SUPPORTING INFORMATION

Photocurrent generation in organic photodetectors with tailor made active layers fabricated by layer-by-layer deposition

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Instrumentation and Analysis

Nuclear Magnetic Resonance

NMR spectra were recorded at room temperature in deuterated solvents on 400 MHz JEOL NMR spectrometers (JEOL Ltd., Japan). Chemical shifts (δ) are reported in units of parts per million relative to tetramethylsilane. All ¹H spectra were referenced to proton signals of residual undeuterated solvents, ¹³C spectra were referenced to carbon signals of the solvent. Coupling constants (J) are given in Hertz (Hz).

Mass spectrometry

ESI accurate masses were measured on a MicroTof (Bruker Daltronics, Bremen, Germnay) with loop injection. Mass calibration was performed using sodium formate cluster ions immediately folled by the sample in a quasi internal calibration.

MALDI mass spectra were recorded on an Autoflex Speed (Bruker Daltonics, Bremen, Germany). A SmartBeamTM NdYAG-Laser with 355nm wavelength was used.

Contact Angle

Water contact angles were measured by the sessile drop method on a DSA 100 goniometer (Krüss GmbH Wissenschaftliche Laborgeräte, Germany).

X-ray photoelectron spectroscopy

XPS measurements were performed with an Axis Ultra DLD (Kratos Analytical Ltd, UK). A monochromatic Al K α source (hv = 1486.6 eV) at 10 mA filament current and 12 kV filament voltage source energies was used. The pass energy was set to 20 eV for high resolution scans and to 160 eV for survey scans. The charge neutralizer was used to compensate for sample charging. All measurements were carried out in the "hybrid mode". The data were evaluated with CasaXPS (version 2.3.15, Casa Software Ltd, UK) and the spectra were calibrated to aliphatic carbon (C1s = 285 eV).

Ellipsometry

Ellipsometry was performed using "The Multiskop" build by "Optrel GBR" (Kleinmachnow, Germany). The build in software of the machine was used to analyze the data.

UV/vis spectroscopy

UV/vis spectra were recorded on a Shimadzu UV-3100PC spectrophotometer.

Photocurrent Measurements

Photocurrents were measured by exposing the samples to chopped light from a blue LED at a wavelength of 427 nm and a frequency of 0.2 Hz in a homebuilt circuit. The chopped light was generated with a Tektronix AFG320 function generator. The photocurrents were amplified with a current amplifier (Femto DLPCA-200, Germany) and recorded on an oscilloscope (Tektronix TDS5104B, USA).

General Procedures and Materials

Chemicals were obtained from commercial suppliers and used without further purification. Dehydrated solvents were obtained from WAKO Pure Chemical Industries Ltd. (Japan). Analytical thin-layer chromatography was performed on TLC silica gel 60 F254 (Merck KGaA, Germany). Purifications by column chromatography over silica were carried out using silica gel C-200E (Wako Ltd., Japan).



Scheme 1. Synthesis of 5,10,15,20-tetra(4-ethynylphenyl)porphyrinzinc(II) 1

5,10,15,20-Tetrakis-(4-[(trimethylsilyl)ethynyl]phenyl)porphyrin S1

Following a published procedure,¹ 4-[(trimethylsilyl)ethynyl]-benzaldehyde (1 g, 5 mmol, 1 eq) was brought to reflux in propionic acid (35 mL) in the dark. Pyrrole (0.35 mL, 5 mmol, 1 eq) was added and the solution was stirred for 2 h. The solution was cooled down to room temperature, filtered and washed with methanol until the filtrate turned colorless. The purple filter cake was then purified by column chromatography (dichlormethane/pentane = 2/3) to give **S1** as a purple solid (365 mg, 30%). The analytical data is in agreement with the reported data.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 8H, β-pyrrole), 8.15 (d, J = 8.0 Hz, 8H, *o*-ArH), 7.87 (d, J = 8.0 Hz, 8H, *m*-ArH), 0.38 (s, 36H, SiMe₃), -2.84 (s, 2H, pyrrole NH).

MS-ESI-ToF (+): found 999.4145, calculated 999.4124 (C64H62N4Si4H)

5,10,15,20-Tetrakis-(4-[(trimethylsilyl)ethynyl]phenyl)porphyrin-zinc(II) S2

S1 was synthesized following a published procedure with small modifications.¹ **S1** (750 mg, 0.75 mmol, 1 eq.) was dissolved in dry dichlormethane (150 mL) under nitrogen and $Zn(OAc)_2 * 2$ H₂O (330 mg, 1.5 mmol, 2 eq.) in dry methanol (20 mL) was added to the solution. The reaction was stirred at room temperature overnight, washed with NaHCO₃ (5%, aq, 3 x 200 mL) and water

 $(2 \times 200 \text{ mL})$ and dried over Na₂SO₄. The solvent was evaporated and S2 was further reacted to the final product 1 without any intermediate purification procedures.

5,10,15,20-Tetrakis-(4-(ethynyl)phenyl)porphyrin-zinc(II) 1

1 was synthesized following a published procedure with small modifications.² Tetrabutylammoniumfluoride (980 mg, 3.75 mmol, 5 eq.) in dry THF (10 mL) was added to a solution of **S2** (800 mg, 0.75 mmol, 1 eq.) in dry THF (130 mL) under a nitrogen atmosphere. Na₂CO₃ (aq, 5%) was added to the reaction mixture after 30 min and a purple solid precipitated, which was filtered off and rinsed with copious amounts of water to give the final product **1** (513 mg, 88%). The analytical data is in agreement with the reported data.

¹H NMR (400 MHz, THF- d_8) δ 8.88 (s, 8H, β-pyrrole), 8.19 (d, J = 8.0 Hz, 8H, o-ArH), 7.88 (d, J = 8.0 Hz, 8H, m-ArH), 3.79 (s, 4H, acetylene H).

¹³C NMR (75 MHz, *d*-DMSO) δ 149.08, 143.25, 134.42, 131.79, 130.02, 121.02, 119.69, 83.62, 81.86.

MS-MALDI (+), DCTB matrix : found 772.13, calculated 772.16 (C52H28N4Zn)



Scheme 2. Synthesis of 1,3,5-tris(azidomethyl)benzene 2

1,3,5-tris(bromomethyl)benzene S3³

Mesitylene (2.78 mL, 20 mmol, 1 eq.), N-bromosuccinimide (12.460 g, 70 mmol, 3.5 eq.) and azobisisobutyronitrile (820 mg, 5 mmol, 25 mol%) were refluxed in benzene (150 mL) overnight and then stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue recrystallized from hot hexane/ethanol (1/1). White needles crystallized out upon cooling (1.390 g, 20%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 (s, 3H, ArylH), 4.45 (s, 6H, CH₂).

1,3,5-tris(azidomethyl)benzene 2⁴

S3 (1.000 g, 2.8 mmol, 1 eq.) and sodium azide (1.092 g, 16.8 mmol, 6 eq.) were warmed up to 80 °C in DMF (15 mL) under a nitrogen blanket. Water was added after 20 h and the mixture extracted with dichlormethane (3 x 25 mL). The combined organic phases were washed with brine, dried over Na₂SO₄ and the solvent was removed under reduced pressure. Column chromatography with DCM/hexane (1/1) yielded the product as a yellow oil (585 mg, 86%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 (s, 3H, ArylH), 4.40 (s, 6H, CH₂).



Scheme 3. Synthesis of Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amin (TBTA)

(Azidomethyl)benzene S3⁵

Sodium azide (4.88 g, 75 mmol, 1.5 eq.) was slowly added to a solution of (bromomethyl)benzene (6 mL, 51 mmol, 1 eq.) in water/acetone (1/4, 375 mL) at room temperature and stirred for 24 h at room temperature. Ethyl acetate was added (100 mL), the organic and aqueous phases were separated and the aqueous phase was extracted with ethyl acetate (3 x 100 mL). The combined organic phases were washed with water (2 x 100 mL), dried over Na_2SO_4 and concentrated under vacuum to yield the product **S3** as a slightly yellow oil (4.47 g, 65%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.10 (m, 5H, ArylH), 4.35 (s, 2H, CH₂).

Tris[(1-benzyl-1H-1,2,3-triazol-4-yl)methyl]amin (TBTA) S4⁶

(Azidomethyl)benzene **S3** (3.000 g, 22.5 mmol, 3 3q.), trispropargyl amine (0.984 g, 7.5 mmol, 1 eq.), CuSO₄ (64 mg, 0.4 mmol, 5 mol%) and sodium ascorbate (218 mg, 1.1 mmol, 15 mol%) were dissolved in a one to one mixture of dichlormethane and water (100 mL) and vigorously stirred under a nitrogen atmosphere at room temperature overnight. The organic and the aqueous phases were separated after the addition of water (50 mL) and DCM (50 mL). The aqueous phase was extracted with DCM (3 x 50 mL) and the combined organic phases were washed with water (100 mL) and brine (100 mL), dried over Na₂SO₄ and concentrated under reduced pressure to yield **S4** as a white solid (2.857 g, 5.4 mmol, 72%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 3H, TriazoleH), 7.39 (m, 9H, *m*-ArH, *p*-ArH), 7.31 (m, 6H, *o*-ArH), 5.55 (s, 6H, Triazole-C*H*₂-Aryl), 3.74 (s, 6H, N-C*H*₂-Triazole).

¹³C NMR (400 MHz, Chloroform-*d*) δ 144.50, 134.93, 129.26, 128.85, 128.18, 123.90, 54.19, 47.17.



Figure S 1. NMR spectra of 5,10,15,20-Tetrakis-(4-(ethynyl)phenyl)porphyrin-zinc(II) 1. Top: proton-NMR in THF, bottom: carbon-NMR in DMSO.



Figure S 2. Proton-NMR spectrum of 1,3,5-tris(azidomethyl)benzene 2 in chloroform.

Preparation of azide functionalized self-assembled monolayers

Patterned ITO substrates were cleaned by sonification for 3 min in dichlormethane, acetone, ethanol and twice in water. Then, they were activated in a mixture of $H_2O:NH_3$ (aq. conc.): H_2O_2 (aq. conc.) (5:1:1 volume fractions), rinsed with copious amounts of water, dried in a stream of nitrogen and transferred into a solution (3-bromopropyl)trichlorosilane (0.1 v% in dry toluene) under a blanket of nitrogen. The samples were taken out of the solution after stirring for 15 min. at room temperature, rinsed with toluene, ethanol and water and dried in a stream of nitrogen. The azide substitution was carried out in a saturated solution of sodium azide in dry DMF for two days at 80 °C under a blanket of nitrogen. The azide functionalized surfaces were sonicated in water for 3 min, rinsed with water and ethanol and dried in a stream of nitrogen in the fridge prior to use.

Self-assembled monolayers on silicon were used for contact angle, ellipsometry and XPS analysis. The silicon was activated in piranha solution ($H_2SO_4(konz)$: $H_2O_2(30\%) = 2:1$) for 30 min. All other steps were performed as on ITO.



Figure S 3. Contact angle of the activated surface (A) and the self-assembled monolayer with terminal bromides (B).



Figure S 4. XPS high resolution spectra for Br3d (A) and N1s (B) of the bromide and azide terminated self-assembled monolayers.

Layer-by-layer assembly of the active layer and device assembly

Two solutions were prepared for the layer-by-layer assembly of the active layer and kept in Schlenk flasks under an atmosphere of nitrogen:

A: Porphyrin 1 (1.3 mM), $CuSO_4*5H_2O$ (0.325 mM), Tris(benzyltriazolylmethyl)amine (0.358 mM) and sodium ascorbate (0.48 mM) in DMSO. Water content ca. 2%.

B: Azide 2 (2.2 mM), $CuSO_4*5H_2O$ (4.4 mM), Tris(benzyltriazolylmethyl)amine (4.8 mM) and sodium ascorbate (8.9 mM) in DMSO. Water content ca. 8%.

The azide terminated SAMs were first brought in contact with solution A for 6 min., rinsed with acetone, ethanol, dichlormethane and water. They were blown dry in a stream of nitrogen before they were immersed in solution B for 6 min. Next, they were rinsed with acetone, ethanol, dichlormethane, a solution of EDTA in water (1 mM) and water and blown dry in a stream of nitrogen. These two dipping steps were repeated until the desired number of layers was assembled on the surface.



Figure S 5. Survey, N1s and Zn2p XPS spectra of samples with one to 5 layers. The signals for nitrogen and zinc increase with layer number. The samples for XPS analysis were prepared on silicon wafers.

A solution of PVDF (4 w%) in 2-butanone was prepared by heating the solution to 120 °C. After cooling the solution, 100 μ L of the solution was dropped on the active layer and immediately spincoated at 2000 rounds per minute for 50 s.

The aluminium top electrodes were deposited by physical vapor deposition at a rate of 1 angstrom/s. The thickness of the aluminium electrodes was estimated with the build in quartz crystal microbalance to be roughly 100 nm.



Figure S 6. Change in transient photocurrent over time. The signal decreases to roughly 65% after 3 h of continuous irradiation.



Figure S 7. Left side: Maximal absorbance as a function of layers of porphyrin for four different batches. Right side: Normalized transient photocurrents for four different batches.

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