Non-Covalent Postfunctionalization of Dye Layers on TiO₂ — A Tool for Enhancing Injection in Dye-Sensitized Solar Cells

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1) Materials and Methods

1.1) Materials

All chemicals and solvents were purchased from Sigma-Aldrich (St. Louis, Mo, USA), VWR (Darmstadt, Germany), Acros Organics (Geel, Belgium), Roth (Karlsruhe, Germany) and ABCR (Karlsruhe, Germany) and, if not otherwise noted, used without further treatment. Column chromatography was carried out on silica gel 60 (particle size, 0.04-0.063 mm) purchased from Macherey-Nagel (Düren, Germany).

2.2) Methods

NMR and Mass spectrometry

NMR spectra were recorded on a Bruker Avance NEO 600 MHz or a Bruker Avance III 400 MHz spectrometer. High resolution mass spectrometry (HRMS) was performed on a Bruker mAxis 4G UHR TOF MS/MS spectrometer with ESI or APPI ionization, a Bruker microTOF II focus ESI or APPI ionization and a Bruker Ultraflex TOF/TOF spectrometer with MALDI ionization.

HPLC

HPLC measurements were performed with a Shimadzu LC20-AT Prominence.

Electrochemistry and spectroelectrochemistry

Cyclic voltammetry and differential pulse voltammetry were performed at room temperature, under argon atmosphere, and the applied potential was controlled with μAutolab III/FRA2 potentiostat from METROHM. Current vs the applied potential was recorded by means of the software NOVA 1.10. Measurements were carried out in THF:ACN mixture (1:1 v/v) in a homemade cell containing a 0.1 M tetrabutylammonium perchlorate (TBAClO₄) as the supporting electrolyte. A three-electrode configuration was
used with a glassy carbon working electrode (3 mm diameter), Pt wire acting as the counter electrode, and a Ag-wire as the quasi-reference electrode. The Fc/Fc$^+$ redox couple was used as an internal standard.

Spectroelectrochemical measurements were carried out using a METROHM potentiostat PGSTAT 101 and a Cary 5000 Varian spectrophotometer. The measurements were performed in a custom built three neck cell with a platinum gauze (working electrode), a platinum wire (counter electrode) versus a silver wire (pseudo reference electrode) in THF under argon atmosphere. Tetrabutylammonium perchlorate (TBAClO$_4$, 0.2M) was used as a supporting electrolyte. The resulting spectroelectrochemical spectra were overlaid with the spectrum of the neutral compound, and the cation spectrum was obtained by subtracting neutral absorption spectrum from the spectroelectrochemical spectrum.

**Absorption and emission spectroscopy**

UV/Vis spectra were recorded at room temperature using a Perkin Elmer Lambda 2 spectrometer or a Varian Carry 5000 was used for UV-VIS measurements. The data were collected with the software UV WinLab using a slit width of 2 nm and a scan rate of 480 nm/min. Steady-state fluorescence studies were carried out with a FlouroMax®-3 spectrofluorometer (Horiba Scientific).

**Transient absorption spectroscopy**

The measurements were carried out with a transient absorption pump/probe system (TAPPS) from Ultrafast Systems (Helios). The excitation was performed with an amplified CPA-2110 Titanium:Sapphire laser (775 nm, 1 kHz, 150 fs pulse width) from Clark-MXR. The 610 nm excitation wavelength was generated with a noncollinear optical parametric amplifier (NOPA, Clark MXR). The 387 nm excitation wavelength was generated via second harmonic generation (SHG) of the 775 nm laser output. Femtosecond transient absorption studies were performed laser pulses (1 kHz, 150 fs pulse width, energy between 200 and 300 nJ) from an amplified Ti:Sapphire fs laser system (Model CPA 2101 and 2110 Clark MXR), using transient absorption pump/probe detection systems (Helios,
Ultrafast Systems). The 610 nm excitation wavelength was generated with a noncollinear optical parametric amplifier (NOPA, Clark MXR). Excitation pulses of 430 nm wavelength were generated by a NOPA with subsequent frequency doubling; a bandpass filter with ±5 nm was used to ensure low spectral width and to exclude 775 and 387 nm photons. All measurements in solution were conducted in a 2 mm quartz cuvettes under argon atmosphere. Obtained data were treated with the multi-wavelength analysis using either mono- or multi-exponential fitting.
2) Synthetic Procedures

Scheme S2. Synthetic pathway towards ethinyl AB$_2$C porphyrin 6a. a) 0.9 eq. BF$_3$OEt$_2$, 2.8 eq. DDQ, CHCl$_3$, 2 h. b) 0.4 eq. I$_2$, 1.5 eq. p-chloranil, DCM, 5 min.

Mesityldipyrromethane (1):[1]

In a procedure modified from the literature, Mesitaldehyde (2.00 g, 13.5 mmol) was dissolved in pyrrole (66 mL) and degassed with nitrogen for 30 min. BF$_3$OEt$_2$ (1.56 g, 10.9 mmol) was added and the mixture was stirred at rt for 2h. After the addition of NaOH (3.6 g) the mixture was stirred for 1h and the precipitate was removed by filtration. The filtrate was evaporated to dryness under reduced pressure. The residue was taken up in DCM and purified via column chromatography (SiO$_2$, CH/EtOAc, 4.75/1). The crude product was further crystallized from cyclohexane to yield the title compound (1.57 g, 5.90 mmol, 44%) an off-white solid.
**1H-NMR** (400 MHz, CDCl$_3$-d, 25°C): (δ) [ppm] = 7.94 (s, 2H, NH), 6.87 (s, 2H, Ar), 6.67 (dd, $^3J = 4.1$ Hz, 2H), 6.18 (dd, $^3J = 5.8$ Hz, 2H), 6.03 – 6.00 (m, 2H, Py), 5.93 (s, 1H, CH), 2.29 (s, 3H, Ph-CH$_3$), 2.07 (s, 6H, Ph-CH$_3$).

**TMS ethinyl-AB$_2$C Porphyrin 4a:**

Procedure A:
Under argon atmosphere, dipyrrromethane 1 (564 mg, 2.13 mmol), 4-[(trimethylsilyl)ethinyl]benzaldehyde (2) (216 mg, 1.06 mmol) and methyl 4-formylbenzoate (3) (175 mg, 1.07 mmol) were dissolved in CHCl$_3$ (280 mL). Under vigorous stirring, BF$_3$·OEt$_3$ (117 μl, 0.94 mmol) was added and the reaction mixture was stirred for 2 h under exclusion of light. After addition of DDQ (672 mg, 0.80 mmol) the solution was stirred for 16 h and subsequently filtered over a plaque of silica. The crude product was further purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$:CH = 2:1) to yield the title compound (217.4 mg, 0.25 mmol, 24%) as a purple solid.

Procedure B:
Procedure B: Under argon atmosphere, dipyrrromethane 1 (281 mg, 1.06 mmol), methyl 4-formylbenzoate (3) (87 mg, 0.53 mmol) and 4((Trimethylsilyl)ethynyl)benzaldehyde (2) (107 mg, 0.529 mmol) were added to a microwave vial and dissolved in DCM (19 mL). Iodine (51.5 mg, 0.202 mmol) dissolved in 0.5 mL DCM was added and the mixture was submitted to microwave irradiation (100 W, 40°C) for 5 min. Subsequently p-chloranil (393 mg, 1.59 mmol) was added and the mixture was heated to 40°C under microwave conditions (100 W) for 1 min. The crude product was adsorbed onto silica and purified by column chromatography (SiO$_2$, DCM) to yield the title compound (96.8 mg, 0.114 mmol, 22%).

**1H-NMR** (600 MHz, CDCl$_3$, 25°C): (δ) [ppm] = 8.77 (d, $^3J = 4.7$ Hz, 2H, β-Py), 8.74 (d, $^3J = 4.8$ Hz, 2H, β-Py), 8.73 – 8.69 (m, 4H, β-Py), 8.43, (d, $^3J = 8.2$ Hz, 2H, Ar), 8.31 (d, $^3J = 8.2$ Hz, 2H, Ar), 8.17 (d, $^3J = 8.1$ Hz, 2H, Ar), 7.87 (d, $^3J = 8.1$ Hz, 2H, Ar), 7.29 (s, 4H, Ar), 4.11 (s, 3H, OCH$_3$), 2.63 (s, 6H, Ph-CH$_3$), 1.84 (s, 12H, Ph-CH$_3$), 0.38 (s, 9H, SiMe$_3$), -2.64 (s, 2H, NH).
**Metallated TMS-ethinyl AB$_2$C Porphyrin 5a:**

Under protective gas, 4a (207 mg, 0.242 mmol) was dissolved in THF (75 mL). Subsequently ZnOAc (159 mg, 0.726 mmol) was added and the mixture was refluxed for 2 h. The volatiles were evaporated under reduced pressure and the crude material was further purified via column chromatography (Cyclohexane : DCM, 1 : 2) to obtain the title compound as a purple solid (209 mg, 0.227 mmol, 95%).

$^1$H-NMR (600 MHz, CDCl$_3$, 25°C): $\delta$ [ppm] = 8.86 (d, $^3$J = 4.6 Hz, 2H, $\beta$-Py), 8.83 (d, $^3$J = 4.6 Hz, 2H, $\beta$-Py), 8.81 – 8.78 (m, 4H, Ar), 8.41 (d, $^3$J = 8.1 Hz, 2H, Ar), 8.32 (d, $^3$J = 8.1 Hz, 2H, Ar), 8.19 (d, $^3$J = 8.0 Hz, 2H, Ar), 7.87 (d, $^3$J = 8.0 Hz, 2H, Ar), 7.28 (s, 4H, Ar), 4.09 (s, 3H, OCH$_3$), 2.63 (s, 6H, Ph-CH$_3$), 1.83 (s, 12H, Ph-CH$_3$), 0.38 (s, 9H, SiMe$_3$).

HRMS (MALDI, dctb): calculated: m/z = 914.2989, measured m/z = 914.2969 [M]$^+$.  

**Metallated ethinyl AB$_2$C Porphyrin 6a:**

Under protective atmosphere 5a (178 mg, 0.194 mmol) was dissolved in dry THF (45 mL) and treated with a 1M solution of TBAF in THF (220 µL, 0.220 mmol). After the mixture was stirred under exclusion of light for 2.5 h, a few drops of water were added and the solvent was removed under reduced pressure. Subsequently the crude product was purified by column chromatography (SiO$_2$, Cyclohexane/DCM 1/1) to afford the title compound as a purple solid (159 mg, 0.189 mmol, 97%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm]= 8.85 (d, $^3$J = 4.6 Hz, $\beta$-Py), 8.81 (d, $^3$J = 4.6 Hz, 2H, $\beta$-Py), 8.78-8.76 (m, 4H, $\beta$-Py), 8.77 (d $^3$J = 3.0, 2H, Ar), 8.38 (d, $^3$J = 8.3 Hz, 2H, Ar), 8.30 (d, $^3$J = 8.4 Hz, Ar), 8.17 (d, $^3$J = 7.9 Hz, 2H, Ar), 7.86 (d, $^3$J = 8.2 Hz, 2H, Ar), 7.26 (s, 4H, Ar), 4.06 (s, 3H, -OCH$_3$), 3.29 (s, 1H, C≡C), 2.61 (s, 6H, Ph–CH$_3$), 1.80 (s, 12H, Ph–CH$_3$).

HRMS (MALDI, dctb): calculated: m/z = 842.2594, measured m/z = 842.2593 [M]$^+$. 

Scheme S2. Synthetic pathway towards ethinyl AB₂C porphyrin 6b. a) 0.9 eq. BF₃ OEt₂, 2.8 eq. DDQ, CHCl₃, 2 h. b) 0.4 eq. I₂, 1.5 eq. p-chloranil, DCM, 5 min.

**Dimethyl 5-((4-formylphenyl)ethynyl)isophthalate (3b):**

Under an argon atmosphere, dimethyl 5-iodoisophthalate (576 mg, 1.80 mmol) was dissolved in THF (30 mL) and triethylamine (18 mL). The solution was degassed with argon for 15 min. Pd(PPh₃)₂Cl₂ (25.6 mg, 0.0364 mmol), Cul (13.9 mg, 0.0728 mmol) and PPh₃ (9.60 mg, 0.0364 mmol) were added and the solution was stirred for 10 min to dissolve the catalysts. Subsequently 4-ethynylbenzaldehyde (237 mg, 1.82 mmol) was added and the mixture was stirred for 4 h at rt. The crude reaction mixture was washed with water (50 mL) and extracted with DCM (3 x 50 mL). The combined organic phases were washed with brine (50 mL) and dried over Na₂SO₄ to yield the crude product as an orange solid. The crude product was purified by flash column chromatography (SiO₂, CH:EtOAc, 9:1 => 2:1) to yield the title compound as a white solid (429 mg, 74 %).
**1H NMR** (400 MHz, CDCl₃): δ [ppm] = 10.04 (s, 1H, CHO), 8.67 (t, J = 1.6 Hz, 1H, Ar), 8.39 (d, J = 1.6 Hz, 2H, Ar), 7.91-7.89 (m, 2H, Ar), 7.71-7.69 (m, 2H, Ar), 3.98 (s, 6H, OCH₃).

**13C-NMR** (100 MHz, CDCl₃, 25°C): (δ) [ppm] = 52.8 (2C), 90.3 (1C), 91.2 (1C), 123.8 (1C), 128.8 (1C), 129.8 (1C), 130.8 (1C), 131.3 (1C), 132.4 (1C), 136.0 (1C), 136.8 (1C), 165.6 (1C).

**HRMS (APPI):** calculated m/z = 323.0914, measured m/z = 323.0909 [M+H]^+.

**TMS ethinyl-AB₂C Porphyrin (4b):**

Procedure A: Under argon atmosphere, 2,2′(mesitylmethylene)bis(1Hpyrrole) (1) (563 mg, 2.12 mmol), dimethyl 5((4formylphenyl)ethynyl)isophthalate (3b) (346 mg, 1.07 mmol) and 4((Trimethylsilyl)ethynyl)benzaldehyde (2) (215 mg, 1.06 mmol) were dissolved in chloroform (250 mL) and stirred for 15 minutes at room temperature. BF₃OEt₂ (0.12 mL) was added and the reaction mixture was excluded from light and further stirred. After 2 h, DDQ (678 mg, 2.98 mmol) was then added and the reaction mixture was stirred for 16 h at room temperature. Purification by column chromatography (SiO₂, DCM) led to the isolation of the title compound as a glittery mauve powder (156 mg, 0.154 mmol, 14%).

Procedure B: Under an argon atmosphere, 2,2′(mesitylmethylene)bis(1Hpyrrole) (1) (281 mg, 1.06 mmol), dimethyl 5((4formylphenyl)ethynyl)isophthalate (3b) (140 mg, 0.53 mmol) and 4((Trimethylsilyl)ethynyl)benzaldehyde (2) (107 g, 0.53 mmol) were added to a microwave vial and dissolved in DCM (19 mL). Iodine(51.5 mg, ) dissolved in 0.5 mL DCM was added and the mixture was submitted to microwave irradiation (100 W, 40°C) for 5 min. Subsequently p-chloranil () was added and the mixture was heated to 40°C under microwave conditions (100 W) for 1 min. The crude product was adsorbed onto silica and purified by column chromatography (SiO₂, DCM) to yield the title compound (92 mg, 0.091 mmol, 17%).
**1H-NMR** (400 MHz, CDCl₃, 25°C): (δ) [ppm] = 8.81 (d, 3J = 4.8 Hz, 2H, β-Py), 8.77 (d, 3J = 4.8 Hz, 2H, β-Py), 8.73 (s, 1H, Ar), 8.71 (m, 4H, β-Py), 8.53 (d, 4J = 1.6 Hz, 2H, Ar), 8.25 (d, 3J = 8.3 Hz, 2H, Ar), 8.17 (d, 3J = 8.2 Hz, 2H, Ar), 7.95 (d, 3J = 8.2 Hz, 2H, Ar), 7.87 (d, 3J = 8.2 Hz, 2H, Ar), 7.72 (s, 4H, Ar), 4.02 (s, 6H, O-CH₃), 2.64 (s, 6H, CH₃), 1.84 (s, 12H, CH₃), 0.38 (s, 9H, TMS), -2.63 (s, 2H, NH).

**13C-NMR** (100 MHz, CDCl₃, 25°C): (δ) [ppm] = 0.23 (3C), 21.61 (2C), 21.78 (4C), 52.72 (2C), 88.65 (1C), 91.49 (1C), 95.68 (1C), 105.20 (1C), 118.54 (2C), 118.80 (2C), 122.09 (2C), 122.69 (1C), 124.61 (4C), 127.95 (4C), 130.28 (4C), 130.38 (1C), 130.51 (2C), 131.28 (4C), 134.53 (4C), 134.77 (4C), 136.81 (2C), 137.99 (2C), 138.45 (2C), 139.51 (2C), 142.45 (2C), 142.88 (8C), 165.85 (2C).

**HRMS (APPI)**: calculated m/z = 1011.4294, measured m/z = 1011.4300 [M+].

**Metallated TMS-ethinyl AB₂C Porphyrin (5b):**

Under an argon atmosphere 4b (175 mg, 0.173 mmol) was dissolved in THF (75 mL). The solution was degassed for 10 min and ZnOAc was added. The reaction mixture was refluxed for 2h and subsequently the volatile components were evaporated under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, DCM:CH₃Cl, 1:1) to obtain the title compound as a purple solid (181 mg, 0.168 mmol, 97%).

**1H-NMR** (400 MHz, CDCl₃, 25°C): (δ) [ppm] = 8.90 (d, 3J = 4.6 Hz, 2H, β-Py), 8.86 (d, 3J = 4.6 Hz, 2H, β-Py), 8.81 (d, 2H, 3J = 4.6 Hz, β-Py), 8.79 (d, 3J = 4.7 Hz, 2H, β-Py), 8.68 (t, 4J = 1.6 Hz, 1H, Ar), 8.48 (d, 4J = 1.6 Hz, 2H), 8.27 (d, 3J = 8.3 Hz, 2H, Ar), 8.19 (d, 3J = 8.3 Hz, 2H, Ar), 7.95 (d, 3J = 8.3 Hz, 2H, Ar), 7.87 (d, 3J = 8.3 Hz, 2H, Ar), 7.29 (s, 4H, Ar), 3.99 (s, 6H, OCH₃), 2.64 (s, 6H, CH₃), 1.84 (s, 12H, CH₃), 0.38 (s, 9H, TMS).

**13C-NMR** (100 MHz, CDCl₃, 25°C): (δ) [ppm] = 0.24 (3C), 21.62 (2C), 21.78 (4C), 52.73 (2C), 88.49 (1C), 91.61 (1C), 95.48 (1C), 105.32 (1C), 119.46 (2C), 119.73 (2C), 121.80 (2C), 122.39 (1C), 127.85 (4C), 130.13 (4C), 130.36 (1C), 131.18 (2C), 131.22 (4C), 131.45 (4C), 131.77 (4C), 132.65 (2C), 142.88 (8C), 165.85 (2C).
132.26 (4C), 134.46 (4C), 134.71 (2C), 136.78 (2C), 137.72 (2C), 139.05 (2C), 139.37 (2C), 143.30 (8C), 149.89 (2C), 149.94 (2C), 150.17 (4C), 150.19 (4C), 165.82 (2C).

**HRMS (MALDI, dctb):** calculated: m/z = 1072.3357, measured m/z = 1072.3347 [M]+.

**Metallated ethinyl AB₂C Porphyrin (6b):**

Under an argon atmosphere. 5b (150 mg, 0.140 mmol) was dissolved in THF (50 mL). Subsequently a 1 M solution of TBAF in THF (150 µL) was added slowly. The reaction mixture was stirred at rt. After 3 h, a few drops of water were added and the volatile components were removed under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, DCM/CH₂Cl₂, 2/1) to obtain the title compound as a purple solid (123 mg, 0.123 mmol, 87%).

**1H-NMR (400 MHz, DCM, 25°C):** (δ) [ppm] = 8.93 (d, ³J = 4.6 Hz, 2H, β-Py), 8.88 (d, ³J = 4.7 Hz, 2H, β-Py), 8.79 (d, ³J = 4.9 Hz, 2H, β-Py), 8.78 (d, ³J = 4.9 Hz, 2H, β-Py), 8.61 (t, ⁴J = 1.6 Hz, 1H, Ar), 8.44 (d, ⁴J = 1.6 Hz, 2H, Ar), 8.27 (d, ³J = 8.2 Hz, 2H, Ar), 8.21 (d, ³J = 8.2 Hz, 2H, Ar), 7.97 (d, ³J = 8.2 Hz, 2H, Ar), 7.89 (d, ³J = 8.1 Hz, 2H, Ar), 7.30 (s, 4H, Ar), 3.94 (s, 6H, OCH₃), 3.36 (s, 1H, C≡CH), 2.62 (s, 6H, CH₂), 1.82 (s, 12H, CH₃).

**13C-NMR (100 MHz, DCM, 25°C):** (δ) [ppm] = 166.1 (2C), 150.6 (4C), 150.4 (2C), 150.3 (2C), 144.2 (1C), 144.1 (1C), 139.7 (4C), 139.5 (2C), 138.3 (2C), 137.0 (2C), 135.2 (2C), 135.0 (2C), 132.7 (2C), 132.7 (2C), 131.8 (2C), 131.4 (4C), 130.9 (2C), 130.5 (2C), 130.5 (1C), 128.2 (4C), 125.0 (1C), 122.3 (1C), 121.3 (1C), 120.1 (2C), 120.0 (1C), 120.0 (1C), 91.8 (1C), 88.8 (1C), 84.2 (1C), 78.5 (1C), 53.0 (2C), 21.9 (4C), 21.7 (2C).

**HRMS (APPI):** calculated m/z = 1000.2961, measured m/Z = 1000.2984 [M+].
Scheme S3. Synthetic pathway towards iodo Hamilton receptor 7.

N-(6-aminopyridin-2-yl)-3,3-dimethylbutanamide (7a):\[^{[2]}\]

The synthesis was carried out according to a procedure previously reported by our group. Under protective atmosphere 2,6-diaminopyridine (5.00 g, 45.80 mmol, 1.0 eq.) was dissolved in dry THF (50 mL) afterwards triethylamine (6.40 mL, 45.80 mmol, 1.0 eq.) was added. The mixture was cooled to 0 °C and a solution of 3,3-dimethylbutyryl chloride (6.35 g, 45.80 mmol, 1.0 eq.) in anhydrous THF (25 mL) was added dropwise within 2 hours. After stirring at room temperature for 45 h the resulting precipitate was filtered off. The solvent was concentrated to small volume and the raw product was purified by filtration through a plug of silica. (silica gel, CH\_2Cl\_2/EtOAc 4:1). Compound 21 was obtained as a yellowish solid. Yield: 6.10 g (64 %), R\_f = 0.18 (CH\_2Cl\_2/EtOAc 4:1).

\[^{1}\text{H NMR}\] (300 MHz, DMSO): \(\delta = 9.65\) (s, 1H), \(7.31\) (dd, \(3J = 7.8\) Hz, \(4J = 7.8\) Hz 1H), \(7.24\) (dd, \(3J = 7.7\) Hz, \(4J = 0.9\) Hz, 1H), \(6.15\) (dd, \(3J = 7.8\) Hz, \(4J = 0.9\) Hz, 1H), \(5.68\) (s, 2H), \(2.21\) (s, 2H), \(0.98\) (s, 9H).

Iodoisophtalic acid (7b):\[^{[3]}\]

According to a literature procedure, a solution of 5-aminoisophthalic acid (5.00 g, 27.6 mmol) in water (45 mL) / conc. HCl (10 mL) was cooled below 5 °C with an ice/NaCl bath.
Upon slow addition of a NaNO$_2$ solution (1.79 g, 25.9 mmol) in water (20 mL) a pale yellow precipitate formed. After complete addition, the reaction mixture was stirred at 0.5 °C for additional 30 min. Then, an ice-cold solution of I$_2$ (355 mg, 1.40 mmol) and KI (4.29 g, 25.8 mmol) in water (25 mL) was added dropwise to the previous solution while maintaining the temperature below 5 °C. The reaction mixture was stirred at room temperature for 90 min and was then refluxed for 1 h. Excess iodine was removed by adding an aqueous solution of NaHSO$_3$. Then, the reaction mixture was cooled down, filtered, washed with water and finally the expected compound was obtained by solving in acetone. The organic solution was concentrated and dried overnight in vacuo at 50 °C. The expected 5-iodoisophthalic acid was isolated in 74% yield (5.54 g, 19.0 mmol) as a pale yellow solid.

$^1$H-NMR (400 MHz, DMSO-d$_6$): $\delta = 13.51$ (br s, 2H, COOH), 8.41 (s, 3H, Ar) ppm.

**Iodo Hamilton receptor (7)[2]**

According to a procedure previously reported by our group, a solution of 5-iodoisophthalic acid (1.50 g, 5.10 mmol) in thionyl chloride (30 mL) was treated with DMF (5 drops) and refluxed for 6 h under dry conditions. Subsequently the excess of thionyl chloride was removed under reduced pressure. The remaining residue was dried under high vacuum to yield an orange oil. This crude product of iodo isophthalic acid chloride (7c) was used without further purification. A solution of diacid chloride 7c (1.68 g, 5.10 mmol) in THF (40 mL) was added dropwise to a solution of 7a (2.12 g, 10.2 mmol) and triethylamine (1.66 mL, 10.2 mmol) in THF (40 mmol) at 0 °C. The reaction mixture was stirred at rt for 12 h. Subsequently the precipitate was filtered off and washed with THF. The crude product was concentrated under reduced pressure and then purified via flash column chromatography (SiO$_2$, DCM/ETOAc 4/1, 1% MEOH) to obtain the Iodo Hamilton receptor 7 as a yellow solid (2.47g, 3.68 mmol, 72 %).

$^1$H-NMR (400 MHz, THF): $\delta = 9.67$ (s, 2H), 9.02 (s, 2H), 8.45 (s, 3H), 8.09 – 7.88 (m, 4H), 7.72 (t, $J = 8.1$ Hz, 2H), 2.25 (s, 4H), 1.08 (s, 18H).
Scheme S4. Sonogashira type cross coupling towards Hamilton receptor porphyrin 9a.

**Hamilton receptor porphyrin (9a):**

Under an argon atmosphere, Iodo-Hamilton receptor 7 (25.5 mg, 0.0388 mol), Cul (1.0 mg, 0.0053 mmol), Pd(PPh₃)₄ (2.0 mg, 0.0018 mmol) and PPh₃ (1.0 mg, 0.0038 mmol) were dissolved in a mixture of THF (10 mL) and NEt₃ (3 mL). After degassing for 10 min, 6a (30 mg, 0.0355 mmol) was added and the reaction mixture was stirred at 80 °C for 3 d. After cooling to room temperature the volatiles were removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, Tol : EtOAc 4:1, 1% MeOH) to yield the title compound as a purple solid (28.1 mg, 0.0204 mmol, 57%).

**¹H-NMR** (400 MHz, THF, 25°C): δ [ppm] = 9.74 (s, 2H), 9.06 (s, 2H), 8.83 (d, J = 4.6 Hz, 2H), 8.76 (d, J = 4.6 Hz, 2H), 8.69 (dd, J = 7.0, 4.6 Hz, 4H), 8.55 (t, J = 1.6 Hz, 1H), 8.44 (d, J = 1.6 Hz, 2H), 8.42 – 8.37 (m, 2H), 8.33 – 8.26 (m, 4H), 8.05 (dd, J = 6.8, 4.3 Hz, 4H), 8.01 – 7.96 (m, 2H), 7.76 (t, J = 8.1 Hz, 2H), 7.30 (s, 4H), 4.04 (s, 3H), 2.61 (s, 6H), 2.28 (s, 4H), 1.85 (s, 13H), 1.09 (s, 18H).
$^{13}$C-NMR (150 MHz, THF, 25°C): $\delta$ [ppm] = 171.03 (2C), 167.5 (1C), 165.14 (2C), 152.1 (2C), 151.5 (2C), 150.9 (2C), 150.9 (2C), 150.6 (2C), 150.5 (2C), 149.4 (1C), 145.5 (1C), 143.3 (1C), 140.8 (2C), 140.7 (1C), 140.0 (2C), 138.4 (2), 137.1 (2C), 135.8 (2C), 135.5 (2C), 134.5 (2C), 132.7 (2C), 132.6 (2C), 131.3 (2C), 131.3 (2C), 130.7 (2C), 130.5 (1C), 129.8 (1C), 129.3 (1C), 128.7 (4c), 128.4 (2c), 127.8 (1C), 126.8 (1C), 125.3 (1C), 122.8 (1C), 120.2 (1C), 119.9 (2C), 119.9 (1C) 110.7 (2C), 110.5 (2C), 92.3 (1C), 89.7 (1C), 52.5 (1C), 51.0 (2C), 31.9 (2C), 30.3 (6C), 22.1 (4C), 21.7 (2C).

HRMS (MALDI, dctb): measured: m/z = 1384.5239, calculated: m/z = 1384.5235 [M]$^+$. 

![Scheme S5](image)

**Scheme S5.** Sonogashira type cross coupling followed by deprotection of the carboxylate groups towards Hamilton receptor porphyrin 9d.

**Hamilton receptor porphyrin (9c):**

Under an argon atmosphere, Iodo Hamilton receptor 7 (18.7 mg, 0.0279 mol), Cul (4.4 mg, 0.023 mmol), Pd$_2$dba$_3$ (5.4 mg, 0.0059 mmol) and AsPh$_3$ (1.08 mg, 0.0035 mmol) were dissolved in a mixture of THF (10 mL) and NEt$_3$ (4 mL). After
degassing for 10 min, porphyrin 6b (30 mg, 0.0279 mmol) was added and the reaction mixture was stirred at 80 °C for 3d. After cooling to room temperature the volatiles were removed under reduced pressure and the crude product was purified by column chromatography (SiO₂, Tol : EtOAc 4:1, 1% MeOH) to yield the title compound as a purple solid (22.3 mg, 0.0144 mmol, 51.6%).

1H-NMR (400 MHz, THF, 25°C): δ [ppm] = 9.72 (s, 2H, NH), 9.03 (s, 2H, NH), 8.83-8.82 (m, 4H, β-H), 8.71-8.69 (m, 4H, β-H), 8.65 (t, 4J = 1.6 Hz, 1H, CH), 8.54 (t, 4J = 1.6 Hz, 1H, CH), 8.49 (d, 4J = 1.6 Hz, 2H, CH), 8.43 (d, 4J = 1.6 Hz, 2H, CH), 8.28 (t, 3J = 8.3 Hz, 4H, CH), 8.08-8.04 (m, 4H, CH), 7.99-7.97 (m, 4H), 7.76 (t, 3J = 8.1 Hz, 2H, CH), 7.31 (s, 4H, CH), 3.98 (s, 6H, OCH₃), 2.61 (s, 6H, Ph-CH₃), 2.28 (s, 4H, CH₂), 1.86 (s, 12H, Ph-CH₃), 1.09 (s, 18H, CH₃).

13C-NMR (150 MHz, THF, 25°C): δ [ppm] = 171 (2C, NHCO), 165.9 (2C, COOMe), 165.2 (2C, NHCO), 152.1 (2C, C-Py), 151.5 (2C, C-Py), 150.9 (2C, C-alpha), 150.9 (2C, C-alpha), 150.7 (2C, C-alpha), 150.6 (2C, C-alpha), 145.6 (2C), 145.5 (2C, Ph), 140.9 (2C), 140.8 (2C), 140.0 (1C), 138.4 (2C), 137.1 (2C), 137.1 (4C), 135.8 (2C), 135.7 (2C), 134.5 (2C), 132.8 (1C), 132.7 (1C), 132.6 (2C), 131.3 (2C), 131.2 (2C), 130.8 (2C), 130.7 (1C), 130.7 (2C), 128.7 (4C), 127.8 (1C), 126.2 (1C) 125.6 (1C), 125.3 (1C), 122.7 (1C), 122.7 (1C), 120.2 (1C), 120.1 (1C), 119.9 (2C), 110.7 (2C), 110.5 (2C), 92.5 (1C), 92.3 (1C), 89.7 (1C), 89.1 (1C), 52.9 (2C), 51.0 (2C), 31.9 (2C), 30.3 (6C), 22.1 (4C), 21.8 (2C).

HRMS (APPI): calculated: m/z = 1543.5681, measured: m/z = 1543.5672. [M+H]+.

Hamilton receptor porphyrin with deprotected anchoring groups (9d):

Hamilton receptor porphyrin 9c (22.3 mg, 0.0144 mmol) was dissolved in THF (2 mL) and 2 M NaOH (0.1 mL) was added dropwise. After stirring at rt overnight, the volatile components were removed under reduced pressure. The residue was dissolved in water (15 mL) and washed with DCM (3 X 10 mL). Subsequently the aqueous phase was slowly acidified with 1 M HCl and extracted with EtOAC (3 X 20 mL). The combined organic
phases were dried over Na$_2$SO$_4$ and evaporated to dryness to yield the title compound as a purple solid (20.4 mg, 0.0134 mmol, 93%).

$^1$H-NMR (400 MHz, THF, 25°C): $\delta$ [ppm] = 9.72 (s, 4H), 9.03 (s, 2H), 8.83 – 8.82 (m, 4H), 8.72 – 8.67 (m, 6H), 8.54 (t, $^4J = 1.6$ Hz, 1H), 8.48 (d, $^4J = 1.6$ Hz, 2H), 8.43 (d, $^3J = 1.6$ Hz, 2H), 8.30 – 8.24 (m, 4H), 8.08 – 8.03 (m, 4H), 7.98 (d, $J = 7.8$ Hz, 4H), 7.76 (t, $^3J = 8.1$ Hz, 2H), 7.31 (s, 4H), 2.61 (s, 6H), 2.28 (s, 4H), 1.86 (s, 12H), 1.09 (s, 18H).

$^{13}$C-NMR (150 MHz, THF, 25°C): $\delta$ [ppm] = 171.0, 166.5, 165.1, 152.1, 151.5, 150.9, 150.9, 150.7, 150.6, 145.4, 140.8, 140.8, 140.0, 138.4, 137.1, 137.1, 135.8, 135.7, 134.5, 133.2, 132.8, 132.6, 131.3, 131.2, 130.7, 130.7, 128.7, 125.3, 125.2, 120.3, 119.8, 110.7, 110.5, 51.0, 31.9, 30.3, 22.1, 21.7. (Acetylenic carbons not visible due to concentration).

HRMS (MALDI): calculated: m/z = 1514.5290, measured: m/z = 1514.5309. [M]$^+$.
Scheme S6. Synthetic procedure towards Iodocyanuric acid 8.

1- (4- Iodophenyl)biuret (8a):[4]

According to a literature procedure, 1- Nitrobiuret (4.56 g, 30.8 mmol, 1 eq.) and 4-Iodoanilin (5.18 g, 25 mmol, 0.83 eq.) were dissolved in water (50 mL) and heated to reflux for 2 h. Subsequently the hot mixture was filtrated and washed with water and methanol to obtain the title compound 8a as a white solid (5.12 g, 16.7 mmol, 55 %). 8a was used without further purification and analysis.

Iodo cyanuric acid (8):[4]

According to a literature procedure, sodium (0.32 g, 13.9 mmol, 4.25 eq.) was dissolved in dry ethanol (33 mL) and treated with 8a (0.999 g, 3.27 mmol, 1 eq.). The reaction mixture was heated to 79 °C for 24 h. Subsequently toluene (10 mL) was added and the mixture was filtrated. The residue was washed with water and toluene and dissolved in water. The aqueous solution was treated with concentrated HCl. The resulting white precipitate was collected by filtration to obtain the title compound as a white solid (0.486 g, 1.47 mmol, 45 %).

$^1$H NMR (300 MHz, DMSO): $\delta$ [ppm]: 11.57 (s, 2H, Ar- NH, 1), 7.85 – 7.78 (m, 2H, Ar, 2), 7.18 – 7.11 (m, 2H, Ar, 3).
Scheme S7. Sonogashira coupling reaction of 6a and 8 towards cyanuric acid porphyrin 10a.

Cyanuric acid porphyrin (10a):
Under argon atmosphere a microwave vial was charged with iodo cyanuric acid 8 (12.5 mg, Pd(PPh₃)₂Cl₂, Cul and PPh₃. Subsequently the solids were dissolved in a mixture of THF and NET₃. Ethynyl porphyrin 6a (30.0 mg, 0.0356 mmol) was added and the reaction mixture was heated to 150°C for 32 minutes under microwave conditions. Reaction analysis by TLC indicated complete conversion. The crude mixture was adsorbed onto silica and purified by column chromatography (DCM/EtOAc, 2% MeOH) to yield the title compound as a purple solid (15.0 mg, 0.0143 mmol, 40%).

**¹H NMR (601 MHz, THF):** δ [ppm] = 10.68 (s, 2H, NH), 8.83 (d, 3J = 4.5 Hz, 2H, β- Py), 8.75 (d, 3J = 4.5 Hz, 2H, β- Py), 8.69 (d, 3J = 4.5 Hz, 2H, β- Py), 8.68 (d, 3J = 4.5 Hz, 2H, β- Py), 8.39 (d, 3J = 8.2 Hz, 2H, Ar), 8.31 (d, 3J = 8.2 Hz, 2H, Ar), 8.23 (d, 3J = 8.2 Hz, 2H, Ar), 7.93 (d, 3J = 8.2 Hz, 2H, Ar), 7.72 (d, 3J = 8.5 Hz, 2H, Ar), 7.38 (d, 3J = 8.5 Hz, 2H, Ar), 7.30 (s, 4H, Ar), 4.04 (s, 3H, -OCH₃), 2.61 (s, 6H, Ar -(CH₃)₂, 1), 1.85 (s, 12H, Ar-(CH₃)₄).

**¹³C-NMR (150 MHz, THF-d8, 25°C):** δ [ppm] = 167.2 (1 C, H₃COOC), 150.65 (2C, α - Cpyrrol), 150.58 (2 C, α - Cpyrrol), 150.46 (2 C, α - Cpyrrol), 150.18 (2 C, α - Cpyrrol), 150.04 (2 C, NH-C=O), 149.17 (1 C, Cmeso-Carom), 149.04 (1 C, NH-C=O), 144.7 (1 C, Cmeso-Carom), 140.46 (2 C, Cmeso-Carom), 139.72 (4 C, C─CH₃), 138.04 (2 C, C─CH₃), 135.34 (2 C, C₆H₅), 135.28 (2 C, N-C₆H₅), 135.25(2 C, C₆H₅), 132.52 (2 C, β - Cpyrrol), 132.46 (2 C,
C6H3), 132.28 (2 C, β -Cpyrrol), 130.97 (2 C, β -Cpyrrol), 130.93 (2 C, β -Cpyrrol), 130.31 (2 C, C6H3), 130.18 (1 C, H3COOC-Carom), 130.11 (2 C, C6H3), 128.4 (4 C, C6H3), 128.08 (2 C, C6H3), 124.8 (1 C, C≡C), 123.04 (1 C, C≡CC), 120.12 (1 C, Cmeso), 119.55 (2 C, Cmeso), 119.48 (1 C, Cmeso), 90.84 (1 C, C≡C), 90.23 (1 C, C≡C), 52.18 (1 C, O─CH3), 21.84 (4 C, C6H3─CH3), 21.45 (2 C, C6H3─CH3).

**HRMS** (MALDI, dctb): measured: m/z = 1045.2925, calculated: m/z = 1045.2934 [M]+.

**Scheme S8.** Synthetic pathway towards cyanuric acid modified porphyrin 10c.

**Cyanuric acid porphyrin 10b:**

Under an Argon atmosphere I-Cya (8.60 mg, 0.0260 mmol), Pd(PPh3)4 (2.0 mg, 0.0018 mmol), Cul (1 mg, 0.0053 mmol) and PPh3 (1 mg, 0.0038 mmol) were dissolved in THF (8 mL) and NEt3 (3 mL). The mixture was degassed with Argon for 15 min. Subsequently ethynyl porphyrin 6b (25.7 mg, 0.0256) was added and the reaction mixture was stirred at 80 °C for 8h. After stirring at rt for further 4d, the volatile components were removed under reduced pressure. The crude product was purified via column
chromatography (SiO\textsubscript{2}, toluene:EtOAc 3:2, 2% MeOH) to yield the target molecule as a purple solid (19.9 mg, 0.0165 mmol, 46%).

\textbf{1H-NMR} (600 MHz, THF, 25°C): (δ) [ppm] = 10.69 (s, 1H, NH), 8.83-8.81 (m, 4H, β-Py), 8.70 (d, J = 4.5 Hz, 4H, β-Py), 8.65 (t, J = 1.6 Hz, 1H, Ar), 8.49 (d, J = 1.6 Hz, 2H, Ar), 8.27 (d, J = 8.0 Hz, 2H, Ar), 8.24 (d, J = 8.0 Hz, 2H, Ar), 7.98 (d, J = 8.0 Hz, 2H, Ar), 7.93 (d, J = 8.0 Hz, 2H, Ar), 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.38 (d, J = 8.3 Hz, 2H, Ar), 7.31 (s, 4H, Ar), 3.98 (s, 6H, OCH\textsubscript{3}), 2.61 (s, 6H, CH\textsubscript{3}), 1.86 (s, 12H, CH\textsubscript{3}).

\textbf{13C-NMR} (150 MHz, THF, 25°C): (δ) [ppm] = 21.62 (2C, C\textsubscript{6}H\textsubscript{3}C\textsubscript{H} \equiv C), 22.00 (4C, C\textsubscript{6}H\textsubscript{3}C\textsubscript{H} \equiv C), 52.75 (2C, H\textsubscript{3}COC=O), 119.68 (2C, C\equiv C\equiv C), 128.57 (2C, C\equiv C\equiv C) 130.28 (2C, Py-C-Py), 130.48 (2C, Py-C-Py), 130.61 (2C, CaromC≡C), 131.08 (1C, CaromC≡CProcam), 132.51 (4C, Carom), 132.62 (4C, Carom), 134.52 (4C, Carom), 135.62 (4C, C-Py), 136.94 (4C, C-Py), 138.21 (2C, Carom), 139.91 (8C, C-Py), 140.67 (4C, Carom), 150.37 (4C, C-Py), 150.54 (4C, C-Py), 150.77 (2C, NCO), 150.80 (1C, NH-C-NH), 165.78 (2C, H3COC=O).

\textbf{HRMS (APPI)}: calculated: m/z = 1203.3292, measured: m/z = 1203.3297. [M]+, calculated: m/z = 1204.3371, measured: m/z = 1204.3393 [M+H]+.

**Cyanuric acid porphyrin with deprotected anchoring groups (10c)**

\textbf{10b} (10 mg, 0.00829 mmol) was dissolved in THF (2 mL) and 2 M NaOH (50 µL) was added dropwise. After stirring at rt for 24 h, the volatile components were removed under reduced pressure. The residue was dissolved in water (20 µL) and washed with DCM (3 X 20 mL). The aqueous phase was slowly acidified with 1M HCl and the resulting purple crystals were collected by vacuum filtration to yield the target molecule (6.8 mg, 0.00577 mmol, 70%).

\textbf{1H-NMR} (600 MHz, THF, 25°C): (δ) [ppm] = 10.67 (s, 2H), 8.83 – 8.81 (m, 4H), 8.71 – 8.67 (m, 5H), 8.48 (d, J = 1.6 Hz, 2H), 8.27 – 8.22 (m, 4H), 7.97 (d, J = 8.2 Hz, 2H), 7.92 (d,
$^3J = 8.2 \text{ Hz, 2H}$, $7.72 \text{ (d,} ^3J = 8.5 \text{ Hz, 2H)}$, $7.38 \text{ (d,} ^3J = 8.5 \text{ Hz, 2H)}$, $7.30 \text{ (s, 4H)}$, $2.61 \text{ (s, 6H)}$, $1.85 \text{ (s, 12H)}$.

$^{13}$C-NMR (150 MHz, THF, 25°C): (δ) [ppm] = 166.5, 150.9, 150.7, 150.7, 150.3, 149.3, 145.4, 145.0, 140.8, 140.0, 138.3, 137.1, 135.7, 135.6, 135.6, 133.2, 132.8, 132.7, 131.2, 131.2, 130.7, 130.6, 130.4, 128.7, 125.2, 124.6, 123.3, 122.8, 120.3, 120.2, 119.8, 92.0, 91.2, 90.5, 89.4, 22.1, 21.7.

**HRMS (APPI):** calculated: m/z = 1175.2975, measured: m/z = 1175.2988. [M]$^+$

![Scheme S9](image)

**Scheme S9.** Synthetic pathway towards ethynyl Hamilton receptor 12.

**TMS ethynyl Hamilton receptor (12a)[$^2$]**

Iodo-Hamilton receptor 7 (719 mg, 1.07 mmol) was dissolved in THF (19 mL) under inert conditions. Subsequently Pd(PPh$_3$)$_2$Cl$_2$ (8 mg, x mmol), PPh$_3$ (2 mg, 0.0057 mmol), Cul (6 mg, 0.0032 mmol) and triethylamine (10 mL) were added. After the mixture was stirred for 15 min to dissolve the catalysts, trimethylsilylacetylene (108 mg, 1.10 mmol) was added dropwise. The reaction mixture was stirred for 24 h at rt, filtered and purified by flash column chromatography (SiO$_2$, CH$_2$Cl$_2$/EtOAc 7:1, MeOH 1 %) to yield 12a as a brown solid (609 mg, 0.950 mmol, 89%).

$^1$H NMR (300 MHz, THF): (δ) [ppm] = 9.61 (s, 2H), 9.00 (s, 2H), 8.46 (t, $J = 1.6$ Hz, 1H), 8.18 (d, $J = 1.6$ Hz, 2H), 8.01 (dd, $J = 7.9$ Hz, 4H), 7.72 (t, $J = 8.1$ Hz, 2H), 2.26 (s, 4H), 1.08 (s, 18H), 0.28 (s, 9H).
**Ethinyl Hamilton receptor (12)**:[2]

TBAF in THF (0.7 mL, 0.7 mmol) was added dropwise to a solution of 12a (403 mg, 0.629 mmol) in THF (10 mL) at rt. After stirring for 3 h at rt the solvent was evaporated and the residue purified by column chromatography (CH$_2$Cl$_2$/EtOAc 4:1) to yield the title compound as a white solid (99%).

$^1$H NMR (300 MHz, THF): (δ) [ppm] = 9.62 (s, 2H), 8.98 (s, 2H), 8.47 (t, $^4J = 1.6$ Hz, 1H), 8.21 (d, $^4J = 1.6$ Hz, 2H), 8.01 (dd, $^3J = 2.2$ Hz, 4H), 7.72 (t, $J = 8.1$ Hz, 2H), 3.81 (s, 1H), 2.26 (s, 4H), 1.08 (s, 18H).

![Scheme S10. Synthetic pathway towards ethynyl cyanuric acid 13.](image)

**TMS ethynyl cyanuric acid (13a)**:[4]

In a procedure modified from the literature, Cya-I (400 mg, 1.21 mmol), Pd(PPh$_3$)$_2$Cl$_2$, Cul and PPh$_3$ were dissolved in a mixture of THF (15 mL) and NEt$_3$(10 mL) under an argon atmosphere. After degassing for 15 min TMS-acetylene (147 mg, 1.50 mmol) was added and the resulting solution was stirred at rt for 20 h. The crude product was concentrated under reduced pressure and purified via column chromatography (SiO$_2$, DCM/EtOAc, 1/1) to yield the title compound as a white solid (300 mg, 0.995 mmol, 82 %).

$^1$H NMR (300 MHz, DMSO): δ [ppm] = 11.58 (s, 2H), 7.57 – 7.48 (m, 2H), 7.39 – 7.31 (m, 2H), 0.24 (s, 9H).
**Ethynyl cyanuric acid (13)**\(^{[4]}\)

In a procedure modified from the literature, 13a (100 mg, 0.322 mmol) and K\(_2\)CO\(_3\) (138 mg, 1.00 mmol) were dissolved in MeOH (20 mL) and water (5 mL). After stirring for 24 h at rt, saturated NH\(_4\)Cl solution (50 mL) was added and the mixture was extracted with EtOAc (3 X 50 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL), dried over sodium sulfate and evaporated under reduced pressure to yield the title compound as a white solid (45 mg, 0.20 mmol, 59 %).

\(^1\)H NMR (400 MHz, DMSO): \(\delta [\text{ppm}] = 11.59 \ (s, 2H), 7.56 \ (d, J = 8.4 \text{ Hz}, 2H), 7.36 \ (d, \ J = 8.4 \text{ Hz}, 2H), 4.27 \ (s, 1H)\).
Scheme S11. A) Synthesis of Iodo BODIPY 11. B) Sonogashira type cross coupling towards Hamilton receptor modified BODIPY 15. C) Sonogashira type cross coupling towards cyanuric acid modified BODIPY 16.

BODIPY (11a):[5]

According to a literature procedure, dipyrromethane 1 (462 mg, 1.75 mmol) was dissolved in DCM under protective gas and cooled to 0 °C. DDQ (398 mg) was added and the mixture was stirred at 0 °C for 10 min. Subsequently NEt₃ (3.5 mL) and BF₃ OEt₂ (3.5 mL, ) were added at once. After stirring at rt for 2h, the solution was washed with water (50 mL), 0.2 M NaOH(50 mL) and water (100 mL). The aqueous phase was extracted with
DCM (100 mL) and the combined organic phases were dried over Na$_2$SO$_4$. Filtrated and concentrated under reduced pressure to obtain the title compound (203 mg, 0.655 mmol, 37%).

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 7.91 (s, 2H), 6.95 (s, 2H), 6.68 (d, $J = 4.2$ Hz, 2H), 6.47 (d, $J = 4.0$ Hz, 2H), 2.36 (s, 3H), 2.10 (s, 6H).

Iodo BODIPY (11):[5]

Following a literature procedure, BODIPY 11a (203 mg, 0.655 mmol) was dissolved in a mixture of DCM and MeOH (25mL /25 mL) and ICl (107 mg, 0.660 mmol) dissolved in MeOH (10 mL) was added. The reaction mixture was stirred for 2.5 h at reflux temperature and then further stirred at rt overnight. Subsequently the mixture was concentrated under reduced pressure and washed with water and brine. The crude product was purified by multiple column chromatographic steps (hexanes : DCM 3:1) to obtain the title compound.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 7.97 (s, 1H), 7.81 (s, 1H), 6.96 (s, 2H), 6.76 (s, 2H), 6.53 (d, $J = 5.7$ Hz, 1H), 2.36 (s, 3H), 2.10 (s, 6H).

Hamilton receptor BODIPY (15):

Under an argon atmosphere 11 (30 mg, 0.069 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (3 mg, ), Cul (2 mg, ) and PPh$_3$ (0.5 mg, ) were dissolved in THF (5 mL) and NEt$_3$ (3 mL). The resulting solution was degassed for 10 min and 12 (45 mg, 0.08 mmol) was added. The reaction mixture was stirred at rt overnight. The volatiles were removed under reduced pressure and the crude product was purified via flash column chromatography (SiO$_2$, DCM:EtOAc, 9:1 => 4:1, 1 % MeOH) to yield the title compound as a purple solid (28 mg, 0.032 mmol, 46%).

$^1$H-NMR (400 MHz, THF, 25°C): ($\delta$) [ppm] = 9.58 (s, 2H, NH), 8.97 (s, 2H, NH), 8.42 (t, $J = 1.6$ Hz, 1H), 8.18 (d, $J = 1.7$ Hz, 2H), 8.17 (m, 1H), 8.12 (s, 1H), 8.04 – 7.98 (m, 5H), 7.72 (t, $J = 8.1$ Hz, 3H), 7.06 (s, 2H), 6.86 (d, $J = 4.3$ Hz, 1H), 6.80 (s, 1H), 6.65 (dd, $J = 4.3$ Hz, 1H), 2.37 (s, 4H), 2.26 (s, 5H), 2.13 (s, 8H), 1.08 (s, 24H).
$^{13}$C-NMR (150 MHz, THF, 25°C): (δ) [ppm] = 171.01, 165.02, 152.02, 151.46, 149.04, 148.59, 145.91, 140.79, 140.27, 137.85, 137.25, 136.93, 135.57, 134.09, 132.83, 130.90, 130.59, 129.31, 127.50, 125.12, 110.61, 110.39, 90.94, 85.29, 50.97, 31.90, 30.26, 21.36, 20.14.

HRMS (APPI): m/z = calculated: 877.4167 measured: 877.4175 [M+].

Cyanuric acid modified BODIPY (16):

Under an argon atmosphere, 11 (30 mg, 0.069 mmol) Pd(PPh3)2Cl2 (3.0 mg, 0.0043 mmol), Cul (2mg, 0.011 mmol) and PPh3 (0.5 mg, 0.0019 mmol) were dissolved in a mixture of THF (5mL) and triethylamine (3 mL). After degassing for 10 min 13 was added and the reaction mixture was stirred overnight under exclusion of light. The volatile components were removed under reduced pressure and the crude product was purified by column chromatography (SiO2, DCM => DCM:EtOAc 1:8, 5% methanol), followed by reverse phase HPLC to yield the title compound as a purple solid (8.7 mg, 0.0016 mmol, 23%). The product contained triphenylphosphineoxide as impurity that could not be removed by several chromatographic procedures.

$^1$H-NMR (400 MHz, THF, 25°C): (δ) [ppm] = 11.59 (s, 2H, NH), 8.37 (s, 1H), 8.34 (s, 1H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.37 (d, $J = 8.6$ Hz, 2H), 7.08 (s, 2H), 6.88 (d, $J = 4.4$ Hz, 1H), 6.78 (s, 1H), 6.73 (d, $J = 5.6$ Hz, 1H), 2.35 (s, 3H), 2.06 (s, 6H).

HRMS (APPI): m/z = calculated: 537.1778 measured: 537.1781 [M+].
Scheme S12. Synthetic procedure towards porphyrin cyanurate 17.\cite{2}

Cyanuric acid porphyrin (17):

The target molecule was previously reported by our group.\cite{2} For this work the synthetic procedure was designed anew to accomplish a highly shortened reaction time. Under argon atmosphere a microwave vial was charged with 8 (12.5 mg, 0.0378 mmol), Pd(PPh$_3$)$_2$Cl$_2$, Cul and PPh$_3$. Subsequently the solids were dissolved in a mixture of THF and NET$_3$. 14 (30.0 mg, 0.0356 mmol) was added and the reaction mixture was heated to 150°C for 32 minutes under microwave conditions. Reaction analysis by TLC indicated complete conversion. The crude mixture was adsorbed onto silica and purified by column chromatography (DCM/EtOAc, 2% MeOH) to yield the title compound as a purple solid (15.0 mg, 0.0138 mmol, 39%).

$^1$H-NMR (400 MHz, THF, 25°C): (δ) [ppm] = 10.68 (s, 2H, NH), 8.96 (d, $^3$J = 4.6 Hz, 2H, β-Py), 8.93 (s, 4H, β-Py), 8.85 (d, $^3$J = 4.6 Hz, 2H, β-Py), 8.23 (d, $^3$J = 8.2 Hz, 2H, Ar), 7.94 (d, $^3$J = 8.2 Hz, 2H, Ar), 7.73 (d, $^3$J = 8.6 Hz, 2H, Ar), 7.41 – 7.36 (m, 8H, Ar), 6.91 (t, $^3$J = 2.3 Hz, 3H, Ar), 3.94 (s, 18H, OMe).

HRMS (MALDI, dctb): measured: m/z = 1083.2565, calculated: m/z = 1083.2549 [M]$^+$. 
3) NMR Data

NMR Data

Figure S1. $^1$H NMR (400 MHz, CDCl$_3$) of compound 3b.
Figure S2. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 3b.
Figure S3. $^1$H NMR (400 MHz, CDCl$_3$) of compound 4a.
Figure S4. $^1$H NMR (400 MHz, CDCl$_3$) of compound 5a.
Figure S5. $^1$H NMR (400 MHz, CDCl$_3$) of compound 6a.
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) of compound 4b.
Figure S7. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 4b.
Figure S8. $^1$H NMR (400 MHz, CDCl$_3$) of compound 5b.
Figure S9. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 5b.
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) of compound 6b.
Figure S11. $^{13}$C NMR (100 MHz, CDCl$_3$) of compound 6b.
Figure S12. $^1$H NMR (400 MHz, THF) of compound 9c
Figure S13. $^{13}$C NMR (150 MHz, THF) of compound 9c.
Figure S14: $^1$H NMR (400 MHz, THF) of compound 9d.
Figure S15 $^{13}$C NMR (150 MHz, THF) of compound 9d (Acetylenic carbon signals not visible due to concentration).
Figure S16. $^1$H NMR (600 MHz, THF) of compound 10a.
Figure S17. $^{13}$C NMR (150 MHz, THF) of compound 10a.
Figure S18. $^1$H NMR (600 MHz, THF) of compound 10b.
Figure S19. $^{13}$C NMR (150 MHz, THF) of compound 10b.
Figure S20 $^{1}$H NMR (600 MHz, THF) of compound 10c.
Figure S21 $^{13}$C NMR (150 MHz, THF) of compound 10c.
Figure S22. $^1$H NMR (400 MHz, CDCl$_3$) of compound 15.
Figure S23. $^{13}$C NMR (150 MHz, THF) of compound 15.
Figure S24. $^1$H NMR (400 MHz, CDCl$_3$) of compound 16.
4) NMR Titrations

Figure S25. NMR titration data of Hamilton receptor 9a with cyanuric acid porphyrin 17. A) Chemical Shift of the NH protons plotted vs the added equivalents of cyanuric acid 17. B) Jobs plot analysis of the NMR titration data.
Figure S26. NMR titration data of Hamilton receptor 15 with cyanuric acid porphyrin 10a. A) Chemical Shift of the NH protons plotted vs the added equivalents of cyanuric acid 10a. B) Jobs plot analysis of the NMR titration data.
5) Electrochemistry

The electrochemical properties of 9d, 16, 9d·16, 15, 10c, and 15·10c were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The relevant CV and DPV are collected in Table S1 and presented in Figures S23-S24. Comparison of CV and DPV voltammograms of 9d, 16, 9d·16 shows changes upon hybrid formation. 16 is characterized by reversible reduction at -1.09 V and oxidation at +0.96 V. In DPV, the oxidation overlaps with solvent features. However, a closer look at the CV voltammogram (Figure S23c) reveals presence of two signals: one solvent related and one assigned to 16. 9d shows one reversible reduction at -1.76 V, and three oxidations at +0.48, +0.86, and +1.04 V. Small changes were observed in the redox properties upon 9d·16 hybrid formation. The first reduction is anodically shifted relative to 16. In contrast to the reduction, the first oxidation is cathodically shifted relative to 9d. Even though the second oxidation at +0.82 V is not clearly detectible in the DPV voltammogram, it is recognizable in the CV. Similar observations were noted for 15, 10c, and 15·10c. 15 exhibits one reduction and one oxidation, at -1.08 and +1.10 V respectively. For 10c, one reduction at -1.81 V and three oxidations waves at +0.45, +0.85, and +1.00 were noted. In 15·10c hybrid, the first reduction at -1.07 is anodically shifted to 15, while the first oxidation at +0.42 is cathodically shifted relative to 10c.

Table S1. Electrochemical data. 

| Compound | $E_{1/2}^{1}$ | $E_{1/2}^{2}$ | $E_{1/2}^{1}$ | $E_{1/2}^{2}$ | $E_{1/2}^{3}$ | $E_{0}^{b}$ | $E_{0}^{a}$ | $E_{0}$ opt$^c$ |
|----------|--------------|--------------|--------------|--------------|--------------|-------------|-------------|--------------|
| 9d       | -            | -1.76        | 0.48         | 0.86         | 1.04         | -1.61       | 2.24        | 2.09         |
| 16       | -            | -1.09        | 0.96         | -            | -            | -1.09       | 2.05        | 2.20         |
| 9d·16    | -1.75        | -1.03        | 0.46         | 0.82         | 1.07         | -           | -           | -            |
| 15       | -            | -1.08        | 1.10         | -            | -            | -1.14       | 2.18        | 2.24         |
| 10c      | -            | -1.81        | 0.45         | 0.85         | 1.00         | -1.66       | 2.26        | 2.11         |
| 15·10c   | -1.81        | -1.07        | 0.42         | 0.82         | 1.1          | -           | -           | -            |

[a] Potentials are reported in V (half-wave potentials: $E_{1/2}$); scan rate 50 mVs$^{-1}$. The values were corrected for ferrocene as an internal standard. The peak potentials obtained from the DPV measurements were converted to $E_{1/2}$ values using the formula $E_{max} = E_{1/2} - (\Delta E/2)$, in which $\Delta E$ is the pulse amplitude (25 mV). Measurements were performed at room temperature in THF/ACN (1:1 v.) mixture containing TBAClO$_4$ as a supporting electrolyte.
[b] $E_{ox}^* = E_{1/2ox}^1 - E_{0-0}$

c] The values of the optical energy gap were obtained from the wavelengths of the crossing points of normalized absorption and fluorescence spectra.
Figure S27. a) Differential pulse voltammograms of 9d (red), 16 (black), 9d·16 complex (blue). The response of the solvent is shown in dashed gray. Cyclic voltammograms of b) 9d (red), c) 16 (black) and solvent (gray), d) 9d·16 complex (blue). The values are corrected for ferrocene as an internal standard.
Figure S28. a) Differential pulse voltammograms of 10c (red), 15 (black), 15-10c complex (blue). The response of the solvent is shown in dashed gray. * indicates presence of oxygen. Cyclic voltammograms of b) 10c (red), c) 15 (black), d) 15-10c complex (blue). The values are corrected for ferrocene as an internal standard.
6) Optical Spectroscopy

(a) 4.50x10^7

Intensity

3.00x10^7

1.50x10^7

0.00

Wavelength / nm

(b) 700

Excitation / nm

600

500

400

300

400 500 600 700 800

Emission / nm

Intensity

6x10^7

5x10^7

3x10^7

0
Figure S29. a) Fluorescence spectra upon 506 nm excitation in chloroform at room temperature. 3D-NIR fluorescence spectra of b) 9d, c) 16, and d) 9d-16 in chloroform at room temperature.
Figure S30. a) Steady-state absorption spectra of 15, 10c, and 15·10c (1:1 ratio) in chloroform. b) Fluorescence spectra upon 506 nm excitation in chloroform at room temperature. 3D-NIR fluorescence spectra of c) 10c, d) 15, and e) 15·10c in chloroform at room temperature.
Figure S31. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 9d in argon-saturated chloroform with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 535, 665, and 837 nm.
Figure S32. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 16 in argon-saturated chloroform with several time delays between 0 and 5500 ps at room temperature.
Figure S33. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 9d·16 in argon-saturated chloroform with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 535, 665, and 837 nm.
Figure S34. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 10c in argon-saturated chloroform with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 535, 665, and 837 nm.
Figure S35. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 15 in argon-saturated chloroform with several time delays between 0 and 5500 ps at room temperature.
Figure S36. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 15·10c in argon-saturated chloroform with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 535, 665, and 837 nm. d) Comparison of time absorption profiles of 15, 10, and 15·10c at 557 nm.
Figure S37. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 9d adsorbed onto TiO$_2$ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 564, 665, and 837 nm.
Figure S38. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 10c adsorbed onto TiO$_2$ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 564, 665, and 837 nm.
Figure S39. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (430 nm) of 15-10c adsorbed onto TiO$_2$ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 564, 665, and 837 nm.
**Figure S40.** a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (610 nm) of 9d adsorbed onto TiO$_2$ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 562, 665, and 837 nm.
Figure S41. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (610 nm) of 9d·16 adsorbed onto TiO₂ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 562, 665, and 837 nm.
**Figure S42.** a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (610 nm) of 10c adsorbed onto TiO$_2$ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 562, 665, and 837 nm.
Figure S43. a) Differential absorption spectra with the depicted time delays and b) 3D representation of differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (610 nm) of 15·10c adsorbed onto TiO$_2$ film with electrolyte with several time delays between 0 and 5500 ps at room temperature. c) Time absorption profiles of the spectra at 562, 665, and 837 nm.
Figure S44. Differential absorption spectrum of electrochemically oxidized 9d in argon-saturated THF with TBAClO$_4$ as supporting electrolyte, Ag/Ag$^+$ as reference electrode, Pt as counter electrode, and Pt mesh as working electrode at an applied voltage of + 1.1 V.

Figure S45. Comparison of differential absorption spectra of 9d and 9d·16 adsorbed onto TiO$_2$ films with electrolyte upon 430 nm excitation depicted at 250 ps time delay.
Figure S46. HOMO and LUMO energy levels of 9d and 16. The energy levels were calculated from electrochemistry measurements; HOMO[eV] = -(E_{ox} (vs. Fc/Fc^+) + 4.8) and LUMO[eV] = -(E_{ox}^-(vs. Fc/Fc^+) + 4.8).[6]

7) Dye sensitized solar cells

Solar cell device fabrication

FTO substrates were cleaned in an ultrasonic bath for each 15 min, firstly, with acetone, secondly, with a soap solution (deconex FPD 120, 1 % vol solution in 150 ml deionized water), and, finally, with pure deionized water. The substrates were dried under a nitrogen flow, sonicated in isopropanol for further 15 min and, subsequently, dried under a nitrogen flow. To eliminate organic residuals, the substrates were further treated in a UV-ozone cleaner model 42-220 (Jelight Company) for 18 min.

Semiconducting TiO_{2} films were prepared employing a commercially available Solaronix (Ti-Nanoxide T/SP) paste. These pastes were subsequently doctor-bladed using a circular Scotch tape template with a diameter of 5 mm and a thickness of 50 µm onto the aforementioned FTO slides. The first layer was dried at 80°C and a second layer was applied following the same procedure. Next, the slides were heated between room
temperature and 500°C with the following temperature ramp. Firstly, from room temperature the slides were heated to 150°C with a ramp of 10°C/min and were held at this temperature for 10 min. Secondly, the temperature was increased to 325°C with a 15°C/min ramp and kept constant for 5 min. Thirdly, the temperature was further increased by 5°C/min to 375°C and kept for further 5 min. Fourthly, the temperature was increased up to 450°C at 7°C/min and kept constant at 450°C for 30 min. Fifthly, the final temperature of 500°C was reached by an increase at 5°C/min, where the samples were kept for 15 min. The slides were then cooled to 80°C. Film thicknesses of 9 μm were measured for the TiO$_2$-based electrodes. The latter were then immersed for 2 h into a THF based 4 x 10$^{-4}$ M porphyrin solution to fully cover the semiconducting surface. Subsequently, all slides were immersed into the next dye solution. For counter-electrode fabrication, FTO plates with two holes of 1 mm diameter at the edge of the active area were used. Prior to the fabrication of the counter-electrodes, the FTO slides were cleaned following the aforementioned procedure. A thin film of 26 μl H$_2$PtCl$_6$ (0.5 mmol in ethanol) was prepared from chloroplatinic acid hydrate (≈ 38 w.t.% Pt content), directly spread over the FTO plates, and dried in air prior to baking at 400°C for 20 min. To finalize the device, both electrodes were sealed together with a transparent film of Surlyn (DuPont Ltd., UK), cut as a frame around the nanocrystalline film. A solution of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide 99%, 0.05 M iodine double sublimed, lithium iodide 0.1 M, and 0.5 M 4-tert-butylpyridine 96 % in a solvent mixture of acetonitrile and valeronitrile (85:15 v/v) was employed as electrolyte. The electrolyte was introduced through the aforementioned holes and the final cell was sealed immediately afterwards using another piece of Surlyn and a piece of microscope slide.

**Solar Cell Device Characterization.**

Electrochemical impedance spectroscopic assays (EIS) were carried out with a potentiostat / galvanostat (PGSTAT30, Autolab) equipped with a frequency response analyzer module (FRA). Measurements were performed at the respective open-circuit voltage of the different devices in the dark and under illumination (AM 1.5 filter, 100 W/cm$^2$).
These EIS analyses were conducted based on the equivalent circuit model presented in Figure S43. It reflects, on one hand, the electrolyte regeneration at the platinum/electrolyte interface at 1-50 kHz and, on the other hand, the electron transfer processes across the electrode/dye/electrolyte interfaces around 1-500 Hz. Considering that the former contribution remains constant, all observable changes are attributable to the latter. The AC signal amplitude was set to 10 mV and modulated in a frequency range from 0.1 to 100 KHz. The Nova 1.11 software was used to obtain the parameters from the equivalent circuit. With this data at hand, the charge collection efficiency yield ($\eta_{\text{coll}}$), the electron lifetime ($\tau$), and the effective carrier diffusion length ($L_{\text{eff}}$) were calculated by means of equations 1, 2, and 3, respectively.

Equivalent circuit employed to fit the data with $R_s$ being the pre-device resistance, $R_{pt}/C_{pt}$ and $R_{sc}/C_{sc}$ being the resistance and capacitance at the platinum interface and semiconductor interface, respectively

\[
\eta_{\text{coll}} = 1 - (R_w/R_k) \quad (1)
\]

\[
\tau = 1/(2 \times \pi \times f_{\text{max}}) \quad (2)
\]

\[
L_{\text{eff}} = (D_{\text{eff}} \times \tau)^{1/2} \quad (3)
\]

where $R_w$, $R_k$, $f_{\text{max}}$, and $D_{\text{eff}}$ are the electron transport resistance, the charge-transfer resistance to recombination of electrons, the maximum frequency taken from the Bode phase plot, and the effective diffusion coefficient, respectively.

Photocurrent measurements were carried out under AM 1.5 conditions using a custom-made solar simulator, including a 350-1000 Watt adjustable Xe lamp source (LOT) combined with an appropriate AM 1.5 filter. Current voltage measurements were performed by using a potentiostat / galvanostat (PGSTAT30, Autolab) in the range from -0.8 to 0.2 V. All measurements were performed with a black mask after calibration of the aforementioned apparatus with a silicon solar cell reference SRC-1000-TC-K-KG5-N pursued from VLSI standards at room temperature. Incident photon-to-current efficiency (IPCE) was measured by using a Newport apparatus model 70104. The IPCE is correlated
to four main factors: the light harvesting efficiency (LHE), the quantum yield of charge injection ($\eta_{\text{inj}}$), dye regeneration ($\eta_{\text{reg}}$), and charge collection ($\eta_{\text{coll}}$) as indicated in equation 4.

$$\text{IPCE} = \text{LHE} \times \eta_{\text{inj}} \times \eta_{\text{reg}} \times \eta_{\text{coll}}$$ (4)

**Figure S48:** SEM images of the highly mesoporous TiO$_2$ layers employed herein. Top: top view; Bottom: cross sectional view.
Figure S49: Profilometry measurement of two TiO$_2$ layers as employed for the work at hand.

8) Literature

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