

Electronic Supplementary Information

Hydrogen bonding mediated orthogonal and reversible self-assembly of porphyrin sensitizers onto TiO₂ nanoparticles

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1) Materials and Methods

General Considerations

All reagents and solvents were purchased from commercial sources (Sigma-Aldrich, Acros). They were all analytical grade and used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica60F₂₅₄ TLC aluminium foils (Merck). Column chromatography was carried out on Silica gel 60 (particle size 0.04 - 0.063 mm; deactivated), purchased from Macherey-Nagel. The titanium oxide (anatase) nanoparticles were purchased from nanograde[®] as a 20 wt.% suspension in isopropanol without any surfactants. TiO₂ paste (Ti-Nanoxide T/SP) and the sealing foil (Meltonix 1170-25) were purchased from Solaronix.

Instruments

NMR spectra were recorded with Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz), and Jeol EX 400 (400 MHz) spectrometers. IR spectra were recorded on a Bruker Tensor 27 (ATR or ZnSe plate) spectrometer. A Varian Cary 5000 and Shimadzu UV-3102 PC were used for UV-Vis measurements. Fluorescence spectra were obtained from a Shimadzu RF-5301 PC. Mass spectrometry was carried out with a Shimadzu AXIMA Confidence (MALDI-TOF, matrices: 2,5-dihydroxybenzoic acid (dcb), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (dctb). High resolution mass spectrometry (HRMS) was performed on a Bruker microTOF II focus and a Bruker maXis 4G. For DLS measurements and determination of the zeta potentials, a Zetasizer Nano series ZEN3600 (Malvern Instruments) was used. The device uses a red laser for measurements. TGA experiments were carried out on a TG-209 F1 Libra (Netzsch) with nitrogen as protective and nitrogen and oxygen as carrier gas. The centrifuge was a Heraeus Multifuge X1R (Thermo scientific).

2) Synthesis

Synthetic procedures

Synthesis of *N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-(4-(*tert*-butoxycarbonyl)phenyl)ethynyl-isophthalamide (**5**):

Under inert conditions 0.27 g (0.90 mmol; 1.0 eq) *tert*-butyl 4-iodobenzoate **4** were dissolved in 15 mL dry THF and 10 mL NEt₃. After addition of 2 mg Pd(PPh₃)₂Cl₂, 1 mg PPh₃ and 2 mg CuI, the mixture was stirred for 15 min at RT before 0.61 g (1.08 mmol; 1.2 eq) *N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-ethynyl-isophthalamide **3** in 5 mL dry THF were added dropwise within a period of 1 min. The yellow solution was stirred for 18 h at RT before the residue was filtered off and the solvent was distilled under reduced pressure. Purification was achieved using column chromatography (SiO₂, DCM/EtOAc 2:1). The Product was obtained as a yellowish solid. Yield: 0.53 g (79 %).

¹H-NMR (THF-d₈, 400 MHz, RT): δ [ppm] = 9.69 (br, 2 H, NH), 9.04 (br, 2 H, NH), 8.51 (s, 1 H, PhH), 8.31 (s, 2 H, PhH), 8.02 (m, 6 H, PhH), 7.73 (t, ³J = 8.1 Hz, 2 H, PhH), 7.64 (d, ³J = 8.5 Hz, 2 H, PhH), 2.27 (s, 4 H, CH₂), 1.60 (s, 9 H, O^tBuCH₃), 1.09 (s, 18 H, ^tBuCH₃); ¹³C-NMR (THF-d₈, 100.5 MHz, RT): δ [ppm] = 170.9 (2 C, C=O), 165.1 (1 C, C=O), 164.8 (2 C, C=O), 151.8 (2 C, PhC), 151.2 (2 C, PhC), 140.6 (2 C, PhC), 136.8 (2 C, PhC), 134.4 (2 C, PhC), 133.1 (1 C, PhC), 132.2 (2 C, PhC), 130.3 (2 C, PhC), 127.9 (1 C, PhC), 127.5 (1 C, PhC), 124.4 (1 C, PhC), 110.5 (2 C, PhC), 110.3 (2 C, PhC), 91.0 (1 C, ethynyl C), 81.7 (1 C, ethynyl C), 60.5 (1 C, O^tBu-C), 50.8 (2 C, CH₂), 31.7 (2 C, ^tBu-^oC), 30.1 (6 C, ^tBuCH₃), 28.3 (3 C, O^tBuCH₃). HRMS (ESI): calculated: m/z = 745.370810, measured: m/z = 745.371667 [M]⁺; UV-Vis (THF): λ = 231, 300 nm; IR (ATR): $\tilde{\nu}_{\max}$ = 3288, 2954, 2868, 1734, 1700, 1696, 1584, 1507, 1443, 1239, 1152, 1117, 1017, 859, 799, 694; M.p.: 168 °C.

Synthesis of *N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-(4-carboxyphenyl)-ethynyl-isophthalamide (**1**):

Under inert conditions 0.18 g (0.24 mmol; 1.0 eq) *N,N'*-Bis[6-(3,3-dimethylbutyrylamino)pyridin-2-yl]-5-(4-(*tert*-butoxycarbonyl)phenyl)ethynyl-isophthalamide **5** was dissolved in 10 mL formic acid and stirred for 16 h at RT. Afterwards, the excess of formic

acid was removed in vacuum to give the deprotected carboxylic acid **1** as a white solid. Yield: 0.16 g (99 %).

$^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz, RT): δ [ppm] = 13.15 (br, 1 H, OH), 10.66 (br, 2 H, NH), 10.01 (br, 2 H, NH), 8.52 (s, 1 H, PhH), 8.34 (s, 2 H, PhH), 8.01 (d, $^3J = 7.9$ Hz, 2 H, PhH), 7.83 (m, 8 H, PhH), 2.30 (s, 4 H, CH_2), 1.01 (s, 18 H, CH_3). $^{13}\text{C-NMR}$ (DMSO- d_6 , 100.5 MHz, RT): δ [ppm] = 170.9 (2 C, C=O), 165.4 (1 C, C=O), 164.5 (2 C, C=O), 150.5 (2 C, PhC), 149.9 (2 C, PhC), 140.0 (2 C, PhC), 134.94 (2 C, PhC), 133.84 (2 C, PhC), 131.8 (1 C, PhC), 128.1 (1 C, PhC), 126.0 (2 C, PhC), 122.3 (2 C, PhC), 110.6 (2 C, PhC), 110.1 (2 C, PhC), 90.4 (1 C, ethynyl C), 89.9 (1 C, ethynyl C), 49.0 (2 C, CH_2), 30.9 (2 C, ^qC), 29.6 (6 C, CH_3); HRMS (ESI): calculated: $m/z = 689.30821$ measured: $m/z = 689.30737$ $[\text{M}+\text{H}]^+$; UV-Vis (THF): $\lambda = 299$ nm; IR (ATR): $\tilde{\nu}_{\text{max}} = 3279, 2954, 2910, 2867, 1700, 1684, 1653, 1558, 1507, 1443, 1293, 1231, 1153, 859, 798, 771$; M.p.: > 300 °C.

$^1\text{H-NMR}$ of **1**

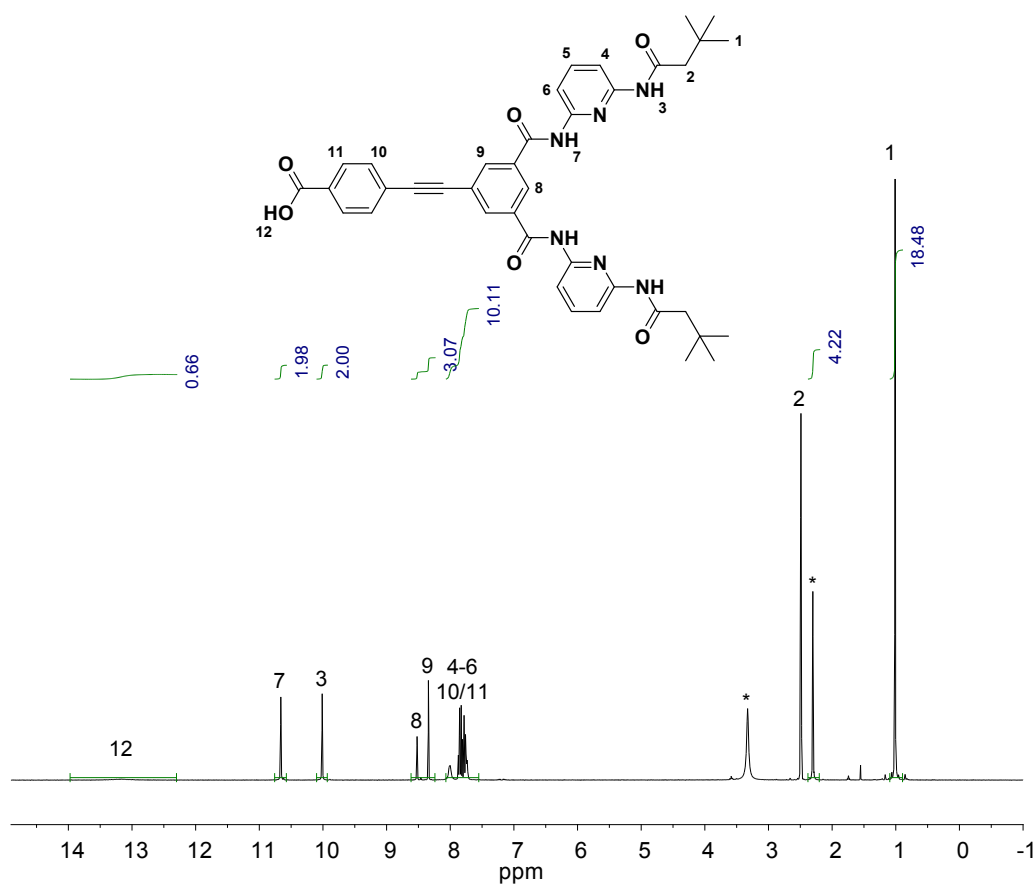


Fig. S1 $^1\text{H-NMR}$ of carboxylic acid Hamilton receptor **1** (400 MHz; rt; DMSO- d_6).

3) Supramolecular Coupling Investigations

Job's Plot Analysis

A Job's plot analysis of the titration data was carried out (Figure S2). To this end, the chemical shift variation of NH1 ($\Delta\delta$) was monitored as a function of the molar fraction of the porphyrin derivative C (**2**) and the product of the mole fraction X (fd) was plotted as a function of C. Well in line with the expectation, we found that the fitted curve showed a maximum at 0.5 C (**2**). Such a finding clearly confirmed the existence of a 1:1 stoichiometry.

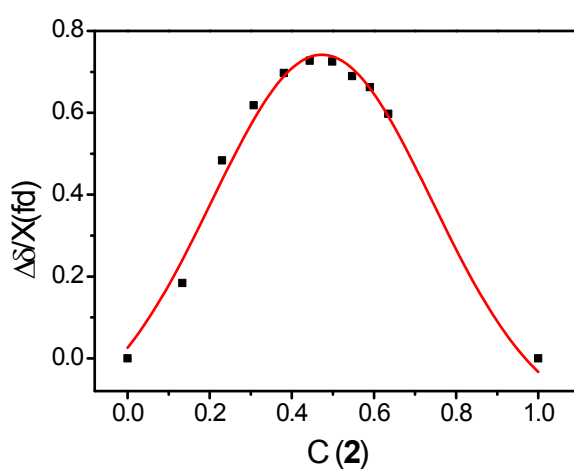


Fig.S2 Job's Plot analysis of the Hamilton receptor **5** – cyanurate **2** supramolecular complex. The maximum at ~ 0.5 demonstrated a 1:1 stoichiometry of the supramolecular complex;

Emission Spectroscopy

For a further characterization of a successful supramolecular coupling of **5** and **2**, emission spectra were recorded. Upon formation of the hydrogen complex a hypsochromic shift of the emission of the Hamilton receptor **5** from 528 nm to 509 nm was observed (Figure S3). The shift indicated electronic communication between the two molecules in the supramolecular complex.^{1,2}

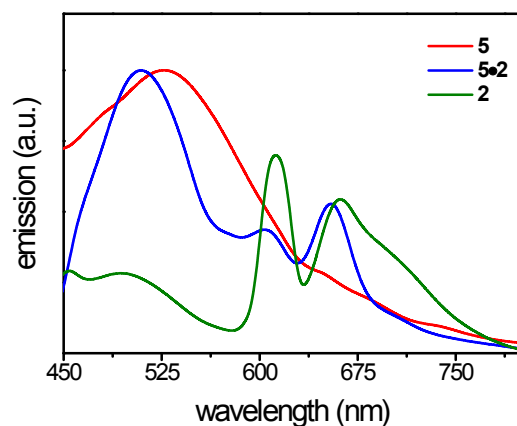


Fig.S3 Emission spectra of a 10^{-4} M solution of **5**, **2**, and **5•2** in chloroform.

4) Wet-chemical Surface Functionalization

Pure TiO₂ Nanoparticles:

The titanium dioxide (anatase) nanoparticles were purchased from nanograde[®] as a 20 wt% suspension in isopropanol without any surfactants. This was confirmed by TGA measurement and by recording IR spectra of the pure particles. Furthermore, DLS measurements gave an average hydrodynamic diameter of ~ 58.8 nm for these particles:

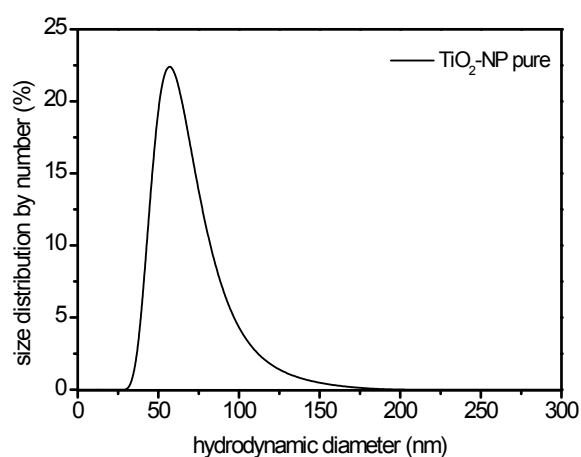


Fig. S4 DLS of initial TiO₂ nanoparticles (0.15wt.% in IPA).

BET Measurement

We performed a BET measurement to determine the specific surface area of the pure TiO₂ nanoparticles:

The particles were heated to 250 °C for 4 h before measurement. Analysis data:

relative pressure	volume @ STP cc/g	relative pressure	volume @ STP cc/g
1.47970e-03	-0.2453	8.66152e-01	55.4425
1.47970e-03	-0.2861	8.95600e-01	70.6593
1.64672e-03	-0.3062	9.26835e-01	111.6540
4.12733e-03	0.5100	9.62886e-01	194.6176
4.92312e-03	0.6672	9.91127e-01	204.9491
6.96989e-03	0.9981	9.93626e-01	206.7272
9.61624e-03	1.2991	9.95307e-01	214.5652
1.22490e-02	1.5584	9.51592e-01	199.5262
3.51518e-02	2.9176	9.50296e-01	199.2264
6.87770e-02	4.2210	9.22516e-01	187.3171
1.03359e-01	5.3801	8.85390e-01	90.6327
1.41452e-01	6.5900	8.49551e-01	58.1823
1.73343e-01	7.5837	8.00426e-01	41.3479
2.05954e-01	8.5863	7.73412e-01	36.5499
2.40930e-01	9.6394	7.39636e-01	32.1058
2.74210e-01	10.6291	6.98742e-01	28.4158
3.04949e-01	11.5244	6.53819e-01	25.3734
3.38728e-01	12.5072	6.17752e-01	23.3308
3.74576e-01	13.5624	5.77336e-01	21.3060

4.07380e-01	14.5282	5.40498e-01	19.7439
4.50741e-01	15.9212	5.02737e-01	18.2679
4.81954e-01	16.9519	4.68978e-01	17.0105
5.13729e-01	18.0645	4.27950e-01	15.5520
5.47527e-01	19.3768	3.90748e-01	14.2885
5.80398e-01	20.7663	3.58999e-01	13.2321
6.22837e-01	22.8402	3.22523e-01	12.0873
6.52489e-01	24.4504	2.83010e-01	10.8350
6.90063e-01	26.8718	2.73332e-01	10.5156
7.19672e-01	29.3519	2.51907e-01	9.8601
7.56272e-01	32.9118	2.11190e-01	8.5164
7.86376e-01	36.7613	1.83723e-01	7.5853
8.40683e-01	47.2766	1.57144e-01	6.6900

MBET summary:

Slope = 63.547

Intercept = 1.106e+01

Correlation coefficient, $r = 0.999949$

C constant = 6.748

Surface Area = 46.680 \sim sm/g

Experimental Functionalization Procedure

The TiO₂ nanoparticles were functionalized in a wet-chemical functionalization process in 0.15 wt% dispersions in isopropanol. To ensure a full coverage the particles were exposed to different concentrations of **1** (from 0.34 mM to 5 mM). The particles were functionalized in a volume of 25 mL, corresponding to \sim 30 mg nanoparticles. After adding the phosphonic acid, the dispersions were sonicated for 30 min. After functionalization the mixture was centrifuged for 10 min (14.000 rpm). The functionalization included three washing steps. A

washing step included redispersion of the particles in isopropanol followed up by another sonication step for 10 min and centrifugation. Finally, the particles were dried (80°C) or converted into a desired solvent for characterization (chloroform) while maintaining the particle concentration (0.15 wt%). To determine the maximum grafting density and the parameters needed for a complete monolayer surface functionalization we performed TGA measurements of all samples. TGA was measured with nitrogen as protective gas and nitrogen and oxygen (80%:20%) as carrier gas.

Determination of the Langmuir Isotherm and maximum monolayer grafting density

For determination of grafting density for each concentration we employed the following formula:³

$$\text{grafting density} = \left(\frac{wt}{100 - wt} \right) \left(\frac{6,022 * 10^{23}}{MW * SSA} \right)$$

(wt: weight loss in TGA; MW: molecular weight of **1**; SSA: specific surface area of TiO₂ nanoparticles)

Functionalization of TiO₂-NPs with carboxylic acid Hamilton receptor **1** yielding **TiO₂•1**:

Experimental results of the TGA measurements:

c (1) (mM)	wt.loss (%)	provided molecules (nm⁻²)	grafting density (θ) (nm⁻²)	1/c (M⁻¹)	1/θ (nm²)
0.34	4.31	3.71	0.86	2941.18	1.1686
0.52	4.95	5.67	0.99	1923.08	1.0111
1.00	5.80	10.91	1.17	1000.00	0.8552
1.95	6.39	21.27	1.30	512.82	0.7718
5.00	6.78	54.55	1.38	200.00	0.7237

A plot of the reciprocal values of the experimental data (1/grafting density vs. 1/concentration) resulted in figure S5. This data was fitted linearly. A linear fit of the experimentally determined data resulted in a linear equation, from which the value of the maximum monolayer grafting density (intercept) was extracted according to the linear form of the Langmuir equation:

$$\frac{1}{\hat{I}_s} = \frac{K_{des}}{\hat{I}_{s,max}} * \frac{1}{c} + \frac{1}{\hat{I}_{s,max}}$$

From the intercept of this linear fit the maximum monolayer grafting density for this functionalization process was determined to 1.4 molecules/nm².

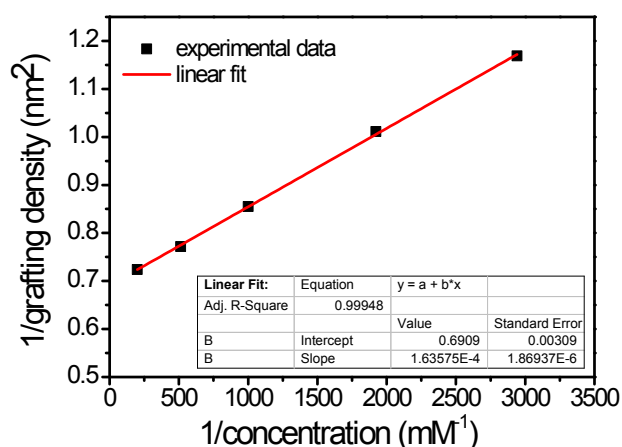


Fig. S5 Plot of the reciprocal values of the calculated grafting density versus the applied concentration during particle functionalization. A linear fit of the experimentally determined data is displayed in red.

linear fit	y = b*x + a	
R ²	0.99	
	value	standard error
intercept (a)	0.6909	0.0031

$$\hat{I}_{s,max} = \frac{1}{a} = \frac{1}{0.6909} = 1.44 \text{ nm}^{-2} \pm 0.01 \text{ nm}^{-2}$$

A binding isotherm was calculated using the data of the linear fit and compared to the experimentally determined grafting densities in a plot versus the applied concentrations of **1**, as depicted in Figure S6.

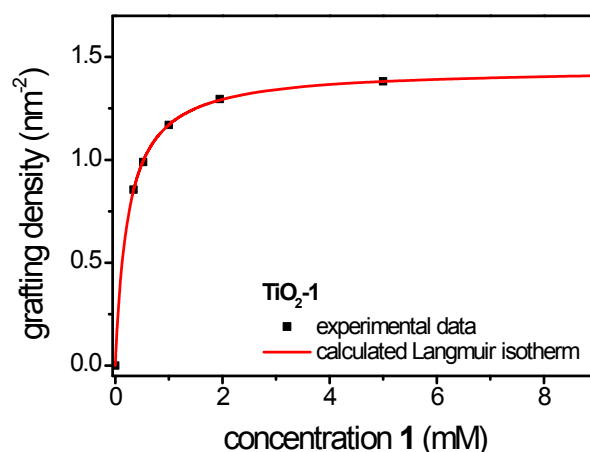


Fig. S6 Experimentally determined Langmuir isotherm for the monolayer adsorption of **1** on TiO₂ nanoparticles (particle concentration: 0.15 wt.% in isopropanol; room temperature; functionalization time: 30 min).

5) Self-assembly of porphyrins on TiO₂ nanoparticles

Experimental procedure for hydrogen bonding interaction driven self-assembly on nanoparticle surfaces

In a typical experimental procedure, the porphyrin cyanurate **2** was added in 0.5 mM concentration to functionalized nanoparticle counterparts TiO₂•**1** in a 0.15 wt.% dispersion. The hydrogen bonding complex formation was accomplished in chloroform. Pristine coated nanoparticles were transferred into the apolar solvent before the supramolecular coupling. The particles were transferred into the chloroform by centrifugation (14.000 rpm; 10 min), removal of the supernatant, and subsequent redispersion of the precipitate in chloroform. The functionalization of coated 2D substrates was accomplished by immersion into a solution of the cyanurate **2** in 0.5 mM concentration for 24 h. A general procedure for supramolecular functionalization of nanoparticles included a sonication step (30 min).

Experimental procedure for hydrogen bonding interaction driven self-assembly on 2D TiO₂ thin layer

For the time-dependent absorption study presented in Figure 3 of the manuscript a transparent nanocrystalline TiO₂ layer (Ti-Nanoxide T/SP, Solaronix; thickness: 7 μm) was prepared on an untreated glass slide by using a doctor blade technique. This glass slide was then exposed to Hamilton receptor **1** in isopropanol (0.5 mM) for 24 h for complete monolayer coverage of the TiO₂ nanoparticles. Aiming for a supramolecular coupling of porphyrin cyanurate **2** the glass slide was immersed into a chloroform solution of porphyrin cyanurates **2** (0.5 mM). In order to exchange the surface-adsorbed porphyrin cyanurates **2** against *tert*-butyl 8-(cyanurato)octanoate⁴ (cy.ac.) the glass slide was immersed into a 2.0 mM chloroform solution of *tert*-butyl 8-(cyanurato)octanoate.

6) Assembly of DSSCs

Fluorine-doped tin-oxide (FTO) substrates were sonicated for 15 min with a detergent solution, washed with deionized water, and again sonicated in isopropanol for 15 min. FTOs were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. Treated substrates were sintered at 450 °C for 30 min. The transparent nanocrystalline TiO₂ layers were prepared on FTO glass plates for DSSCs by using a doctor blade technique and pre-dried at 125 °C for 6 min. The TiO₂ anodes were gradually heated under air flow to 325 °C and held for 5 min, further heated to 375 °C and held for 5 min, heated to 450 °C and held for 30 min, and finally sintered at 500 °C for 15 min. The final thickness of TiO₂-based electrodes was 7 μm. For the TiO₂ functionalization, the electrodes were immersed at around 80 °C in the corresponding solutions.

For preparation of the counter-electrodes two holes (0.1 mm) were drilled into FTOs *via* sandblasting prior to the cleaning procedure (*vide supra*). FTOs were coated with a thin film of chloroplatinic solution (4.88 mM) in isopropanol. Thereby, always the same amount of chloroplatinic solution (26 μL) was used to assure the same coverage of the FTO. Then, the slides were annealed to 390 °C for 15 min. For every measurement counter-electrodes were freshly prepared to assure reproducible results.

The photoanodes and the counter-electrodes were assembled into a sealed sandwich-type cell by heating at 130 °C with a controlled pressure using a hot-melt ionomer film (Surlyn). The electrolytes were introduced *via* capillary forces. Finally, the two holes were sealed using an additional Surlyn and a cover glass.

Afterwards, the electrolyte was filled into the cell *via* capillary forces. The electrolyte composed of 0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M I₂, 0.1 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in a mixture of acetonitrile/valeronitrile (85:15, v/v). For every experiment four cells were assembled to prove good reproducibility.

7) Characterization of DSSCs

The photocurrent measurements were performed using a 150 W lamp (Xenon lamp, calibrated to 1000 W m⁻² under AM 1.5G conditions with a Si-Reference cell (Oriel SRC-1000-TC-K-KG5-N). Current-voltage measurements were measured by using a potentiostat/galvanostat (PGSTAT30N, Autolab equipped with a frequency response analyzer module – FRA) in the range of -0.9 to 0.2 V. DSSCs were measured by using a shading mask with an aperture size according to the literature.⁵ Incident photon-to-current efficiency (IPCE) spectra were measured by using Newport apparatus model 70104. For alpha-step thickness measurements of the TiO₂-based electrodes a Dektak XT profilometer from Bruker was utilized.

7) References

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