Electronic Supplementary information for

A Covalent Cobalt Diimine-Dioxime – Fullerene Assembly for Photoelectrochemical Hydrogen Production from Near-Neutral Aqueous Media

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Materials and methods

Chemical used and general characterization methods and equipments.

All chemical reagents used in this study were of analytical grade and were used as received without further purification Anhydrous $NiCl_2$ and Pluronic F108 polymer were purchased from Strem Chemicals and Sigma-Aldrich, respectively. Poly(3-hexylthiophene) (P3HT, M102, 95.7% RR) was purchased from from Ossila, UK, [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM >99.5%) was purchased from Solenne BV, The Netherlands and 2,9-dimethyl-4,7-diphenyl-1,10-phenantroline (BCP) was purchased from Luminescence Technology Corp, Taiwan. Other chemical reagents were purchased from Sigma-Aldrich and used as received. Whenever needed, solvents were dried from appropriate drying agents (calcium hydride for CH_2Cl_2 and CH_3CN, 4Å molecular sieves for methanol and sodium clippings for toluene) and freshly distilled under argon before use. $(DOH)_2pnN_3$(**5**) was synthesized as previously described.[1] The preparation of $[Cu(DO)(DOH)N_3pn]ClO_4$ (**4**) was adapted from a reported procedure,[2] using $(DOH)_2pnN_3$ instead of $(DOH)_2pn$. Unless otherwise specified crude mixtures were purified via flash column chromatography on an automated Puriflash 450 setup (Interchim, Lyon, France) on normal phase silica (regular particles SI-HP, 30 µm), using dry loading deposition technique (dry load on celite® 545). FTO-coated glass substrates (20 mm × 40 mm × 1.1 mm; 80 $\Omega \cdot sq^{-1}$) were obtained from Solems, France.

^1H NMR spectra were recorded at 298 K in 5 mm o.d. tubes on a Bruker Avance 300 spectrometer equipped with a QNP probe head operating at 300.0 MHz. Chemical shift values are given in ppm with reference to solvent residual signals. FTIR spectra were recorded on an Perkin-Elmer Spectrum100 spectrometer equipped with a Pike MIRacle single reflection ATR module using a Germanium prism. UV-Visible spectra were recorded on an Agilent Cary 60 UV-Visible Spectrometer. Melting point measurements were carried on a Büchi Melting Point B-540, using a gradient of 1 °C. min^{-1}. High resolution spectra (HRMS) were obtained on a Bruker MaXis ESI Q-TOF Mass Spectrometer by the "plateforme HRMS" (Insitiut de chime Organique et Anlytique, Université d'Orléans) and elemental analysis recorded on a Thermofisher Scientific "Flash 2000" by the "Plateforme d'analyse pour la chimie" (GDS 3648, Strasbourg).

Synthesis.

N-Methyl-2-(4'-ethynyl)phenyl-3,4-fulleropyrrolidine (nmep-pC$_{60}$): This protocol was adapted from ref. 3. A solution of 500 mg of C_{60} (0.693 mmol, 1 equivalent), 189.9 mg of 4-ethynylbenzaldehyde (1.39 mmol, 2 equivalents) and 630 mg of sarcosine (6.93 mmol, 10 equivalents) in 300 ml of toluene was refluxed for 3 hours then the solvent was removed under reduced pressure. The purification was performed by flash column chromatography on silica, using cyclohexane and toluene as solvents. After complete elution of unreacted C_{60} by cyclohexane, the product was eluted by a 1:1 mixture of cyclohexane and toluene. The desired compound was obtained as the first brown band. Following bands corresponded to the products resulting from multiple cyclo-addition reactions. After evaporation of the solvent, the desired product was obtained as a brown powder. Yield: 302.5g (0.35 mmol, 50%). FTIR (cm^{-1}): 2194 ($C\equiv C$), 1461 (C—H pyrrolidine), 1430 (C—H Pyrrolidine). ^1H NMR (300 MHz, $CDCl_3/CS_2$ 1/1): 7.85 (d, 2H), 7.58 (d, 2H), 5.10 (d, 1H), 5.07 (s, 1H), 4.34 (d, 1H), 3.10 (s, 1H), 2.88 (s, 3H). HRMS (ESI-MS): *m/z* calc. for $C_{71}H_{12}N$ 878.0964 $[M+H]^+$, found 878.0952. mp: > 350 °C.

Synthesis of 3: 54 µl N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, 0.226 mmol, 0.2 equivalent) was introduced in 10 mL oxygen-free CH_3OH, then 33.0 mg CuBr (0.226 mmol, 0.2 equivalent) was added under argon. The mixture was stirred and immediately after the complete dissolution of CuBr, it was added to a solution of 500 mg [Cu(DO)(DOH)N_3pnClO_4] (1.13 mmol, 1 equivalent) and 181.6mg 4-ethynylbenzaldehyde (1.35 mmol, 1.2 equivalents) in 140 ml of oxygen-free CH_3OH. The mixture was stirred for 3h at 50°C under argon. The solvent was evaporated in vacuum and the residue was purified by flash chromatography on silica using CH_3CN:KNO_3 10% saturated in water (95:5) as eluent. The product was eluted as the second band. The solvent was removed under reduced pressure, and the crude material was suspended in acetone. The excess KNO_3 was filtered off, washed with acetone, and the solvent was evaporated to yield the desired product as a dark red powder. Two subsequent columns were necessary to obtain the desired compound as a pure product. Yield: 610mg (1.13mol, 94%). FTIR (cm^{-1}): 1695 (C=O), 1611, 1520 (C=N Cu(DO)(DOH)pn), 1454 (N=N). HRMS (ESI-MS): *m/z* calc. for $C_{20}H_{24}CuN_7O_3$ 473.1231 $[M- ClO_4]^+$, found 473.1231. mp: degradation > 185 °C.

Synthesis of 2: 610 mg of ***3*** (1.06 mmol, 1 equivalent) and 698 mg of $CoBr_2$ (3.19 mmol, 3 equivalents) were dissolved in 200 ml acetone. The mixture was stirred for 3h while bubbling air. The solvent was removed under reduced pressure to afford a crude solid, which was washed with H_2O and diethyl ether. The filtrate was dried under vacuum to remove the diethyl ether then extracted with ethyl acetate. The crude solid was purified by column chromatography on silica using acetone as the solvent. The desired product was collected as the second band yielding a light green powder after the evaporation of the solvent. Yield: 522 mg (0.88 mmol, 83%). FTIR (cm^{-1}): 1688 (C=O), 1610, 1507 (C=N Co(DO)(DOH)pn), 1453 (N=N). ^1H NMR (300 MHz, DMSO-d_6): 19.31 (s, 1H, H_9), 10.05 (s, 1H, H_1), 9.26 (s, 1H, H_4), 8.15 (d, *J* = 9 Hz, 2H, H_2), 8.06 (d, *J* = 9 Hz, 2H, H_3), 5.82 – 5.74 (m, 1H, H_5), 4.84 – 4.80 (m, 2H, $H_6/H_{6'}$), 4.54 – 4.44 (m, 2H, $H_6/H_{6'}$), 2.71 (s, 6H, H_7/H_8), 2.56(s, 6H, H_7/H_8). ^{13}C NMR (75.5 Mhz, DMSO-d_6): 193.06, 177.70, 157.26, 145.86, 136.66, 135.99, 130.94, 126.01, 123.71, 58.29, 54.75, 18.49, 14.01. HRMS (ESI-MS): *m/z* calc. for $C_{20}H_{25}Br_2CoN_7O_3$ 627.9712 $[M+H]^+$, found 627.9720. Elem.Anal.: calc. for $C_{20}H_{24}Br_2CoN_7O_3$: C 38.18, H 3.84, N 15.58; found: C 38.60, H 3.95, N 15.34. mp: degradation > 312 °C.

Synthesis of 1: 507.6 mg of C_{60} (0.704 mmol, 1.2 equivalents), 369 mg of **2** (0.586 mmol, 1 equivalent) and 538.6 mg of sarcosine (5.86 mmol, 10 equivalents) were suspended in an oxygen-free mixture of 1.5L of toluene:1,2-dichloroethane 2:1. The mixture was stirred under reflux for 4h under argon. After removal of the solvent under reduced pressure, the crude mixture was purified by flash column chromatography with a gradient of cyclohexane:toluene and then of toluene:acetone. **1** was obtained as the third band as a brown powder. Yield: 121 mg (0.088 mmol,15%). Due to the poor solubility of the compound in most solvent only ^1H NMR could be recorded under diluted conditions. FTIR (cm^{-1}): 1513 (C=N Co(DO)(DOH)pn), 1461 (C–H pyrrolidine), 1453 (N=N), 1430 (C–H pyrrolidine). ^1H NMR (300 MHz, CD_2Cl_2): 19.29 (s, 1H, H_9), 8.09 – 8.01 (m, 5H, $H_{2\text{-}4}$), 5.98 – 5.90 (m, 1H, H_5), 5.16 (br s, 1H, H_1), 4.77 – 4.69 (m, 2H, $H_6/H_{6'}$), 4.60 – 4.55 (m, 2H, $H_6/H_{6'}$), 4.42 – 4.38 (m, 1H, $H_{10}/H_{10'}$), 3.72 (br s, 1H, $H_{10}/H_{10'}$), 2.94 (s, 3H, H_{11}), 2.63 (s, 12H, $H_{7\text{-}8}$). HRMS (ESI-MS): calc. for $C_{82}H_{30}Br_2CoN_8O_2$ 1375.0184 $[M+H]^+$; found, 1375.0177. Elem. Anal.: calc. for $C_{82}H_{29}Br_2CoN_8O_2$: C 71.53, H 2.12, N 8.14; found: C 69.74, H 2.57, N 9.03. mp: > 350 °C.

Electrochemical measurements

Electrochemical measurements were carried out with a *Biologic VSP 300* potentiostat in a 3-electrode cell, using a glassy carbon electrode (1.6 mm or 3 mm diameter), a Pt wire and a Ag/AgCl/3M KCl reference electrode. 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 or a leakless Ag/AgCl (ET072, eDAQ). The supporting electrolyte was 0.1 M nBu_4NBF_4 in dry CH_3CN (or a CH_3CN/1,2-dichlorobenzene 1:1 (v/v) solvent mixture). The supporting electrolyte was degassed with a flow of N_2 at least for 5 min before the measurements and a N_2 blanket was kept above the solution for the duration of the experiment. 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 ferrocene in the supporting electrolyte. The potential of the Fc/Fc$^+$ couple is 0.52V vs Ag/AgCl in CH_3CN/1,2-dichlorobenzene 1:1 (v/v) mixture and 0.47V vs Ag/AgCl in CH_3CN. Taking into account junction potentials, the potential of the Fc$^+$/Fc couple in CH_3CN is measured at +0.53 V vs NHE or +0.80 V vs RHE at pH 4.6.[4] The conditions used for the CV and DPV measurements are indicated in the corresponding figure captions.

The position of the different energy levels of the components of solid-state heterojunctions in Figure 1 are reported against vacuum. We used the following formula to calculate the estimated "absolute" mid-wave potential for the catalysis:

$$E_{cat}^{abs}(V) = E^{abs}(SHE) + E°(Fc^+/Fc) + E^{1/2}_{cat} = 4.66\ V$$

where E_{cat}^{abs} is the estimated "absolute" mid-wave potential for the catalysis, $E_{abs}(SHE) = 4.77$ V vs vacuum the absolute potential of the standard hydrogen electrode in acetonitrile recently recalculated by Busch et al.,[5] E(Fc$^+$/Fc) = +0.53 V vs SHE in acetonitrile, and $E^{1/2}_{cat} = -0.62$ V vs Fc$^+$/Fc measured in acetonitrile (Figure 3).

Electrochemical study of ***1*** *deposited on the electrode*.

A solution of 5 mg of **1** in 1 ml of 1,2-dichlorobenzene was prepared. Then, 1 µl of this solution was deposited onto a glassy carbon disk (0.07 cm^2, catalyst loading of 52±1 nmol·cm^{-2}). After drying, the working electrode modified with **1** was used in a standard three-electrode electrochemical cell configuration. Electrochemical measurements were carried out in CH_3CN (with 0.1 M of n-Bu_4NBF_4 supporting electrolyte) in the absence and in the presence of p-cyanoanilinium tetrafluoroborate (10 mM). The electrochemical experiments have been performed using a leakless Ag/AgCl reference electrode.

Photoelectrochemical measurements

Photoelectrochemical measurements were carried out in sodium acetate buffer electrolyte (0.1 M, pH 4.5) in a standard three-electrode configuration in a specific glass cell. A Ti wire and a Ag/AgCl, KCl (3M) were used as the counter and reference (Ref.) electrodes, respectively. All potentials reported have been referred to the reversible hydrogen electrode (RHE): E(V vs RHE)=E(V vs Ref.) +E(V of Ref. vs NHE)+0.059 × pH. The fabricated photocathodes were used as working electrode, clamped to the cell, so that only the catalyst side of the photocathodes was interfaced with the electrolyte. The surface of working electrode in contact with the electrolyte was 0.50 cm². Photoelectrodes were back-illuminated with a 300 W ozone-free xenon lamp

(Newport) operated at 280 W coupled to a water-filled Spectra-Physics 6123NS liquid filter for elimination of IR radiation and a Spectra-Physics 59472 UV cut-off filter (λ>400 nm). Irradiance at the substrate surface was measured to 65 $mW.cm^{-2}$ (corresponding to 1 sun) using the Newport power-meter. The electrolyte was degassed prior measurements under a N_2 flow. Linear scan voltammograms (LSVs) have been recorded in under light on, light off and under chopped light at a scan rate of 5 $mV\cdot s^{-1}$. Chronoamperometry (CA) measurements were performed at 0.065 V vs RHE with chopped light for 10 min. CA measurements at 0.065 V vs RHE under light coupled with gas chromatography measurements (PerkinElmer Clarus 500 gas chromatograph) were used to determine the faradic hydrogen production efficiency of each photocathode. The faradaic efficiency for hydrogen production is calculated according to the equation: $\eta_F(\%) = [(\text{mols of } H_2 \times 2F)/Q]\times100$, where F is the Faraday constant (96485 $C\cdot mol^{-1}$) and Q is the charged passing through the electrode. The action spectra of the films were recorded at 0.065 V vs RHE using Asahi spectra band pass filters (FWHM 10 nm) centered at 400, 450, 500, 550, 600, 650, and 700 nm. The intensity of the photocurrent was recorded under continuous illumination and the value obtained after equilibration for 150 s was used for the calculations. Incident photon to charge efficiency (IPCE) values were calculated at 400, 450, 500, 550, 600, 650, and 700 nm using the following equation: $\text{IPCE}(\%) = [(1240/\lambda_{ex})(I_{light}\text{-}I_{dark})/P_{light}] \times 100$ where λ_{ex} and P_{light} are the center wavelength of the band pass filter and power density of the incident light (nm and $mW.cm^{-2}$), respectively, I_{light} the current density under irradiation ($mA.cm^{-2}$), and I_{dark} the current density in the dark.[6] For each band pass filter the power density of the light (P_{light}) was measured using a Newport power meter (model 1918-R) equipped with a silicon Detector (model 918D-UV-OD3R) used with the attenuator on.

Photoelectrode fabrication

Cleaning of the substrates. FTO-coated glass substrates were placed in a sample holder and cleaned through (i) sonication for 15 minutes in an aqueous detergent solution (Gigapur 10 %), (ii) rinsing twice with deionized water, (iii) sonication for 10 min in deionized water, (iv) rinsing with ethanol, (v) sonication for 15 min in ethanol and (vi) 15 min treatment in a UV-ozone cleaner.

Synthesis and deposition of NiO thin films. 1.5 g of anhydrous $NiCl_2$ and 1.5 g of Pluronic F108 polymer were dissolved in a mixture of 4.5 ml of deionized water and 11.2 ml of ethanol.[7] The resulting viscous solution was sonicated overnight, and then centrifuged for 30 min at 5000 rpm. After centrifugation, the supernatant was collected for deposition by spin-coating onto FTO-coated glass substrates. The solution was spin-coated in two steps (3000 rpm/30 s and 5000 rpm/30 s). Two layers were deposited, each followed by immediate annealing at 100 °C for 2 min in air (on a hot plate). Finally, the substrates were then annealed at 450 °C in air for 30 min (450°C/ramp: 30 min/dwelling time: 30 min/cooling down to RT) allowing the formation of the NiO hole-transport layer.

Deposition of P3HT:PCBM BHJ. The P3HT:PCBM weight ratio used was 1:1 for a total concentration of 25 mg·ml^{-1} of each material (25 mg P3HT and 25 mg PCBM in 1 ml of anhydrous 1,2-dichlorobenzene). The solution prepared in the glovebox is stirred 2 h at 55 °C, then overnight at room temperature and 1 h at 55 °C prior deposition. The solution is spin-coated in the glovebox (500 rpm/10 s and then 1500 rpm/50 s). A polyvinylidene fluoride filter (PVDF, 45 µm) is used to remove particles. Contact is cleaned with a cotton bud and 1,2-dichlorobenzene. Annealing is carried out at 140 °C for 5 min in the glovebox. The substrates were transferred out of the glove box only after the catalyst deposition and just before the photoelectrochemical measurements.

*Deposition of [P3HT:PCBM+**1**] BHJ*. A solution of 4 mg of **1**/1 ml of 1,2-dichlorobenzene was prepared in the glove-box and added to 0.5 ml solution of P3HT:PCBM. The P3HT:PCBM weight ratio used was 1:1 for a total concentration of 25 mg·ml^{-1} of each material (25 mg P3HT and 25 mg PCBM in 1 ml of anhydrous 1,2-dichlorobenzene). The as-prepared solution of P3HT:PCBM in the glovebox is stirred 2 h at 55 °C, then overnight at room temperature before mixing with the solution of **1**. Then, 500 µl of the final solution deposited onto the whole surface of the substrate, was spin-coated (500 rpm/10 s and then 1500 rpm/50 s). Annealing is carried out at 100 °C for 10 min in the glove box.

Figure S1a. Selected region (2300 cm^{-1} – 1300 cm^{-1}) of the FTIR spectra of **1**, **nmep-C60**, and **2** and partial attribution of significant absorption bands.

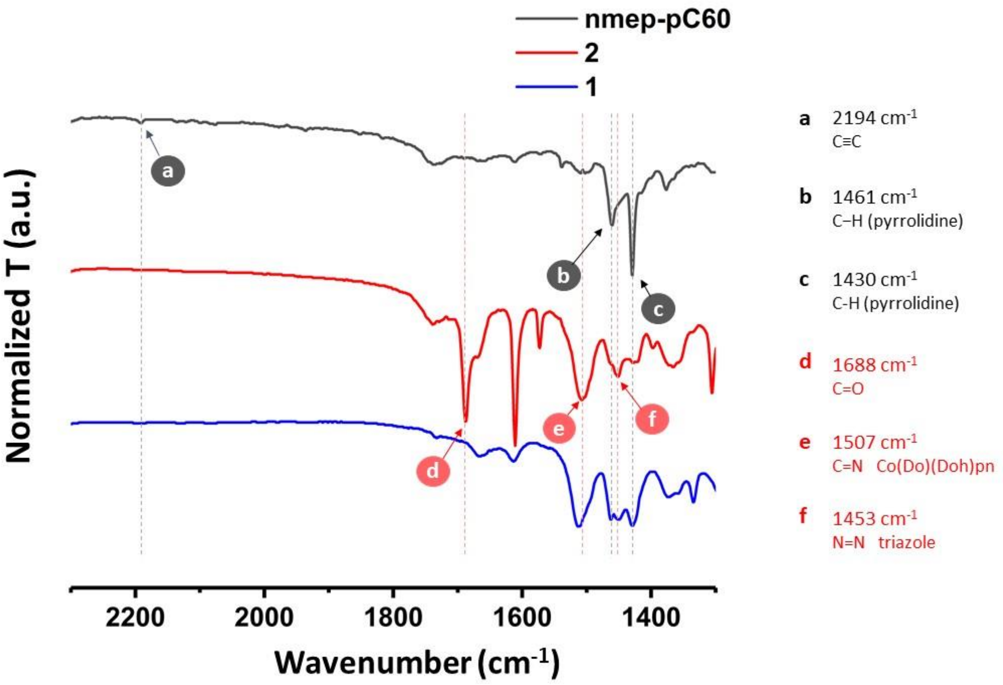


Figure S1b. Comparison between the FTIR spectra of **1** and the compound described by as given by Tian *et al*. The spectrum form Tian *et al*. was digitalized from the data published in the original article using WebPlotDigitizer 4.4 (https://apps.automeris.io/wpd/). The digitalized spectra was calibrated according to the spectral window given by the authors.

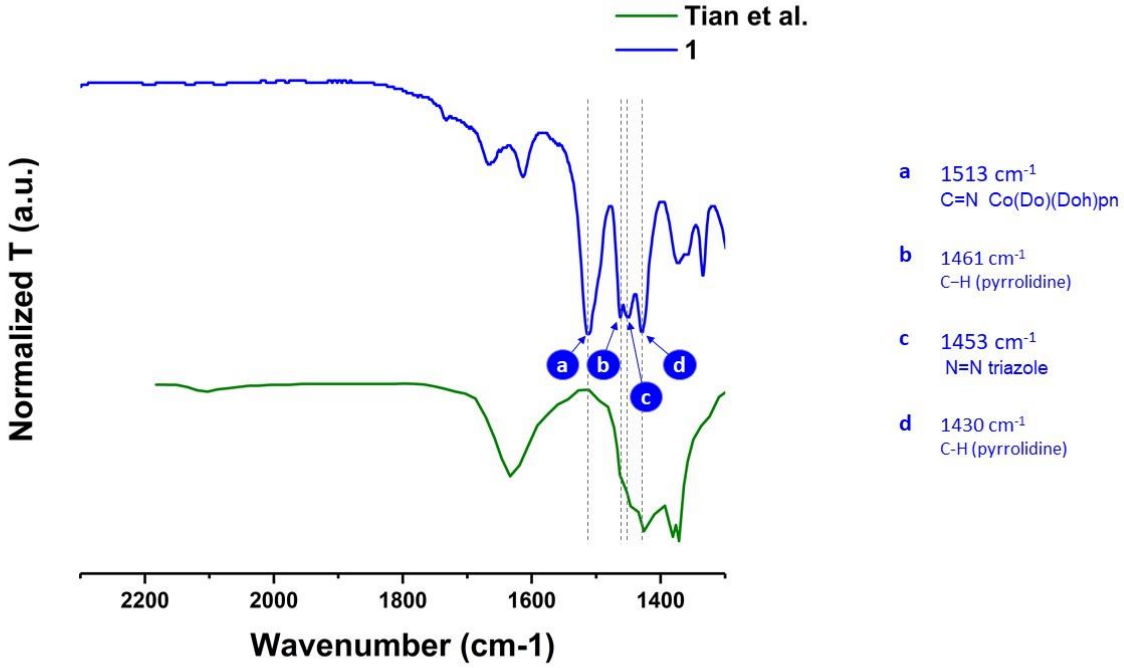


Figure S2a. ^{1}H NMR (300 MHz) spectra for compound **2** recorded in DMSO-d$_6$ at 25 °C and assignation of residual trace solvents.

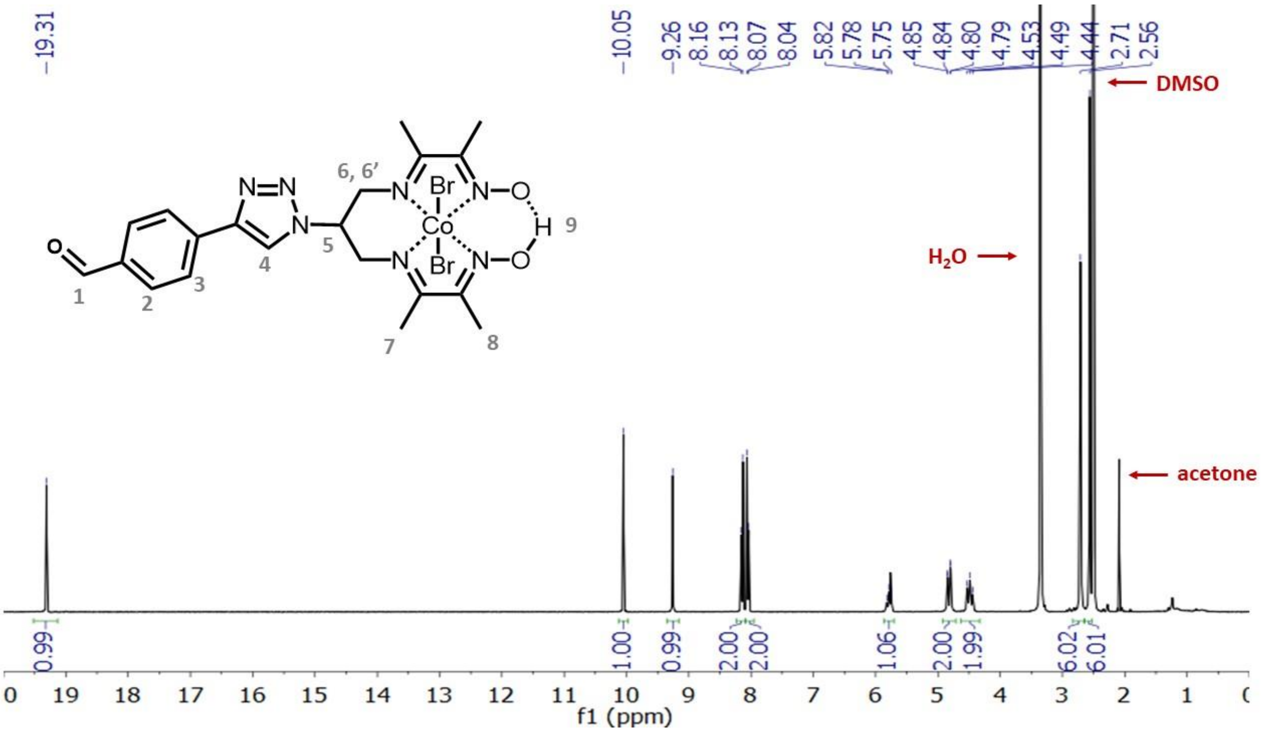


Figure S2b. ^{13}C NMR spectra for compound **2** recorded in DMSO-d$_6$ at 25 °C and assignation of residual trace solvent.

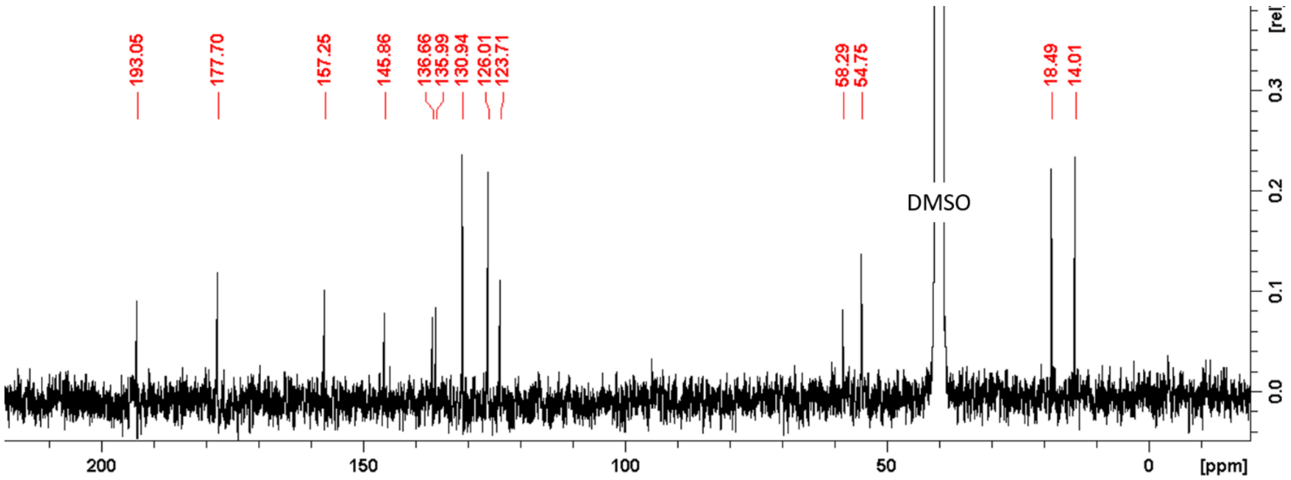


Figure S3. ^{1}H NMR (300 MHz) spectra for compound **1** recorded in CD_2Cl_2 at 20 °C, top full spectral range (20 ppm – 0 ppm), bottom 8.5 ppm - 2 ppm. Residual solvents are indicated in red.

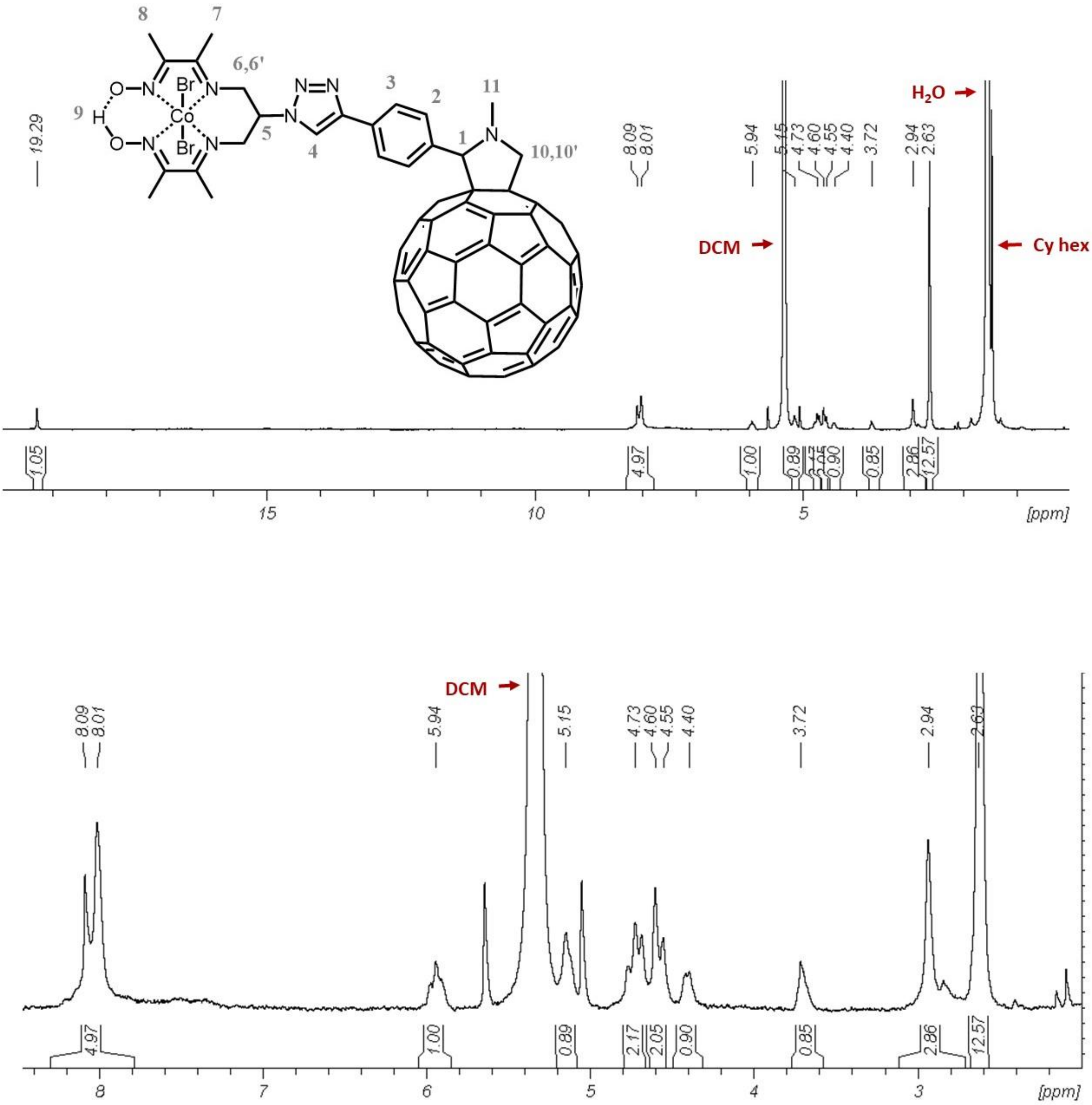


Figure S4. Differential pulse (cathodic scan, parameters: P_{Height} = 10 mV, P_{Width} = 50 ms, S_{Height} = -1 mV, S_T = 200 ms) voltammograms of **1** and **2** (0.3 mM) recorded at a glassy carbon electrode (ϕ 1.6 mm) in a 0.1 M n-Bu_4NBF_4 solution in CH_3CN/1,2-dichlorobenzene 1:1 (v/v), under N_2.

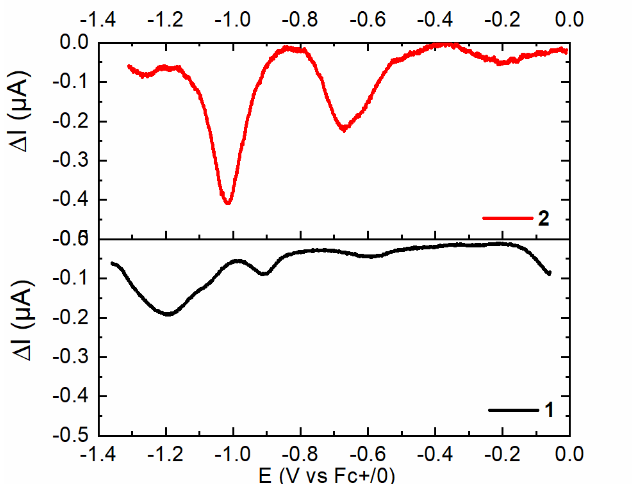


Figure S5. LSV for GC electrode (ø 3 mm) modified (red) or not (black) with compound **1** (52 ± 1 nmol.cm^{-2}) recorded at 10 mV.s^{-1} in acetate buffer (0.1 M, pH 4.5).

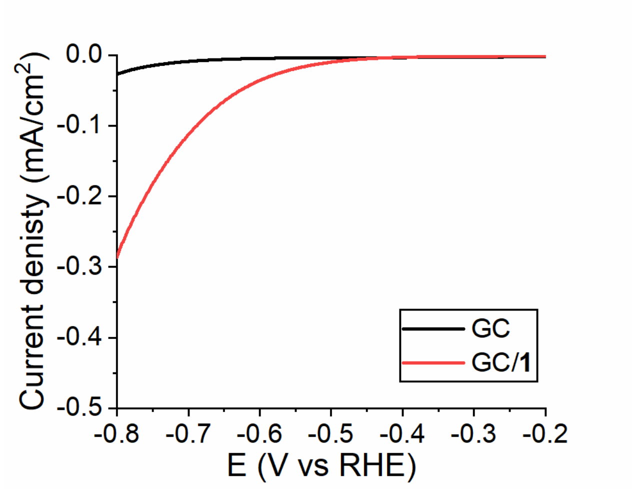
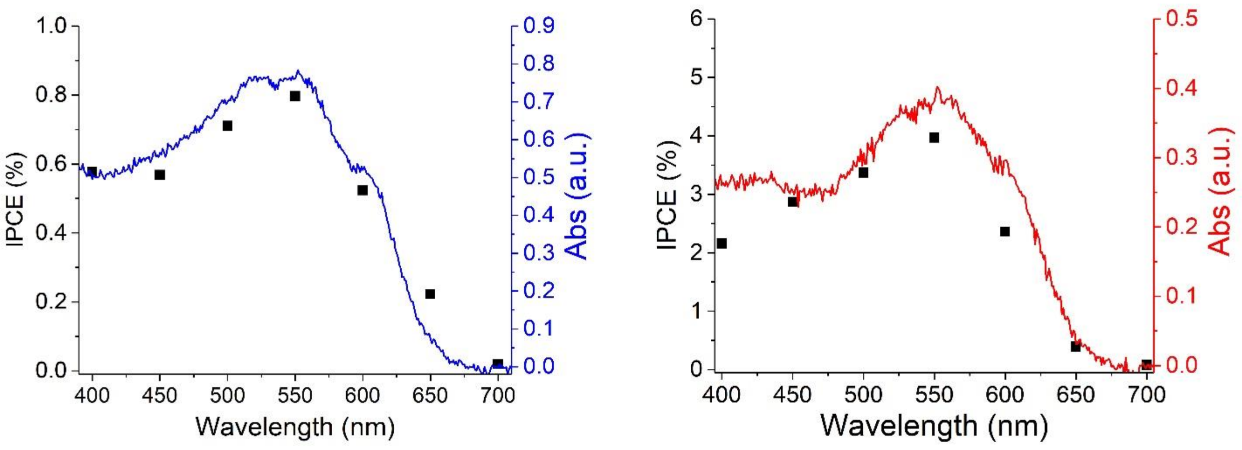
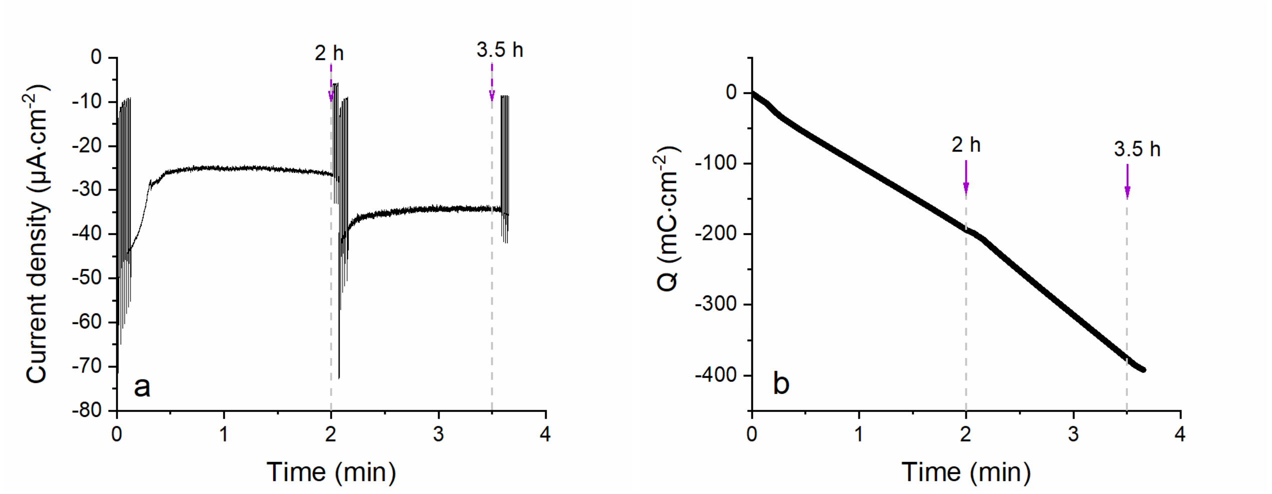


Figure S6. UV-Vis absorption spectra and action spectra for FTO/NiO/[P3HT:PCBM] (left) and FTO/NiO/[P3HT:PCBM+1] (right) assemblies. The action spectra where obtained at an applied potential of 0.065 V vs RHE in 0.1 M acetate buffer (pH 4.5) using band-pass filters centered at 400, 450, 500, 550, 600, 650, and 700 nm.



Figures S7. Photocurrent (a) and charge (b) density measured at an applied potential of 0.065 V vs RHE in 0.1 M acetate buffer (pH 4.5) for FTO/NiO/[P3HT:PCBM+**1**] electrode.



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