# Supporting information materials for

# Chemistry on the electrodes: post-functionalization and stability enhancement of anchored dyes on mesoporous metal oxide photoelectrochemical cells with copper-free Huisgen cycloaddition reaction

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## 1) General methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on an *AVANCE 300 MHz BRUKER*, *AVANCE III* 400 *MHz BRUKER*. Chemical shifts for <sup>1</sup>H NMR spectra are calibrated on residual protons in the deuterated solvent (**CDCl**<sub>3</sub>  $\delta$  = 7.26 ppm for <sup>1</sup>H and  $\delta$  = 77.16 ppm for <sup>13</sup>C; **CD**<sub>3</sub>**OD**  $\delta$  = 3.31 ppm for <sup>1</sup>H and  $\delta$  = 49.00 ppm for <sup>13</sup>C; **CD**<sub>3</sub>**CN**  $\delta$  = 1.94 ppm for <sup>1</sup>H and  $\delta$  = 1.32 ppm for <sup>13</sup>C; **CD**<sub>6</sub>**SO**  $\delta$  = 2.50 ppm for <sup>1</sup>H and  $\delta$  = 39.52 ppm for <sup>13</sup>C). Spectra were recorded at room temperature, chemical shifts are given in ppm and coupling constants in Hz.

High-resolution mass spectra (HRMS) were obtained either by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific) or by MALDI-TOF (Autoflex III, Bruker), both working in ion-positive mode or ion negative mode and with 2,5-dihydroxybenzoic acid (DHB) or dithranol matrix. Static ToF-SIMS spectra were acquired in negative mode using a ToF-SIMS IV instrument from ION-TOF GmbH. An Ar<sup>+</sup>10 keV ion beam was used as analysis beam at a current of 2 pA, and rastered over a scan area of  $300\times300 \ \mu\text{m}^2$ . Several different locations (up to 5) on the surface were accounted for ensuring the reproducibility of the results. For each spectrum, the mass scale was calibrated by using well-identified ions, namely H<sup>-</sup>, C<sup>-</sup>, CH<sup>-</sup>, CH<sub>2</sub><sup>-</sup>, O<sup>-</sup>, OH<sup>-</sup>, C<sub>2</sub><sup>-</sup> and C<sub>2</sub>H<sup>-</sup>.

Electrochemical measurements were performed with a potentiostat-galvanostat *Autolab PGSTAT 302N* controlled by resident GPES software (General Purpose Electrochemical System 4.9) or NOVA software using a conventional single-compartment three-electrodes cell. The working electrode was a glassy carbon one. The auxiliary electrode was a stainless wire and the reference one was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N Bu<sub>4</sub>NPF<sub>6</sub> in DCM or CD<sub>3</sub>CN and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the presented experiments the scan rate was 100 mV/s.

UV-Visible absorption spectra were recorded on a *UV-2401PC Shimadzu* spectrophotometer using 1 cm path length cells. Emission spectra were recorded on a *SPEX Fluoromax-4 Jobin Yvon* fluorimeter (1 cm quartz cells). Emission spectra are corrected in near-infrared part.

The ultrafast transient absorption setup was described in ref. 1. Excitation was performed at 530 nm using the output of an optical parametric amplifier (TOPAS Prime) pumped at 800 nm using part of the output of a Ti:Sapphire amplified system (Spectra Physics, Solstice Ace). The irradiance on the samples was ca. 0.2 mJ cm<sup>-2</sup>. The polarization of the pump pulses was set to magic angle relative to the probe pulses. Probing was achieved using white-light pulses generated by focusing 800 nm pulses into a CaF<sub>2</sub> plate. The experimental arrangement was the same as that described in ref. 2 except that all lenses, after white light generation, were replaced by spherical mirrors to prevent chromatic aberration. The full width at half maximum of the instrument response function was below 130 fs. Before the TA measurements, the films were wetted with propylene carbonate and protected with a microscope cover slip. The samples were continuously moved laterally and vertically according

to Lissajoux functions to avoid prolonged irradiation of the same spot. No sample degradation was observed over the measurements.

# 2) Synthesis of the DPP dyes 1 and 2

Crosslinking agent **3**,<sup>3</sup> DPP **5**,<sup>4</sup> 4-(*tert*-butoxycarbonyl)phenylboronic acid pinacol ester **7**,<sup>5</sup> boronate **11**,<sup>6</sup> and benzyl-1,2,3-triazole -4-carboxylic acid methyl ester **15**<sup>7</sup> were prepared according to already published procedures. Chemical were purchased from Sigma-Aldrich, Alfa Aesar, Fluorochem or TCI Europe and used as received. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 nm mesh).



Scheme S1. Synthetic route to the DPP 1.



Scheme S2. Synthetic route to the DPP 2.





**DPP 5** (2 g, 4.48 mmol) and a few grains of molecular sieves were added to 25 mL of THF under argon atmosphere. A solution of 1,6-diiodohexane (7.38 mL, 44.8 mmol) in 5 mL of THF, cesium carbonate (7.3 g, 22.4 mmol) and dibenzo-21-crown-7 (181 mg, 0.448 mmol) were added, and the solution was stirred overnight at 70°C. The reactional mixture was evaporated and the crude product was extracted with dichloromethane. The organic phase was washed

with brine, dried over magnesium sulfate and evaporated. The crude product was purified by flash column chromatography (silica gel, petroleum ether/DCM, 3/1), affording the title product **6** as a red solid (1.26 g, 33%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{H}$  = 7.66 (s, 8H), 3.73 (t, 4H, <sup>3</sup>J = 7.5 Hz), 3.11 (t, 4H, <sup>3</sup>J = 6.9 Hz), 1.73 (q, 4H, <sup>3</sup>J = 7.5 Hz), 1.59-1.50 (m, 4H), 1,37-1.19 (m, 8H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_{C}$  = 162.4, 147.5, 132.4, 130.2, 126.9, 126.0, 110.0, 41.7, 33.2, 30.0, 29.3, 25.7, 6.8.

**MS-ESI(+):** m/z calculated for 886.8818 [M+Na]<sup>+</sup>; found 886.8807 [M+Na]<sup>+</sup>; Δ = 1.2 ppm.

# Synthesis of the DPP 7



**DPP 6** (200 mg, 0.231 mmol) and 4-(*tert*-butoxycarbonyl)phenylboronic acid pinacol ester **7** (35 mg, 0.115 mmol) were solubilized in 1 mL of THF and 1 mL of water. The solution was degassed by argon purging under sonication for 20 minutes. Potassium carbonate (48 mg, 0.346 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (6.7 mg, 5.78 µmol) were added and the mixture was stirred overnight at 80°C. After cooling to room temperature, the crude product was extracted with dichloromethane, washed with brine and dried over magnesium sulfate. The crude product was purified by flash column chromatography (silica gel, DCM) affording the title product **8** as a red solid (40 mg, 36%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_H$  = 8.09 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.91 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.78 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.72-7.66 (m, 6H), 3.78 (q, 4H, <sup>3</sup>J = 7.5 Hz), 3.11 (td, 4H, <sup>3</sup>J = 6.7 Hz, <sup>4</sup>J = 3.1 Hz), 1.74 (m, 4H), 1.62 (s, 9H), 1.60 (m, 4H), 1.31 (m, 8H).

<sup>13</sup>**C NMR (75 MHz, CDCl<sub>3</sub>):**  $\delta_c$  = 165.5, 162.7, 162.6, 148.3, 147.1, 143.7, 143.0, 132.4, 131.7, 130.2, 130.1, 129.3, 127.8, 127.6, 127.0, 125.9, 110.2, 110.0, 81.3, 41.9, 41.7, 33.2, 30.0, 29.3, 28.3, 25.7, 6.87, 6.82.

**MS-ESI(+):** m/z calculated for 985.0550 [M+Na]<sup>+</sup>; found 985.0552 [M+Na]<sup>+</sup>; Δ = 0.2 ppm.

## Synthesis of the DPP 9



**DPP 8** (40 mg, 41  $\mu$ mol) was solubilized in 3 mL of anhydrous DMF under argon atmosphere. Sodium azide (22 mg, 332  $\mu$ mol) was added and the solution was stirred overnight at 50°C. The major part of DMF was eliminated under reduced pressure with the rotary evaporator, then the mixture was diluted with dichloromethane and water and the two layers were separated. The organic phase was washed with water to remove DMF and dried over anhydrous magnesium sulfate. The crude product was purified by flash column chromatography (silica gel, DCM/petroleum ether, 1/1), affording the title product **9** as a red solid (33 mg, 99%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_H$  = 7.97 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.74 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.54 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.51-7.43 (m, 6H), 3.78 (q, 4H, <sup>3</sup>J = 7.5 Hz), 3.20 (td, 4H, <sup>3</sup>J = 6.8 Hz, <sup>4</sup>J = 2.9 Hz), 1.68-1.58 (m, 13H), 1.52 (m, 4H), 1.30 (m, 8H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_c$  = 165.5, 162.7, 162.6, 148.4, 147.1, 143.7, 143.0, 132.4, 131.7, 130.3, 130.2, 129.3, 127.8, 127.6, 127.0, 125.9, 110.2, 110.0, 81.3, 51.4, 41.9, 41.8, 29.4, 28.7, 28.3, 26.4, 26.3.

**MS-ESI(+):** m/z calculated for 793.2820 [M+H]<sup>+</sup>; found 793.2817 [M+H]<sup>+</sup>; Δ = 0.3 ppm.



**DPP 9** (28 mg, 35  $\mu$ mol) was solubilized in 2 mL of DCM and 2 mL of TFA. The mixture was stirred at room temperature for two hours and then solvents were evaporated, affording the

title product as a red solid (26 mg, 99%).

Synthesis of the DPP 1

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_H$  = 8.09 (d, 2H, <sup>3</sup>J = 8.2 Hz), 7.91 (d, 2H, <sup>3</sup>J = 8.2 Hz), 7.78 (d, 2H, <sup>3</sup>J = 8.2 Hz), 7.72-7.66 (m, 6H), 3.69 (m, 4H), 3.12 (td, 4H, <sup>3</sup>J = 8.0 Hz, <sup>3</sup>J = 7.0 Hz), 1.50-1.35 (m, 8H), 1.28-1.08 (m, 8H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $δ_c$  = 171.1, 162.4, 148.4, 147.3, 144.6, 142.2, 132.1, 130.8, 130.2, 129.5, 128.8, 127.7, 127.5, 126.8, 126.9, 126.8, 126.0, 109.9, 109.7, 51.3, 41.5, 41.4, 29.8, 29.2, 28.7, 26.3, 26.2.

**MS-ESI(-):** m/z calculated for 735.2043  $[M-H]^{-}$ ; found 735.2047  $[M-H]^{-}$ ;  $\Delta = 0.5$  ppm.

Synthesis of the DPP 12



In a sealed tube were added **DPP 6** (200 mg, 0.23 mmol) and boronate **11** (66 mg, 0.116 mmol). 7 mL of THF and 1 mL of distilled water were added. The solution was degassed by argon purging under sonication for 20 minutes. Potassium carbonate (48 mg, 0.23 mmol) and tetrakis(triphenylphosphine)palladium were added, and the mixture was stirred overnight at 80°C. The mixture was extracted with dichloromethane, washed with brine and dried over magnesium sulfate. The crude product was purified by flash column chromatography (silica gel, DCM/petroleum ether, 1/1), affording the title product as a red solid (54 mg, 38%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{H}$  = 7.93-7.86 (m, 6H), 7.75 (d, 2H, <sup>3</sup>J = 8.6 Hz), 7.68 (s, 4H), 7.60 (d, 2H, <sup>3</sup>J = 8.6 Hz), 7.21 (d, 2H, <sup>3</sup>J = 8.6 Hz), 7.17-7.09 (m, 4H), 3.78 (q, 4H, <sup>3</sup>J = 7.5 Hz), 3.11 (td, 4H, <sup>3</sup>J = 6.7 Hz, <sup>4</sup>J = 3.1 Hz), 1.75 (q, 4H, <sup>3</sup>J = 8.6 Hz), 1.67-1.53 (m, 22H), 1.31 (m, 8H).

<sup>13</sup>C NMR (**75** MHz, CDCl<sub>3</sub>):  $δ_c$  = 165.4, 162.7, 162.6, 150.7, 150.5, 148.7, 146.8, 146.6, 145.6, 143.1, 135.9, 132.4, 131.0, 130.9, 130.1, 129.3, 128.4, 128.1, 127.2, 127.1, 126.8, 126.7, 126.4, 126.3, 126.0, 125.8, 123.0, 122.7, 110.2, 109.8, 80.9, 80.8, 77.5, 77.1, 76.7, 41.9, 41.8, 33.2, 30.0, 29.3, 28.3, 25.7, 6.89, 6.83.

**MS-ESI(+):** m/z calculated for 1230.1990 [M+H]<sup>+</sup>; found 1230.1989 [M+H]<sup>+</sup>; Δ = 0.1 ppm.



**DPP 12** (62 mg, 50  $\mu$ mol) was solubilized in 2.5 mL of anhydrous DMF under argon atmosphere. Sodium azide (26 mg, 403  $\mu$ mol) was added and the solution was stirred overnight at 50°C. The major part of DMF was eliminated under reduced pressure with the rotary evaporator, then the mixture was diluted with dichloromethane and water and the two layers were separated. The organic phase was washed with water to remove DMF and dried over anhydrous magnesium sulfate. The crude product was purified by flash column chromatography (silica gel, DCM/petroleum ether, 3/1), affording the title product as a red solid (47 mg, 88%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{H}$  = 7.90 (m, 6H), 7.74 (d, 2H, <sup>3</sup>J = 8.5 Hz), 7.67 (s, 4H), 7.59 (d, 2H, <sup>3</sup>J = 8.7 Hz), 7.21 (d, 2H, <sup>3</sup>J = 8.7 Hz), 7.12 (m, 4H, <sup>3</sup>J = 8.7 Hz), 3.78 (q, 4H, <sup>3</sup>J = 8.4 Hz), 3.20 (td, 4H, <sup>3</sup>J = 6.8 Hz, <sup>4</sup>J = 2.8 Hz), 1.69-1.46 (m, 26H), 1.29 (m, 8H).

<sup>13</sup>**C** NMR (**75** MHz, CDCl<sub>3</sub>):  $\delta_c$  = 165.5, 162.8, 162.6, 150.7, 150.6, 148.7, 146.8, 146.6, 145.6, 143.2, 135.9, 132.4, 131.0, 130.9, 130.1, 129.3, 128.4, 128.1, 127.3, 127.1, 126.8, 126.7, 126.4, 126.3, 126.0, 125.8, 123.0, 122.7, 110.3, 109.8, 80.9, 51.4, 41.9, 41.8, 29.4, 28.8, 28.3, 26.4, 26.3.

**MS-ESI(+):** m/z calculated for 1059.4001 [M+H]<sup>+</sup>; found 1059.4003 [M+H]<sup>+</sup>; Δ = 0.2 ppm.

Synthesis of the DPP 2



**DPP 13** (47 mg, 44  $\mu$ mol) was solubilized in 2 mL of DCM and 2 mL of TFA. The mixture was stirred at room temperature for two hours and then solvents were evaporated, affording **DPP2** as a red solid (42 mg, 99%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{H}$  = 8.09-7.95 (m, 4H), 7.95-7-83 (m, 2H), 7.82-7.71 (m, 2H), 7.70-7.55 (m, 6H), 7.25-7.10 (m, 8H), 3.77 (m, 4H), 3.21 (m, 4H), 1.68-1.44 (m, 8H), 1.38-1.17 (m, 8H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $δ_c$  =165.9, 162.9, 151.4, 148.7, 136.7, 132.4, 132.0, 130.2, 129.4, 127.9, 127.3, 126.7, 123.8, 123.0, 51.4, 29.8, 29.4, 28.8, 26.4, 26.3.

**MS-ESI(-):** m/z calculated for 946.2676  $[M-H]^-$ ; found 946.2694  $[M-H]^-$ ;  $\Delta = 1.9$  ppm.



## Absorption and emission spectra of the DPP dyes in solution

Figure S1. Overlay of the absorption (straight line) and emission (dashed line) spectra of DPP 1 recorded in CH<sub>2</sub>Cl<sub>2</sub>.

 $\lambda_{\text{excit}}$  = 484 nm.



Figure S2. Overlay of the absorption (straight line) and emission (dashed line) spectra of DPP 2 recorded in CH<sub>2</sub>Cl<sub>2</sub>.  $\lambda_{excit}$  = 486 nm.

**Table S1.** Absorption and emission properties of the dyes **1** and **2** recorded in  $CH_2Cl_2$ , energy level of the singlet excited state ( $E_{00}$ ) and the redox potentials referenced *versus* SCE recorded in acetonitrile solution with  $Bu_4NPF_6$  as supporting electrolyte.

dye	λ <sub>abs</sub> (nm)/ε(M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{em}$ (nm)	E <sub>00</sub> (eV) <sup>a</sup>	E <sub>Ox</sub> (DPP <sup>+</sup> /DPP)	E <sub>Red</sub> (DPP/DPP <sup>-</sup> )
DPP1	486 (1.85×10 <sup>4</sup> )	554	2.36	1.08 V	-1.21 V
DPP2	489 (2.22x10 <sup>4</sup> )	564	2.33	1.18 V	-1.20 V

<sup>a</sup>calculated according to the equation:  $E_{00}$  = 1240/  $\lambda_{inter}$ , with  $\lambda_{inter}$  wavelength at the intersection of the normalized absorption and emission spectra.

## **Gibbs free energies of the charge transfer reactions**

**Table S2.** Gibbs free energy for the electron injection into TiO<sub>2</sub> ( $\Delta G_{einj}$ ) or hole injection into NiO ( $\Delta G_{hinj}$ ) and for the dye regeneration reaction ( $\Delta G_{reg}$ ) by iodide electrolyte or cobalt electrolyte.

dye	$\Delta G_{einj}(eV)^{a}$	$\Delta G_{hinj}(eV)^{b}$	$\Delta G_{reg}(eV)$		
			I₃⁻/I⁻°	Co(III)/Co(II) d	
DPP1	-0.58	-	-0.97	-0.76	
DPP2	-	-0.83	-0.88	-1.09	

<sup>a</sup>Calculated according to the equation:  $\Delta G^{\circ}_{einj} = E_{Ox}(DPP1^{+}/DPP1^{*}) - E_{CB}(TiO_2)$  with  $E_{Ox}(DPP1^{+}/DPP1^{*}) = E_{Ox}(DPP1^{+}/DPP1) - E_{00}$  and  $E_{CB}(TiO_2) = -0.70$  V vs SCE. <sup>b</sup>Calculated according to the equation:  $\Delta G^{\circ}_{inj} = E_{BV}(NiO) - E_{Red}(DPP2^{*}/DPP2^{-})$  with  $E_{Red}(DPP2^{*}/DPP2^{-}) = E_{Red}(DPP/DPP^{-}) + E_{00}$  and  $E_{BV}(NiO) = 0.30$  V vs SCE. <sup>c</sup>Calculated according to the equation:  $\Delta G_{reg} = E(I_3^{-}/I^{-}) = E_{Ox}(DPP1^{+}/DPP1)$  with  $E(I_3^{-}/I^{-}) = 0.11$  V vs SCE and  $\Delta G_{reg} = E_{Red}(DPP2^{*}/DPP2^{-}) - E(I_3^{-}/I_2^{-\bullet})$  with  $E(I_3^{-}/I_2^{-\bullet}) = -0.32$  V. <sup>d</sup>Calculated according to the equation:  $\Delta G_{reg} = E_{Red}(DPP2^{*}/DPP2^{-}) - E(I_3^{-}/I_2^{-\bullet})$  with  $E(Co^{III}/Co^{II}) = 0.32$  V for ligand = 2,2'-bipyridine and  $\Delta G_{reg} = E_{Red}(DPP2/DPP2^{-}) - E(Co^{III}/Co^{II})$  with  $E(Co^{III}/Co^{II}) = 0.11$  V for ligand = 4,4'-diterbutyI-2,2'-bipyridine.

## ATR-IR spectra of DPP dye 2



*Figure S3.* ATR-IR spectra of DPP dye **2** grafted on NiO film before crosslinking (black) and after crosslinking (red) with **3**. The blue trace corresponds to the ATR-IR spectrum of **3** powder.



**Figure S4.** ATR-IR spectra of DPP dye **2** grafted on TiO<sub>2</sub> film before (black) and after being heated at 140°C in orthodichlorobenzene (red).

Reaction of DPP 1 with ethyl-propiolate ester 4



**Scheme S3.** Reaction of DPP **1** with ethyl-propiolate ester **4** conducted in dichlorobenzene at 140°C.

## Synthesis of the DPP 14

**DPP 1** (40 mg, 0.05 mmol) was solubilized in 10 mL of anhydrous *o*-dichlorobenzene under argon atmosphere. Ethyl-propiolate ester **4** (600 mg, 6 mmol) was added and the solution was stirred overnight at 140°C and then solvent was evaporated. The crude product was purified by column chromatography (silica gel, DCM then DCM/ethanol, 96/4), affording the title product as a red solid (49 mg, 99%).



**Figure S5.** <sup>1</sup>H NMR spectrum of the reaction products of **1** with **4** in dichlorobenzene at 140°C recorded in d<sup>6</sup>-DMSO.



**Figure S6.** ES-MS mass spectrum of the reaction products of **1** with **4** in dichlorobenzene at 140°C.

### 3) Preparation and characterizations of the DSSCs

## **Glass substrate cleaning**

Conductive glass substrates (F-doped SnO<sub>2</sub>) were purchased from Solaronix SA (Switzerland) (TCE7, sheet resistance 7  $\Omega$ /square; or TEC15, sheet resistance 15  $\Omega$ /square). Conductive glass were successively cleaned by sonication in soapy water (15 min), then ethanol containing 1% of concentrated HCl (15 min). After rinsing with ethanol and dried in ambient air, they were fired at 450°C for 30 min.

#### Fabrication of TiO<sub>2</sub> electrodes

TiO<sub>2</sub> films were prepared in three steps. A first treatment was applied by immersion for 30 min in an aqueous TiCl<sub>4</sub> solution (0.3 mL of pure TiCl<sub>4</sub> in 500 mL of deionized water) at 80°C. Layers of TiO<sub>2</sub> were then screen printed with transparent colloidal paste 18NR-T (from Dyesol), with drying steps at 150°C for 20 min between each layer. A final light scattering overlayer was eventually screen printed (18NR AO, Dyesol) over the transparent layer. The obtained substrates were then sintered at 450°C, following a progressive heating ramp (135°C for 15 min, 325°C for 5 min, 375°C for 5 min, 450°C for 30 min). A second TiCl<sub>4</sub> treatment was applied while cells are still hot, followed by a final firing at 450°C for 30 min. The prepared  $TiO_2$  electrodes were soaked while still hot (80°C) in a solution of **DPP 1** (0.2 mM in a mixture DCM/EtOH, 1/1) for one night and finally rinsed with the mixture DCM/EtOH: 1/1.

# Fabrication of NiO electrodes

NiO electrodes were prepared by screen-printing of a NiO paste on clean FTO substrates, using a commercial semiautomatic screen printer. The NiO screen-printing paste was produced by preparing a slurry of 3 g of NiO nanopowder (Inframat) suspended in 10 mL of distilled ethanol and ball-milled (500 rpm) for 24h. The resulting slurry was mixed in a round-bottom flask with 10 mL of 10 wt% ethanolic ethyl cellulose (Sigma Aldrich) solution and 20 mL of terpineol, followed by slow ethanol removal by rotary evaporation. The dried film was first calcined in air at 400°C for 0.5h followed by sintering at 550°C for 10 min. The prepared NiO electrodes were soaked while still hot (80°C) in a solution of **DPP 2** (0.1 mM in a mixture DCM/EtOH, 1/1) for one night and finally rinsed with the mixture DCM/EtOH: 1/1.

# **Cross-linking reaction**

<u>Copper free cross-linking</u>: The above electrodes initially coated with DPP **1** or PP **2** were introduced in 15 ml of a cross-linking agent **3** solution (2 mg/mL in orthodichlorobenzene) and the solution was heated while being protected from the light with an aluminum foil. The crosslinking is completed after 15 minutes at 140°C or after 60 minutes at 90°C. Finally, the electrode was rinsed with 1/1 mixture of  $CH_2Cl_2/EtOH$ , and EtOH and dried with jet of argon.

<u>Copper catalysed cross-linking</u>: The above electrodes initially coated with DPP **1** or DPP **2** were introduced in 15 mL of a solution of DMF containing 14% water, 1.2 mM of the crosslinking-agent **3**, 0.9 mM CuSO<sub>4</sub>.5H<sub>2</sub>O, 1 mM of tris(benzyltriazolylmethyl)amine, and 1.4 mM of sodium ascorbate. The solution was heated at 30 °C while being protected from the light with an aluminum foil. After ten minutes, the electrodes were removed and washed with acetone, then with a mixture of DCM/MeOH: 95/5, pure MeOH, and with a solution of 1 mM of disodium ethylenediaminetetraacetate in a mixture 1/1: ethanol/deionized water, and finally with pure deionized water. The electrode was dried with jet of argon.

# Solar cells preparation and characterizations

The compositions of the electrolytes are:

- for TiO<sub>2</sub> based n-DSSCs: 0.1 M LiI, 0.03 M I<sub>2</sub>, 0.1 M guanidinium thiocyanate, 1,2-dimethyl-3butylimidazolium iodide 0.6 M in acetonitrile for  $I_3^-/I^-$  electrolyte and 0.1 M Co<sup>II</sup>(bpy)<sub>3</sub>-2ClO<sub>4</sub><sup>-</sup>, 0.1 M Co<sup>III</sup>(bpy)<sub>3</sub>-3ClO<sub>4</sub><sup>-</sup> and 0.1 M LiClO<sub>4</sub> in propylene carbonate for cobalt complex as redox shuttle.

- for NiO based p-DSSCs: Electrolytes used are composed of: 1 M lithium iodide and 0.1M diiodine in acetonitrile for  $I_3^-/I^-$  electrolyte and 0.1 M Co<sup>II</sup>(dtb-bpy)<sub>3</sub>-2ClO<sub>4</sub><sup>-</sup>, 0.1 M Co<sup>III</sup>(dtb-bpy)<sub>3</sub>-3ClO<sub>4</sub><sup>-</sup>, and 0.1M LiClO<sub>4</sub> in propylene carbonate for cobalt complex as redox shuttle.



Figure S7. Structures of the cobalt based redox mediators.

Pt counter-electrodes were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (10 mg/mL) and sintered at 380°C in the oven for 30 minutes. The photoelectrode and the counter-electrode were placed on top of each other using a thin transparent film of Surlyn<sup>®</sup> polymer (DuPont, 25  $\mu$ m), as a spacer to form the electrolyte space. The empty cell was tightly held, and the edges were heated to 110°C to seal the two electrodes together. A drop of electrolyte was introduced through a predrilled hole in the counter electrode by vacuum backfilling, and was sealed afterward. The cell had an active area of *ca*. 0.25 cm<sup>2</sup>.

The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2400 digital source meter. The solar simulator is an Oriel Lamp calibrated to 100 mW/cm<sup>2</sup>. The overall conversion efficiency ( $\eta$ ) of the photovoltaic cell is calculated from the integral photocurrent density (J<sub>SC</sub>), the open-circuit photovoltage (V<sub>OC</sub>), the fill factor of the cell (FF), and the intensity of the incident light (IPh).

## **ToF-SIMS** spectra



**Figure S8.** ToF-SIMS spectra (negative ions) recorded between m/z = 37.5 and 38.5 for (a) bare TiO<sub>2</sub> film; (b) TiO<sub>2</sub> film coated with DPP **1** without crosslinking and (c) TiO<sub>2</sub> film coated with DPP **1** and crosslinked with **3**.



**Figure S9.** ToF-SIMS spectra (negative ions) recorded between m/z = 37.5 and 38.5 for (a) bare NiO film ; (b) NiO film coated with DPP **2** without crosslinking and (c) NiO film coated with DPP **2** and crosslinked with **3**.

The figures S7-S8 show that the relative intensity of the  $C_2N^-$  fragment increases after loading of DPP dye (b) relative to that of bare metal oxide film (a) and reaches the highest intensity after crosslinking (c).



**Figure S10.** ToF-SIMS spectra (negative ions) recorded between m/z = 95.8 and 96.2 for (a) bare TiO<sub>2</sub> film; (b) TiO<sub>2</sub> film coated with DPP **1** without crosslinking and (c) TiO<sub>2</sub> film coated with DPP **1** and crosslinked with **3**. The SO<sub>4</sub><sup>-</sup> fragment at m/z = 95.954 occurs as trace surface contaminants, and is therefore unspecific of the surface. It shows up because the sensitivity is high in ToF-SIMS experiments.



**Figure S11.** ToF-SIMS spectra (negative ions) recorded between m/z = 57.5 and 58.5 for (a) bare NiO film ; (b) NiO film coated with DPP **2** without crosslinking and (c) NiO film coated with DPP **2** and crosslinked with **3**.



**Figure S12.** ToF-SIMS spectra (negative ions) recorded between m/z = 73.8 and 74.1 for (a) bare NiO film ; (b) NiO film coated with DPP **2** without crosslinking and (c) NiO film coated with DPP **2** and crosslinked with **3**.

The figures S8-S10 show that the relative intensity of the inorganic fragments coming from the SC ( $TiO_3^-$  for  $TiO_2$  and  $NiO^-$  for NiO) steadily decrease after loading of DPP dye (b) relative to that of bare metal oxide film (a) and reaches the lowest intensity after crosslinking (c) most certainly due to restricted access of the bombardment ion beam to the SC surface.

## Spectra of the desorption experiments



**Figure S13.** Evolution of the absorption spectrum of the DMF phenyl-phosphonic (100 mM) solution as a function of the time when a TiO<sub>2</sub> film coated with **DPP 1** was soaked: non-crosslinked (up) and cross-linked with **3** (down).







**Figure S15.** Evolution of the absorption spectrum of a DMF phenyl-phosphonic (100 mM) solution as a function of the time when a TiO<sub>2</sub> film coated with **DPP 1** and then cross-linked with ethyl propiolate **4** was soaked.



**Figure S16.** Cyclic voltammograms of TiO<sub>2</sub> electrodes coated with DPP **1** non-crosslinked (left) and crosslinked with **3** (right) recorded in acetonitrile with Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte with scan rate 25 mV/sec. Inset: picture of the electrode after 4 scans (left) and 12 scans (right).



**Figure S17.** Picture of the TiO<sub>2</sub> film coated with non-crosslinked DPP **1** showing the detachment of the dye after the first reduction process during cyclic voltammetry. Conditions: acetonitrile with  $Bu_4NPF_6$  as supporting electrolyte, scan rate 25 mV/sec.

#### Transient absorption spectroscopy spectra



**Figure S18.** Transient absorption spectra measured at different time delays after 530 nm excitation of DPP 1 on  $TiO_2$  and DPP 2 on NiO before and after cross-linking with 3.



**Figure S19.** Evolution-associated difference absorption spectra and time constants obtained from a global analysis of the TA data assuming a series of four exponential steps with increasing time constants,  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow$ .

Current/voltage characteristics of the solar cells



**Figure S20.** Current/voltage characteristics of the TiO<sub>2</sub> based DSSC sensitized with **1** with iodide/triiodide electrolyte; non-crosslinked (black) and copper-free crosslinked with **3** (red); solid line = under AM1.5 and dashed-line under the dark.







**Figure S22.** Current/voltage characteristics of the NiO based DSSC sensitized with **2** with the iodide/triiodide electrolyte; non-crosslinked (black) and copper-free crosslinked with **3** (red); solid line = under AM1.5 and dashed-line under the dark.



**Figure S23.** Current/voltage characteristics of the NiO based DSSC sensitized with **2** with the cobalt electrolyte; non-crosslinked (black) and copper-free crosslinked with **3** (red); solid line = under AM1.5 and dashed-line under the dark.

# <sup>1</sup>H NMR spectra of the titration of benzyl-1,2,3-triazole -4-carboxylic acid methyl ester with



**Figure S24.** <sup>1</sup>H NMR (300 MHz, d<sup>6</sup>-DMSO)spectrum of benzyl-1,2,3-triazole -4-carboxylic acid methyl ester **15** without (blue, up) and with 10 equivalents of Bu<sub>4</sub>NI (red, down).





**Figure S25.** ATR-IR spectra of DPP dye **1** grafted on TiO<sub>2</sub> film before crosslinking (black) and after copper catalyzed crosslinking (red) with **3**.



**Figure S26.** ATR-IR spectra of DPP dye **2** grafted on NiO film before crosslinking (black) and after copper catalyzed crosslinking (red) with **3**.

# Table of the photovoltaic performances of copper catalyzed cross-linked DSSCs

**Table S3.** Photovoltaic performances of the DSSCs with the iodine based electrolyte and recorded under simulated sunlight AM1.5 (100mW/m<sup>2</sup>). w/o = without cross-linking and with thermally induced copper free and copper catalyzed cross-linking with **3**.

Electrode	Conditions	J <sub>sc</sub> (mA/cm²)	V <sub>oc</sub> (mV)	FF (%)	PCE (%)
TiO2/DDP <b>1</b>	w/o	4.98±0.5	470±10	68±1	1.58±0.06
	thermal cross-linking	5.37±0.3	475±11	70±1	1.77±0.07
	copper catalyzed cross-linking	2.46±0.5	428±10	67±1	0.70±0.06
NiO/DDP <b>2</b>	w/o	2.02±0.1	89±4	33±1	0.060±0.008
	thermal cross-linking	1.23±0.4	151±8	38±1	0.070±0.006
	copper catalyzed cross-linking	1.33±0.1	92±11	34±3	0.042±0.01

# <sup>1</sup>H and <sup>13</sup>C spectra of the new compounds



Figure S28. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of DPP 6.



Figure S29. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of DPP 8.



Figure S30. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of DPP 8.







Figure S32. <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) spectrum of DPP 9.



Figure S33. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of DPP 1.



Figure S34. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of DPP 1.







Figure S36. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of DPP 12.



Figure S37. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of DPP 13.



Figure S38. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) spectrum of DPP 13.



Figure S39. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) spectrum of DPP 2.



Figure S40.  $^{\rm 13}C$  NMR (300 MHz, CDCl<sub>3</sub>) spectrum of DPP 2.

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