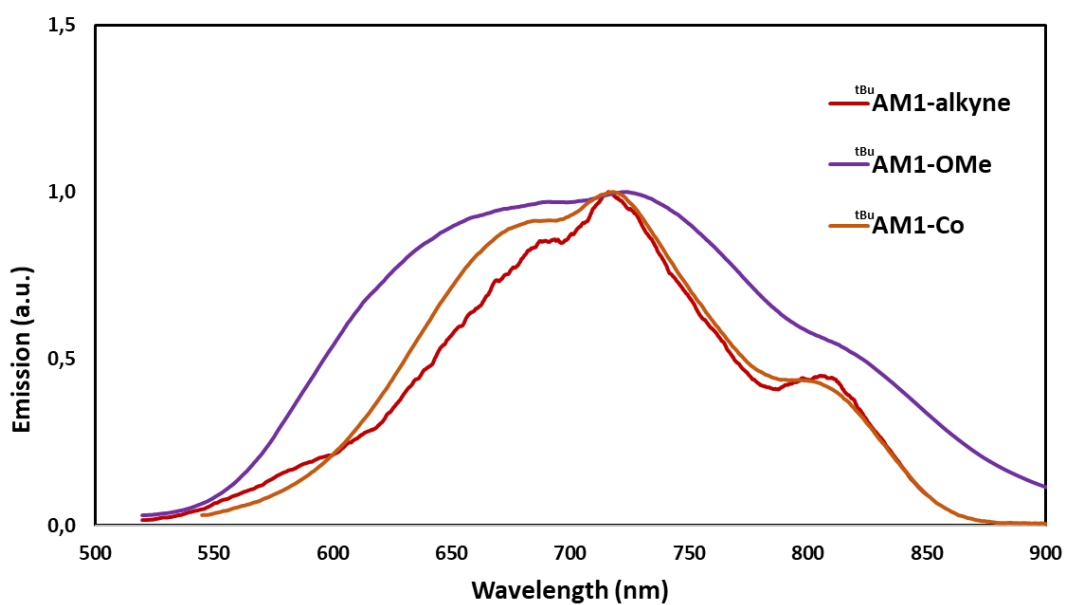
**Figure S5:**  $^1\text{H}$  NMR (400 MHz) spectrum of compound  $^t\text{BuAM1-Co}$  recorded in  $\text{THF-d}_8$  at  $25^\circ\text{C}$



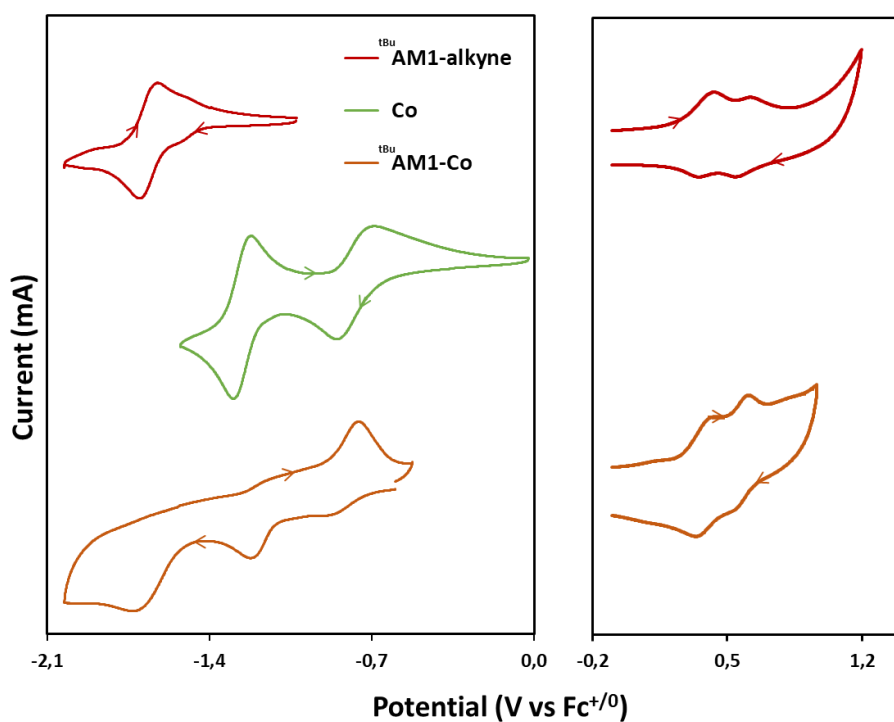
**Figure S6:**  $^1\text{H}$  NMR (400 MHz) spectrum of compound **AM1-OMe** recorded in  $\text{THF-d}_8$  at  $25^\circ\text{C}$



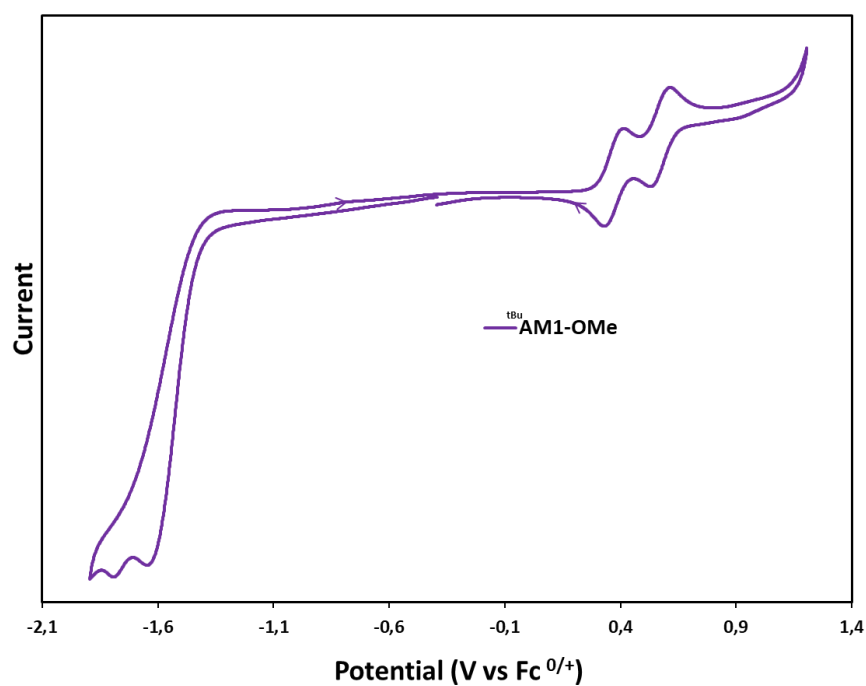
**Figure S7:**  $^1\text{H}$  NMR (400 MHz) spectrum of compound **AM1-Co** recorded in  $\text{THF-d}_8$  at  $25^\circ\text{C}$



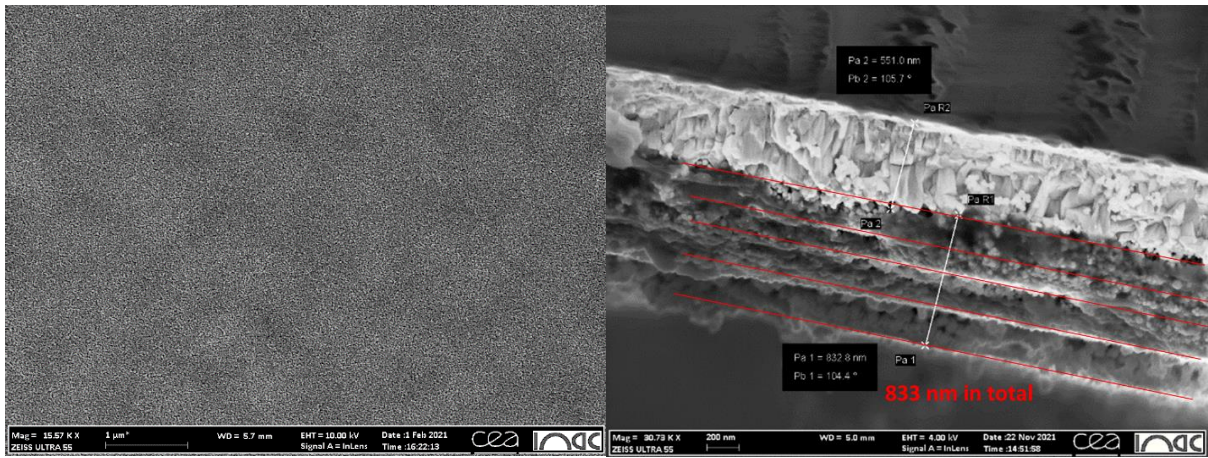
**Figure S8:** Emission spectra of the <sup>t</sup>BuAM1-alkyne (red trace), <sup>t</sup>BuAM1-OMe (purple trace) dyes and <sup>t</sup>BuAM1-Co dyad (orange trace) recorded in DCM at 25°C with an excitation wavelength of 510 nm.



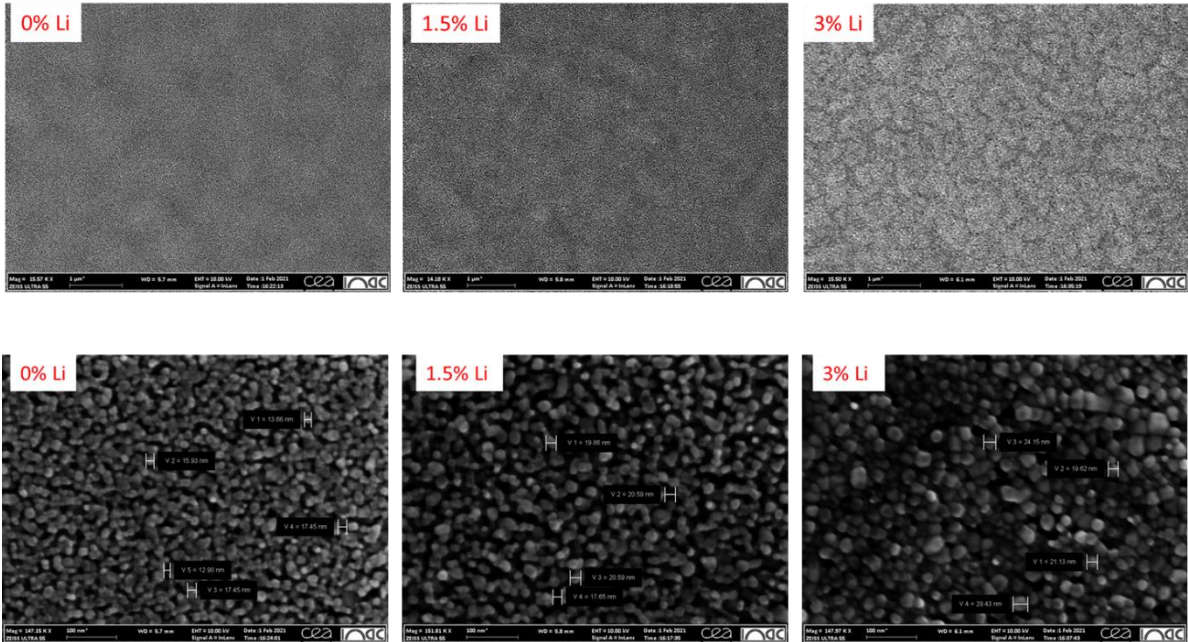
**Figure S9:** Cyclic voltammetry traces of the <sup>t</sup>BuAM1-alkyne (red trace), Co (green trace) catalyst and <sup>t</sup>BuAM1-Co dyad (orange trace). Measurements were carried out at 50 mV.s<sup>-1</sup> at a Pt electrode in dichloromethane (0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>) at 25 °C for oxidation (right window) and in DMF (0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>) at 25 °C for reduction (left window).



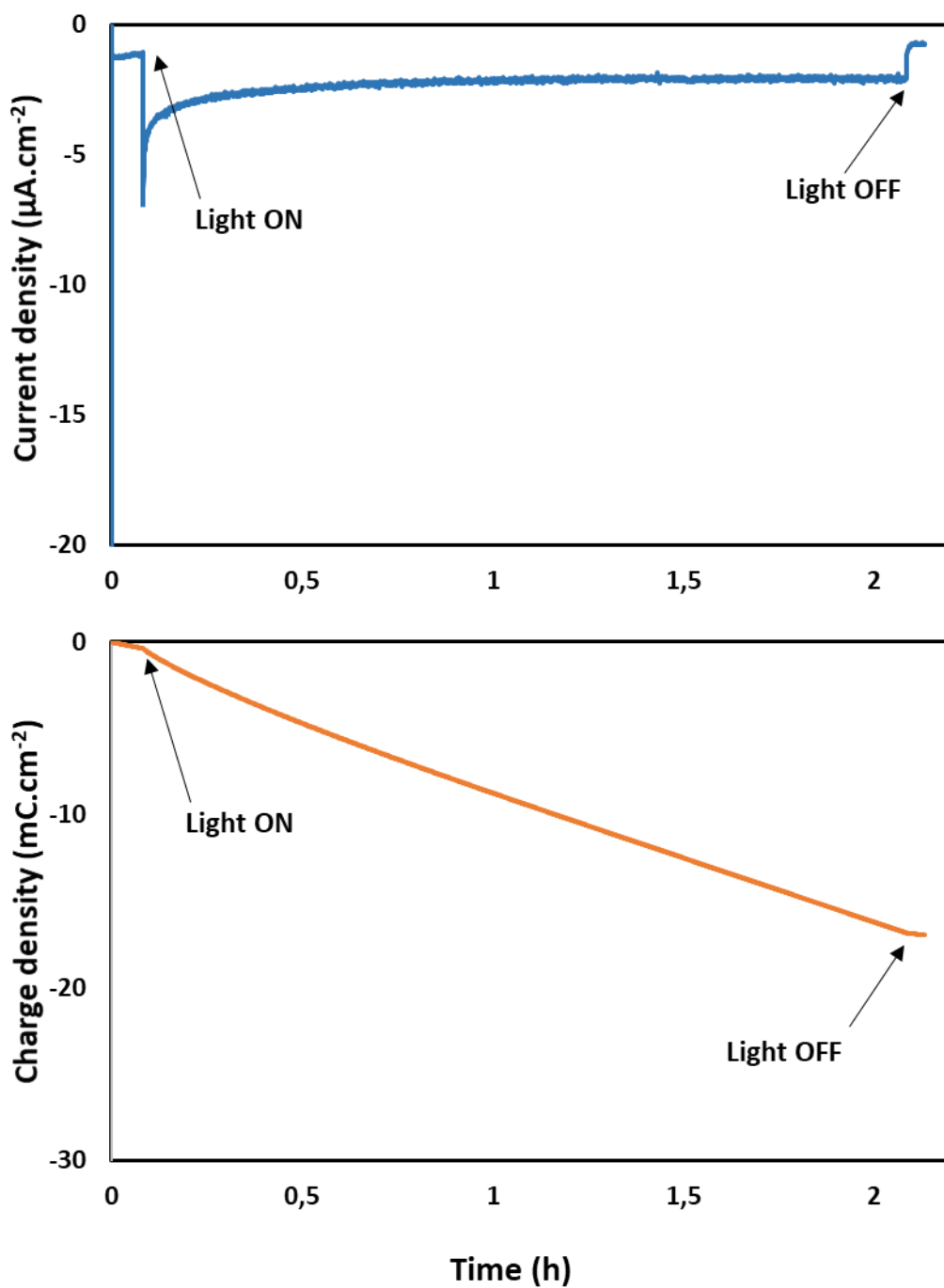
**Figure S10:** Cyclic voltammetry traces of the <sup>t</sup>BuAM1-OMe (purple trace) dye recorded at 50 mV.s<sup>-1</sup> at a Pt electrode in dichloromethane (0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>) at 25 °C.



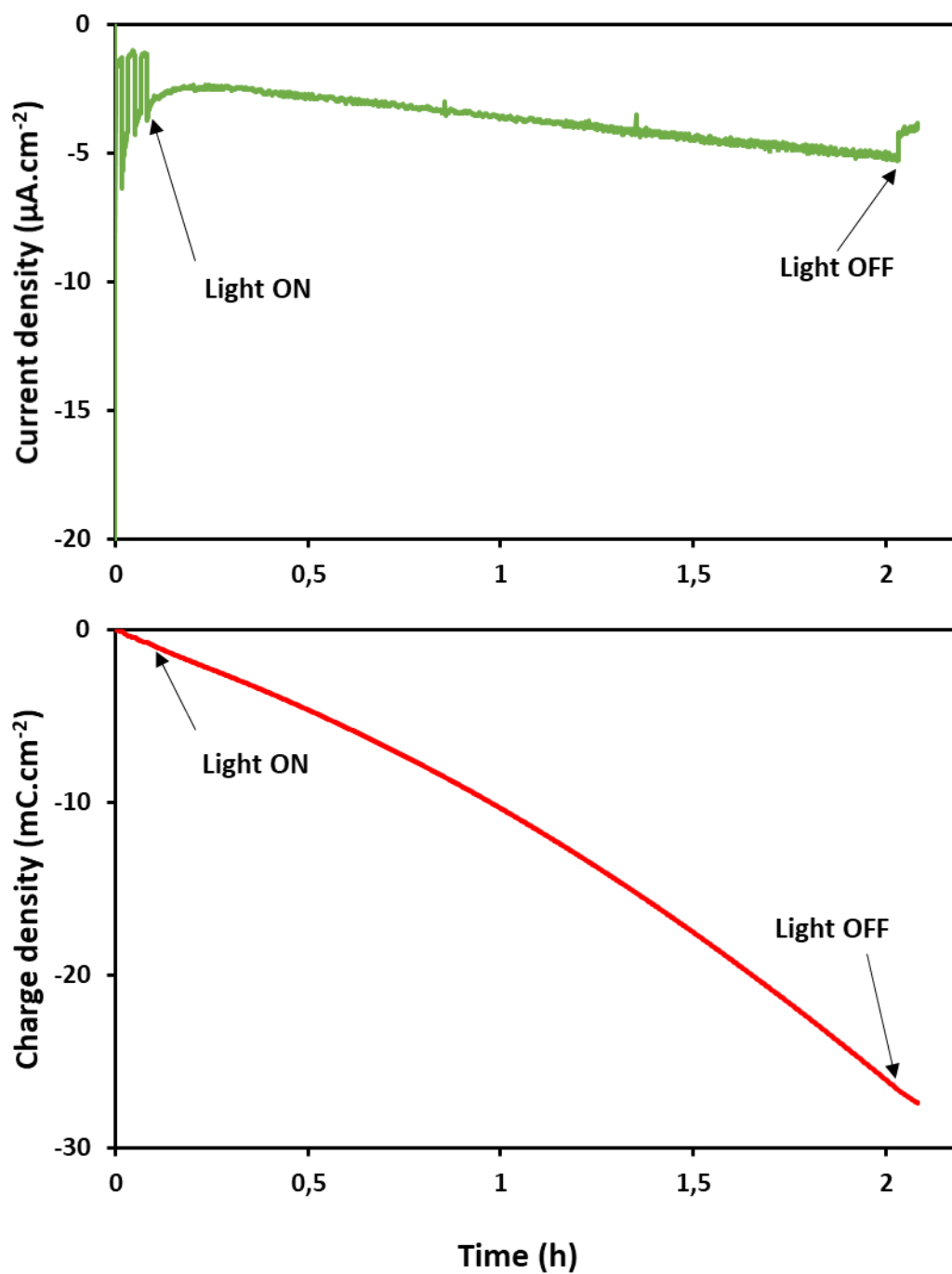
**Figure S11:** SEM images from the NiO films surface (left) and of a cross-section of a NiO film (4 layers) (right) on FTO-coated glass.



**Figure S12:** SEM images from the NiO films surface at various Li-doping concentration. Bottom images show the particles sizes.

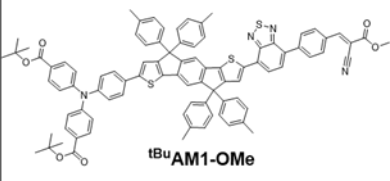
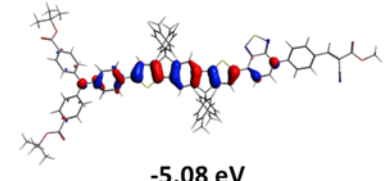
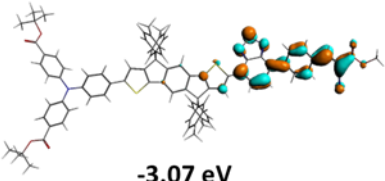
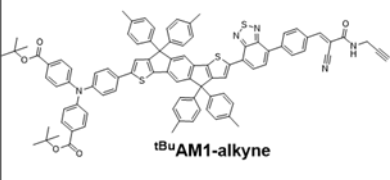
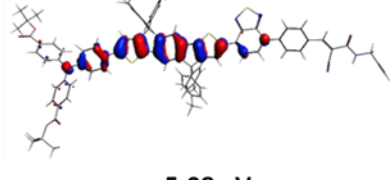
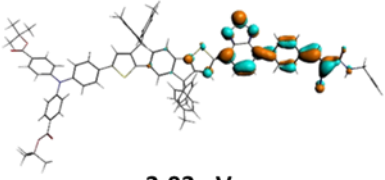
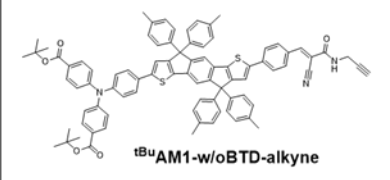
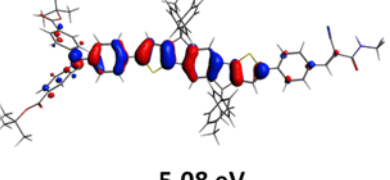
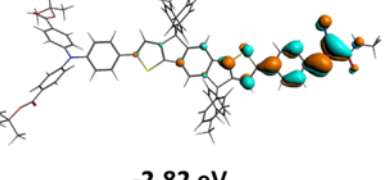


**Figure S13** : Photocurrent density (top) and corresponding charge density (bottom) recorded during the course of two-hour chronoamperometric measurements under continuous light irradiation at an applied potential of + 0.14 V vs RHE on a **AM1-Co**-sensitized NiO electrode. Irradiation conditions: visible light (400-800 nm).



**Figure S14:** Photocurrent density (top) and corresponding charge density (bottom) recorded during the course of two-hour chronoamperometric measurements under continuous light irradiation at an applied potential of + 0.14 V vs RHE on a **AM1-Co**-sensitized 1.5% Li-doped NiO electrode. Irradiation conditions: visible light (400-800 nm).

**Table S1:** HOMO and LUMO localization for the dyes from the B3LYP single-points after geometry optimisation with RevPBE functional.

Molecular structure	HOMO	LUMO
 <p>tBuAM1-OMe</p>	 <p>-5.08 eV</p>	 <p>-3.07 eV</p>
 <p>tBuAM1-alkyne</p>	 <p>-5.08 eV</p>	 <p>-3.03 eV</p>
 <p>tBuAM1-w/oBTD-alkyne</p>	 <p>-5.08 eV</p>	 <p>-2.82 eV</p>

**Table S2:** Electronic conductivity measurement of NiO mesoporous films at different lithium concentration recorded with a Four-Point Probe.

Percentage of lithium doping	0%	1.5%	3%
Measure 1	1.7	24.1	32.3
Measure 2	8.1	26.9	54.8
Measure 3	2.4	15.4	52.3
Measure 4	3.1	23.9	61.0
Measure 5	2.7	27.2	89.1
Average conductivity ( $S \cdot m^{-1}$ )	$3.6 \pm 2.6$	$23.5 \pm 4.8$	$57.9 \pm 20.5$



**Table S3:** Particle size of NiO mesoporous films at different lithium concentration determined by SEM.

<b>Pourcentage of lithium doping</b>	<b>0%</b>	<b>1.5%</b>	<b>3%</b>
Measure 1	15.9	19.9	24.2
Measure 2	13.7	20.6	19.6
Measure 3	17.5	20.6	21.1
Measure 4	12.9	17.7	29.4
Measure 5	17.5	-	-
<b>Average particle size (nm)</b>	<b>15.5 ± 2.2</b>	<b>19.7 ± 1.4</b>	<b>23.6 ± 4.3</b>

**Table S4:** Figures of merit determined from the photoelectrochemical (PEC) measurements (continuous irradiation for 2 hours; MES buffer, pH 5.5; applied potential: +0.14 V vs RHE): dyad/dye loading, amount of H<sub>2</sub> produced, charge passed, faradaic efficiency (F.E.) and turnover numbers (TON<sub>Co</sub>).

Photocathode	NiO layer thickness (nm)	Dyad/dye loading (nmol.cm <sup>-2</sup> )	H <sub>2</sub> in the headspace (nmol.cm <sup>-2</sup> )	Charge passed (mC.cm <sup>-2</sup> )	F.E. (%)	TON <sub>Co</sub>
NiO <sup>1</sup>			<b>1 ± 1</b>	<b>3 ± 1</b>	<b>5 ± 2</b>	
NiO   <b>AM1-OMe</b>	930 ± 80	3.0	18 <sup>2</sup>	25	14	
	950 ± 80	5.5	19 <sup>2</sup>	17	21	
NiO-Li 1.5%   <b>AM1-OMe</b>	825 ± 60	2.8	26 <sup>2</sup>	13	40	
	N.D.	3	5 <sup>2</sup>	8	14	
NiO   <b>AM1-Co</b>	850 ± 60	N.D.	41	36	22	N.D.
	1100 ± 100	3.0	86	104	16	30
	N.D.	3.0	19	10	38	6
	780 ± 50	1.3	13	15	16	10
	800 ± 60	5.5	12	14	17	3
	830 ± 70	4.4	18	17	21	4
NiO-Li 1.5%   <b>AM1-Co</b>	950 ± 80	1.7	31	27	22	19
	1000 ± 100	0.6	27	26	20	45

1. From already reported measurements.<sup>14</sup>

2. A plausible explanation for this photoelectrochemical hydrogen production activity might be the light-driven reduction of electrically disconnected NiO particles, forming Ni(0) catalytic sites as previously observed for a related push-pull dye sensitized NiO photocathode.<sup>16</sup>

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