

Electronic Supplementary Information

Highly improved performance of Zn^{II} tetraarylporphyrinates in DSSCs by the presence of octyloxy chains in the aryl rings

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Experimental

General

All reagents and solvents used in the synthesis were purchased by Sigma Aldrich and used as received, except Et₃N (freshly distilled over KOH) and THF (freshly distilled from Na/benzophenone). Silica gel for gravimetric chromatography (Geduran Si 60, 63-200 µm) and for flash chromatography (Geduran Si 60, 40-63 µm) were purchased by Merck.

Glassware has been flame-dried under vacuum before use when necessary.

Microwave assisted reactions were performed using a Milestone MicroSYNTH instrument.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinate]Zn^{II} (**4**) was synthesized as previously reported in literature.¹

¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX-400 in CDCl₃ as solvent (Cambridge Isotope Laboratories, Inc.). Elemental analyses were carried out with a Perkin-Elmer CHN 2400 instrument in the Analytical Laboratories of the Department of Chemistry at the University of Milan. Mass spectra were collected with a VG Autospec M246 magnetic mass spectrometer with a LSIMS ionic source (FAB) or with a Bruker-Daltonics ICR-FTMS APEX II with an electrospray ionization source (ESI). Electronic absorption spectra were recorded using a Jasco V-530 spectrometer.

Electrochemical measurements

The voltammetric studies have been performed in a 4 cm³ cell, in 5 × 10⁻⁴ - 10⁻³ M solutions in dimethylformamide (Aldrich, 99.8%) with 0.1 M tetrabutylammonium perchlorate (TBAP, Fluka) as the supporting electrolyte. The solutions were de-aerated by N₂ bubbling. The ohmic drop has been compensated by the positive feedback technique.²

The experiments were carried out using an AUTOLAB PGSTAT potentiostat (EcoChemie, The Netherlands) run by a PC with GPES software. Cyclic voltammetry (CV) investigations were carried out at scan rates typically ranging 0.05 to 2 V s⁻¹, with ohmic drop compensation.

The working electrode was a glassy carbon one (AMEL, diameter = 1.5 mm) cleaned by synthetic diamond powder (Aldrich, diameter = 1 μm) on a wet cloth (STRUERS DP-NAP); the counter electrode was a platinum disk or wire. The operating reference electrode was an aqueous saturated calomel electrode, but the potentials were ultimately referred to the Fc⁺/Fc (ferrocinium/ferrocene) couple (the intersolvental redox potential reference currently recommended by IUPAC^{3, 4} by both external and internal standardization). To prevent water and chloride leakage into the working solution a compartment filled with the operating medium and ending with a porous frit was interposed between the reference electrode and the cell.

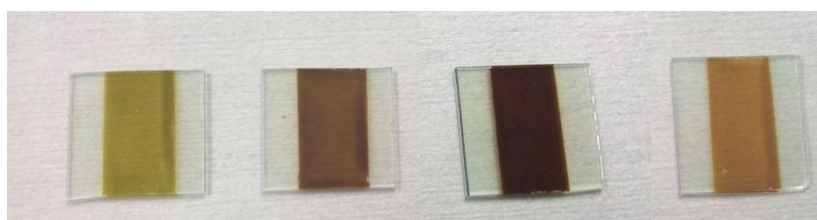
Preparation of DSSCs

Fluorine-doped tin oxide (FTO, 10 Ω/sq, provided by Solaronix S.A.) were cleaned in a detergent solution for 15 min and in EtOH for 30 min using an ultrasonic bath, rinsed with absolute EtOH. Therefore FTO plates were treated with a 40 mM aqueous solution of TiCl₄ for 30 min at 70 °C and then rinsed with EtOH. The photoelectrodes, deposited by doctor blading, were composed of a double layer of pastes with anatase nanoparticles of different dimensions: Dyesol 18NR-T, which gave transparent 9-μm TiO₂ films, and Solaronix D/SP, which was used as active opaque overlayer with thickness of 6 μm, resulting in an active layer of 15 μm. The coated films were dried at 125 °C for 5 min, after each layer deposition, and then thermally treated 450 °C for 30 min. The sintered layer was treated again with 40 mM aqueous TiCl₄ (70 °C for 30 min), rinsed with EtOH and heated at 450 °C for 30 min. After cooling to 80 °C the TiO₂ coated plate was immersed into a 0.2 mM solution of the dye in EtOH/THF 9:1 containing chenodeoxycholic acid (CDCA, 2 mM) for 4 h at room temperature in the dark. The thickness and the active area (0.16 cm²) of the photoanode was measured by means of a profilometer (DEKTAK 150TM from VEECO). The counter electrode was prepared according to the following procedure: a 1.8-mm hole was made in a FTO plate using diamond drill bits. The electrode was then cleaned for 30 min using a solution of EtOH and HCl and finally with acetone for 15 min, in an ultrasonic bath. After heating at 450 °C for 30 min, a 5 × 10⁻³ M solution of H₂PtCl₆ in EtOH was dropped on the cooled substrates and thus has been thermally treated at 530 °C for 1h. The dye adsorbed TiO₂ photo-electrode and counter electrode were assembled by heating a gasket made of a hot-melt ionomer-class resin (Surlyn 50-μm thickness). The electrolyte Z960⁵ (1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I₂, 0.05 M LiI, 0.10 M guanidinium thiocyanate, and 0.50 M 4-*tert*-butylpyridine in acetonitrile/valeronitrile,

85:15), identified among different electrolytes tested varying the components of the solution, was introduced inside the cell by vacuum backfilling.

Dye loading measurements

The surface concentrations (dye loading) of the dyes were assessed by spectrophotometric determination as follows: the sensitized photoelectrodes were placed in a solution of KOH (0.01 M) in THF/EtOH 1:1 for 4 h; the complete desorption was testified by the substrate discoloration; the calculation of the dye concentration in the desorbing solvent, obtained by UV-Vis measurements, allowed the evaluation of the amount of the adsorbed sensitizer, expressed in terms of moles of dye anchored per projected unit area of the photoelectrode.



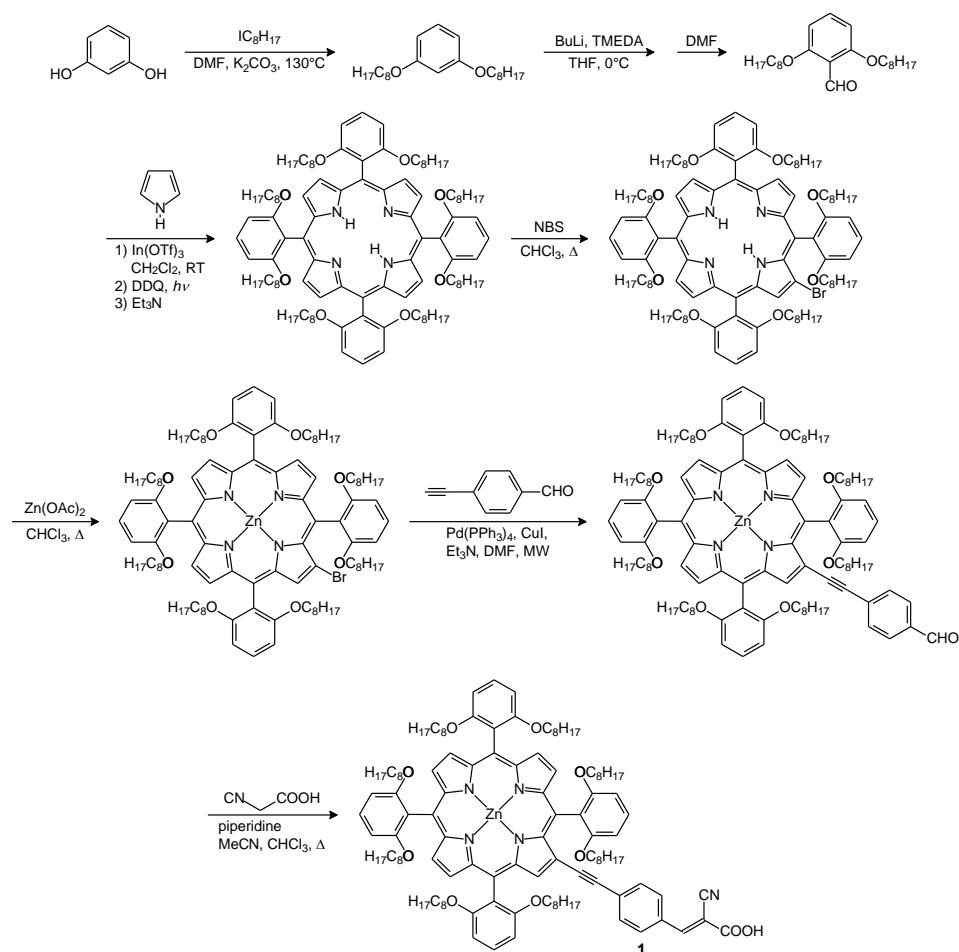
TiO₂ mesoporous electrodes sensitized with dyes **1-4**

Photoelectrochemical measurements

Photocurrent–voltage IV measurements were performed using a Keithley unit (Model 2400 Source Meter), while a Newport Sol3A Class AAA Solar Simulator (Model 94063A equipped with a 1000W xenon arc lamp) served as a light source. The light intensity (or radiant power) was calibrated to 100 mW cm⁻² using as reference a Si solar cell. Incident photon-to-current conversion efficiency (IPCE) measurements were carried out with a computerized setup consisting of a xenon arc lamp (140 W, Newport, 67005) coupled to a monochromator (Cornerstone 260 Oriel 74125). Light intensity was measured by a calibrated UV silicon photodetector (Oriel 71675) and the short circuit currents of the DSCs were measured by using an optical power/energy meter, dual channel (Newport 2936-C).

Electrochemical impedance spectroscopy (EIS) measurements were performed at different bias potentials under 1.0 sun illumination by using a PGSTAT 302N AUTOLAB operating in a frequency range between 300 kHz and 30 mHz. The resulting impedance spectra were fitted with the ZView software (Scribner Associates). EIS spectra were analyzed through the well-known equivalent circuit.

Synthesis of 1



1,3-Dioctyloxybenzene

In a dry Schlenk tube, 15.3 g of K_2CO_3 (0.11 mol, 2.4 equiv.) were suspended in 40 ml of DMF anhydrous over molecular sieves. Under stirring 5.0 g of resorcinol (45.0 mmol, 1.0 equiv.) and 20.1 ml of 1-iodooctane (0.11 mol, 2.4 equiv.) were added.

The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about $-90\text{ }^{\circ}\text{C}$, using a bath of liquid nitrogen and acetone. After the reaction mixture was allowed to warm to room temperature, it was heated at $130\text{ }^{\circ}\text{C}$ for 48 h under nitrogen atmosphere and stirring. It was left to return at room temperature again, then filtered and the solvent was evaporated to dryness *in vacuo*. The residual products were dissolved in 100 ml of AcOEt and washed with H_2O , the aqueous phase was extracted with AcOEt ($2 \times 100\text{ ml}$) and the combined organic phase was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (*n*-hexane/AcOEt 98:2). It was obtained 9.35 g of pure product (yield 62%).

1H -NMR (400.1 MHz, $CDCl_3$) δ , ppm: 7.17 (1H, t), 6.50 (3H, m), 3.95 (4H, t), 1.79 (4H, m), 1.47 (4H, m), 1.33 (16H, m), 0.91 (6H, t).

2,6-Dioctyloxybenzaldehyde

In a 250 ml three-neck round-bottom flask, equipped with a pressure-equalizing dropping funnel, 9.35 g of 1,3-dioctyloxybenzene (28.0 mmol, 1.0 equiv.) were de-aerated with three vacuum/nitrogen cycles and then dissolved in 76.7 ml of THF under nitrogen atmosphere. 1.12 ml of tetramethylethylenediamine (TMEDA) were added and the reaction mixture was cooled at 0 °C, then under stirring 22.7 ml of *n*-buthyllithium (1.6 M in *n*-hexane) were added dropwise in 30 min. After stirring for 3 h at 0 °C, the reaction mixture was allowed to warm to room temperature and 4.3 ml of DMF (56.0 mmol, 2 equiv.) were added dropwise and allowed to react overnight. The reaction was quenched with 150 ml of H₂O at 0 °C, then extracted with Et₂O (3 × 150 ml). The collected organic phase was dried over anhydrous MgSO₄ and the solvent was removed *in vacuo*. The solid crude product was recrystallized from the minimum quantity of *n*-hexane and then dried *in vacuo* overnight. 8.6 g of pure product were obtained (yield 85%).

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 10.56 (1H, s), 7.39 (1H, t), 6.55 (2H, d), 4.05 (4H, m), 1.85 (4H, m), 1.49 (4H, m) 1.33 (16H, m), 0.91 (6H, t).

5,10,15,20-Tetrakis(2,6-dioctyloxyphenyl)porphyrin

In an anhydrous 3 l round-bottom flask, to a solution 4.59 g of 2,6-dioctyloxybenzaldehyde (12.67 mmol, 1.0 equiv.) in 1.2 l of CH₂Cl₂, 0.878 ml of pyrrole (12.67 mmol, 1.0 equiv.) were added and N₂ was bubbling for 15 min. Under vigorous stirring 411.0 mg of In(OTf)₃ (0.731 mmol, 0.06 equiv.). Under nitrogen atmosphere the reaction was stirred for 24 h in the dark. Then 4.313 g of DDQ (19.0 mmol, 1.5 equiv.) and the reaction was stirred under light for 1 h. Finally 3.53 ml of Et₃N (25.3 mmol, 2.0 equiv.) were added and the stirring was maintained overnight. The solution were concentrated and filtrated onto chromatographic column with CH₂Cl₂, and the resulting product was purified by flash chromatography (*n*-hexane/CH₂Cl₂ 7:3) obtaining 0.795 g of product (yield 16%).

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 8.71 (8H, s), 7.68 (4H, t), 7.00 (8H, d), 3.80 (16H, t), 1.05-0.65 (120H, m), -2.51 (2H,s).

MS-FAB(+) *m/z*: calcd for C₁₀₈H₁₅₈N₄O₈ 1639, found 1640 [M+H]⁺.

2-Bromo-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrin

In a 100 ml round-bottom flask, equipped with an Allihn condenser ending with a CaCl₂ valve, 879.4 mg of 5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrin were dissolved in 60 ml of CHCl₃. Under stirring 133.6 mg of NBS (0.751 mmol, 1.4 equiv.) were added and then the reaction mixture was refluxed at 70 °C for 18 h. The solvent was removed at the rotary evaporator and the crude

product was purified by flash column chromatography (*n*-hexane/ CH₂Cl₂ 85:15 gradient to 65:35) obtaining 510.3 mg of product (yield 56%).

¹H-NMR (400.1 MHz, CDCl₃) δ , *ppm*: 8.81 (1H, s), 8.75 (4H, m), 8.62 (2H, s), 7.67 (4H, m), 6.97 (8H, m), 3.81 (16H, m), 1.06-0.62 (120H, m), -2.62 (2H, br s).

[2-Bromo-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrinate]Zn^{II}

In a two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 510.3 mg of 2-bromo-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrin (0.297 mmol, 1 equiv.) were dissolved in 60 ml of CHCl₃ and the resulting solution was heated to reflux. Under stirring a solution of 162.9 mg of Zn(OAc)₂·2H₂O (0.742 mmol, 2.5 equiv.) in 5 ml of CH₃OH was added dropwise, then the reaction mixture was refluxed for additional 6 h. The solvent was removed *in vacuo* and the crude product was dissolved in 30 ml di CHCl₃ again and washed with H₂O (3 × 50 ml), the organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated to dryness. 529.2 mg of product were obtained (quantitative yield).

¹H-NMR (400.1 MHz, CDCl₃) δ , *ppm*: 8.96 (1H, s), 8.79 (6H, m), 7.67 (4H, m), 6.98 (8H, m), 3.82 (16H, m), 1.01-0.60 (120H, m).

MS-FAB(+) *m/z*: calcd for C₁₀₈H₁₅₅BrN₄O₈Zn 1783, found 1783 [M]⁺.

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 21.6 mg of 4-ethynylbenzaldehyde (165.5 μ mol, 5 equiv.), 3.9 mg of Pd(PPh₃)₄ (3.31 μ mol, 10 mol-%) and 59.0 mg of [2-bromo-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrinate]Zn^{II} (33.1 μ mol, 1 equiv.) were dissolved in 4 ml of DMF anhydrous over molecular sieves and 12 ml of Et₃N. The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90 °C, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 1.0 mg of CuI (5.0 μ mol, 15 mol-%) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120 °C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/AcOEt 98:2), obtaining 6.6 mg of product (yield 11%).

¹H-NMR (400.1 MHz, CDCl₃) δ , *ppm*: 10.07 (1H, s), 9.15 (1H, s), 8.74 (6H, m), 7.87 (2H, d), 7.64 (6H, m), 6.96 (8H, m), 3.79 (16H, m), 1.06-0.57 (120H, m).

MS-FAB(+) *m/z*: calcd for C₁₁₇H₁₆₀N₄O₉Zn 1832, found 1832 [M]⁺.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrinate]Zn^{II} 1

In a dry Schlenk tube 65.0 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2,6-dioctyloxyphenyl)porphyrinate]Zn^{II} (36.0 μ mol, 1 equiv.) were dissolved in 3 ml di CHCl₃. A solution of 90.6 mg of cyanoacetic acid (1.064 mmol, 30 equiv.) in 3 ml of CH₃CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85 °C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di CHCl₃ and washed with 20 ml of brine. The organic phase was dried over anhydrous Na₂SO₄ and then purified by flash column chromatography (CH₂Cl₂/MeOH 95:5 gradient to 80:20), obtaining 49.9 mg of product (yield 73%).

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 9.04 (1H, s), 8.62 (6H, m), 8.13 (1H, s), 7.91 (2H, d), 7.58 (6H, m), 6.93 (8H, m), 3.76 (16H, m), 0.98-0.60 (120H, m).

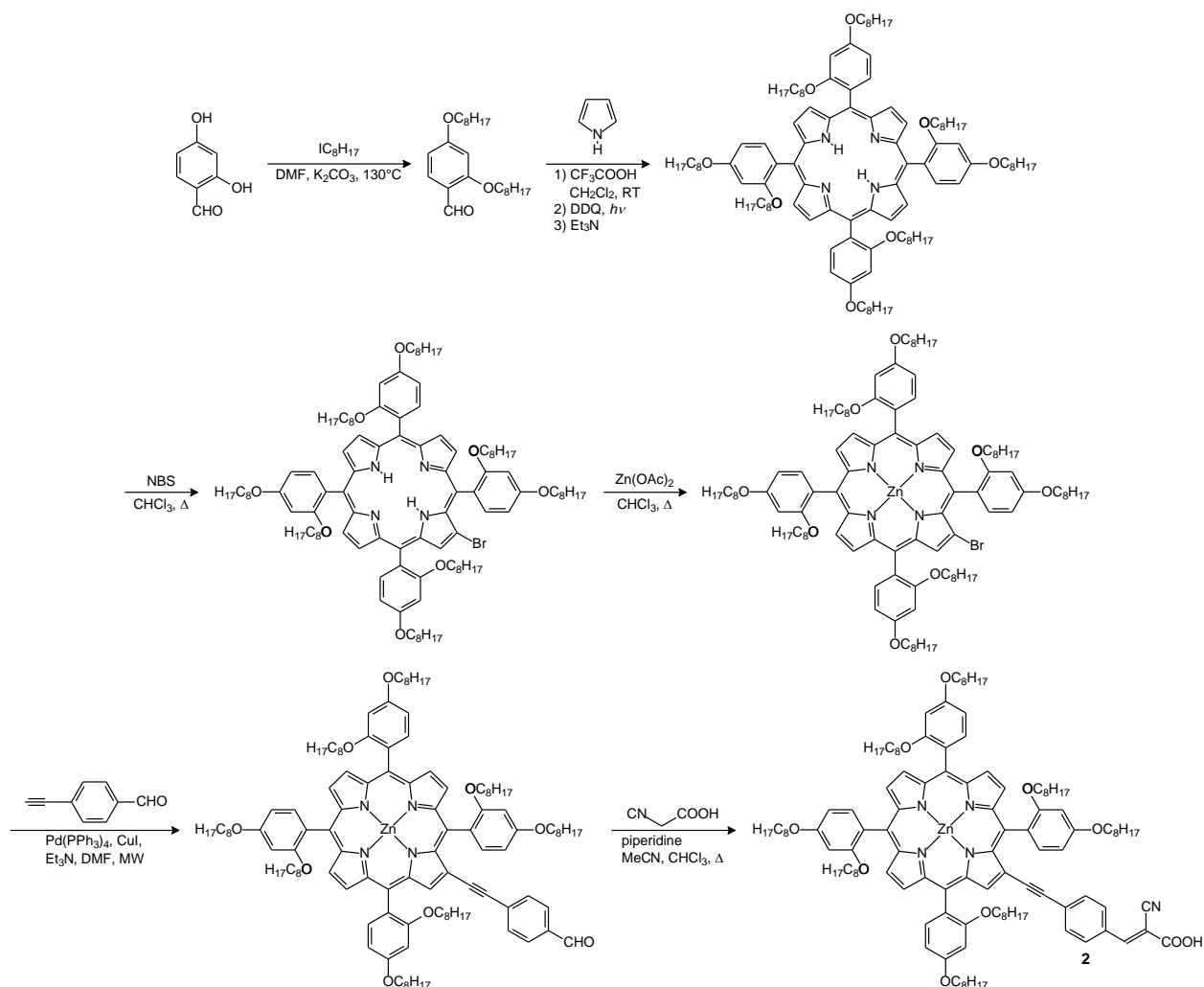
¹³C-NMR (400.1 MHz, CDCl₃) δ , ppm: 150.09, 137.99, 132.31, 130.68, 129.73, 129.02, 105.15, 68.43, 31.63, 28.79, 28.16, 25.19, 13.92.

Elemental analysis calcd (%) for C₁₂₀H₁₆₁N₅O₁₀Zn: C 75.90, H 8.55, N 3.69; found C 76.12, H 8.57, 3.67.

MS-FAB(+) *m/z*: calcd for C₁₂₀H₁₆₁N₅O₁₀Zn 1899, found 1899 [M]⁺.

MS-ESI(-) *m/z*: calcd for C₁₂₀H₁₆₀N₅O₁₀Zn (-1) 1895.14622, found 1897.14533 [M-H]⁻.

Synthesis of 2



2,4-Dioctyloxybenzaldehyde

In a dry Schlenk tube 2.28 g of K_2CO_3 (16.4 mmol, 2.3 equiv.) were suspended in 30 ml of DMF anhydrous over molecular sieves. Under stirring 1.0 g of 2,4-dihydroxybenzaldehyde (7.25 mmol, 1 equiv.) e 5.0 ml of 1-iodooctane (16.4 mmol, 2.3 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about $-94\text{ }^{\circ}\text{C}$, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at $130\text{ }^{\circ}\text{C}$ under nitrogen atmosphere for 24 h. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 150 ml of H_2O and extracted with of AcOEt ($3 \times 60\text{ ml}$). The combined organic phase was washed with 200 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 2.52 of product (yield 96%).

1H -NMR (400.1 MHz, $CDCl_3$) δ , ppm: 10.34 (1H, s), 7.80 (1H, d), 6.52 (1H, dd), 6.43 (1H, d), 4.03 (4H, m), 1.82 (8H, m), 1.47 (8H, m), 1.33 (8H, m), 0.90 (6H, m).

5,10,15,20-Tetrakis(2,4-dioctyloxyphenyl)porphyrin

In an anhydrous 3 l round-bottom flask 2.52 g of 2,4-dioctyloxybenzaldehyde (6.96 mmol, 1 equiv.) were dissolved in 759 ml of CH₂Cl₂ and 483.0 µl of pyrrole (6.96 mmol, 1 equiv.) were added. The solution was de-aerated bubbling nitrogen for 15 min. Under vigorous stirring 480.0 µl of trifluoroacetic acid (6.26 mmol, 0.9 equiv.) was slowly added dropwise. The reaction mixture was stirred for additional 3 h in the dark. Then 2.56 g of di DDQ (11.2 mmol, 1.6 equiv.) were added and the reaction was stirred under light for 1 h. Finally the reaction was quenched by addition of 3.5 ml di Et₃N (2.51 mmol, 3.6 equiv.) and allowed to stir overnight. The solution was concentrated and filtered through column chromatography (CH₂Cl₂) and then the product was purified by flash column chromatography (CH₂Cl₂) obtaining 376.0 mg of pure product as atropisomeric mixture (yield 13%).

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 8.80 (8H, s), 7.87 (4H, m), 6.89 (4H, s), 6.87 (4H, m), 4.28 (8H, m), 3.86 (8H, m), 2.01 (8H, m), 1.66 (8H, m), 1.55-0.51 (104H, m), -2.60 (2H, s).

MS-FAB (+) m/z : calcd for C₁₀₈H₁₅₈N₄O₈ 1639, found 1640 [M+H]⁺.

2-Bromo-5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrin

In a 50 ml round-bottom flask, equipped with an Allihn condenser, 100.0 mg of 5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrin (61.0 µmol, 1.0 equiv.) were dissolved in 20 ml of CHCl₃. 21.0 mg of NBS (112.0 µmol, 1.5 equiv.) were added and the reaction mixture was heated to reflux at 70 °C for 18 h. Then the solvent was removed *in vacuo*.

The preliminary analysis by mass spectrometry has revealed the presence, even if in trace amounts, of the di-bromo derivative, however from TLC analysis (*n*-hexane/CH₂Cl₂ 7:3) it was noticed that the mono-bromo and the di-bromo derivatives are not easily separable by chromatography, thus the crude product was used for the successive step of the synthesis without other purification.

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 8.79 (7H, m), 7.84 (4H, m), 6.88 (8H, s), 4.27 (8H, t), 3.89 (8H, m), 2.01-0.12 (120H, m), -2.66 (2H, m).

MS-FAB (+) m/z : calcd for C₁₀₈H₁₅₇BrN₄O₈ 1719, found 1720 [M+H]⁺.

[2-Bromo-5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrinate]Zn^{II}

In a 50 ml two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 104.0 mg of crude 2-bromo-5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrin (60.1 µmol, 1 equiv.) were dissolved in 30 ml of CHCl₃ and heated to reflux. A solution of 48.7 mg of Zn(OAc)₂·2H₂O (0.22 mmol, 2.6 equiv.) in 4 ml of CH₃OH was added dropwise, then the reaction mixture was allowed to reflux for 6 h. The solvents were removed and the crude product was

dissolved in 30 ml CHCl_3 , extract with H_2O (3×50 ml), dried over anhydrous Na_2SO_4 filtered and evaporated *in vacuo* to dryness, obtaining 105.6 mg of product (quantitative yield).

^1H -NMR (400.1 MHz, CDCl_3) δ , ppm: 8.93 (7H, m), 7.79 (4H, m), 6.87 (8H, m), 4.25 (8H, m), 3.86 (8H, m), 2.01 (8H, m), 1.65 (8H, m), 1.51-0.10 (104H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrinate] Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 426.0 mg of 4-ethynylbenzaldehyde (327 μmol , 5.5 equiv.), 70.0 mg of $\text{Pd}(\text{PPh}_3)_4$ (6.06 μmol , 10 mol-%) and 105.6 mg of [2-bromo-5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrinate] Zn^{II} (59.3 μmol , 1 equiv.) were dissolved in 4 ml of DMF anhydrous over molecular sieves and 12 ml Et_3N . The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about -90°C , using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 1.6 mg of CuI (8.9 μmol , 15 mol-%) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at 120°C in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/ AcOEt 9:1), obtaining 59.7 mg of product (yield 55%).

^1H -NMR (400.1 MHz, CDCl_3) δ , ppm: 10.07 (1H, s), 9.21 (1H, m), 8.84 (6H, m), 7.87 (4H, m), 7.61 (2H, d), 6.88 (8H, m), 6.77 (2H, m), 4.29 (8H, m), 3.85 (8H, m), 2.02 (8H, m), 1.66 (8H, m), 1.54-0.49 (104H, m).

MS-FAB (+) m/z : calcd for $\text{C}_{117}\text{H}_{160}\text{N}_4\text{O}_9\text{Zn}$ 1829, found 1831 $[\text{M}+\text{H}]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2,4-dioctyloxyphenyl)porphyrinate] Zn^{II} 2

In a dry Schlenk tube 59.7 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrinate] Zn^{II} (32.6 μmol , 1 equiv.) were dissolved in 5 ml di CHCl_3 . A solution of 55.4 mg of cyanoacetic acid (654.0 μmol , 20 equiv.) in 1.5 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to 85°C overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 30 ml di CHCl_3 and washed with 50 ml of H_2O . The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2 gradient to $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 9:1), obtaining 38.4 mg of product (yield 62%).

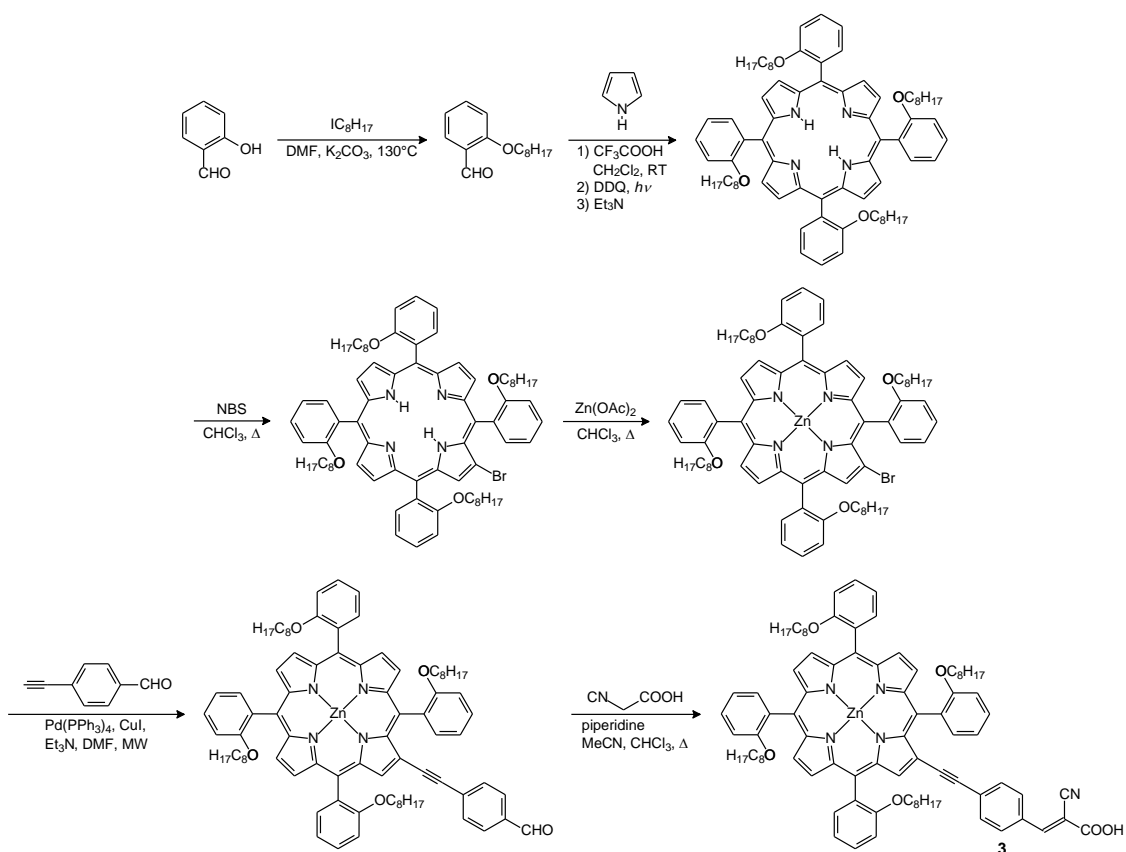
^1H -NMR (400.1 MHz, CDCl_3) δ , ppm: 9.22 (1H, br s), 8.81 (6H, m), 8.45 (1H, m), 8.16 (2H, m), 7.83 (4H, m), 7.57 (2H, m), 6.84 (8H, m), 4.26 (8H, m), 3.83 (8H, m), 1.98 (8H, m), 1.64 (8H, m) 1.48-0.11 (104H, m).

Elemental analysis calcd (%) for $\text{C}_{120}\text{H}_{161}\text{N}_5\text{O}_{10}\text{Zn}$: C 75.90, H 8.55, N 3.69; found C 76.19, H 8.61, 3.65.

MS-FAB (+) m/z : calcd for $\text{C}_{120}\text{H}_{161}\text{N}_5\text{O}_{10}\text{Zn}$ 1899, found 1899 $[\text{M}]^+$.

MS-ESI (-) m/z : calcd for $\text{C}_{120}\text{H}_{160}\text{N}_5\text{O}_{10}\text{Zn}$ 1895.14622, found 1895.15160 $[\text{M}-\text{H}]^-$.

Synthesis of 3



2-Octyloxybenzaldehyde

In a dry Schlenk tube 3.11 g of K_2CO_3 (22.5 mmol, 1.2 equiv.) were suspended in 25 ml of DMF anhydrous over molecular sieves. Under stirring 2.0 ml of salicylaldehyde (18.8 mmol, 1 equiv.) and 4.1 ml of 1-iodooctane (22.5 mmol, 1.2 equiv.). The reaction mixture was de-aerated with three freeze-pump-thaw cycles at about $-94^\circ C$, using a bath of liquid nitrogen and acetone. The mixture was allowed to warm to room temperature and then was heated at $130^\circ C$ under nitrogen atmosphere for 24 h. It was allowed to cool at room temperature, diluted with AcOEt and filtered. The obtained solution was diluted in 250 ml of H_2O and extracted with 300 ml of AcOEt. The combined organic phase was washed with 150 ml of an aqueous solution of KOH 1 M, separated and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* obtaining 4.35 g of product (quantitative yield).

1H -NMR (400.1 MHz, $CDCl_3$) δ , ppm: 10.54 (1H, s), 7.85 (1H, m), 7.54 (1H, m), 7.00 (2H, m), 4.18 (2H, m), 1.88 (2H, m), 1.53 (2H, m), 1.35 (8H, m), 0.91 (3H, m).

5,10,15,20-Tetrakis(2-octyloxyphenyl)porphyrin

In an anhydrous 3 l round-bottom flask 4.40 g of 2-octyloxybenzaldehyde (18.8 mmol, 1 equiv.) were dissolved in 1.88 l of CH_2Cl_2 and 1.3 ml of pyrrole (18.8 mmol, 1 equiv.) were added. The solution was de-aerated bubbling nitrogen for 15 min. Under vigorous stirring 1.3 ml of trifluoroacetic acid

(16.9 mmol, 0.9 equiv.) was slowly added dropwise. The reaction mixture was stirred for additional 3 h in the dark. Then 6.40 g of di DDQ (28.2 mmol, 1.5 equiv.) were added and the reaction was stirred under light for 1 h. Finally the reaction was quenched by addition of 9.4 ml di Et₃N (67.7 mmol, 3.6 equiv.) and allowed to stir overnight. The solution was concentrated and filtered through column chromatography (CH₂Cl₂) and then the product was purified by flash column chromatography (CH₂Cl₂) obtaining 1.95 g of pure product as atropisomeric mixture (yield 37%).

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 8.75 (8H, m), 7.98 (4H, m), 7.74 (4H, m), 7.32 (8H, m), 3.88 (8H, m), 1.06-0.57 (60H, m), -2.62 (2H, s).

MS-ESI (+) m/z : calcd for C₇₆H₉₄N₄O₄ 1127.73478, found 1127.73581 [M+H]⁺, 1149.72012 [M+Na]⁺.

2-Bromo-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrin

In a 50 ml round-bottom flask, equipped with an Allihn condenser, 100.0 mg of 5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrin (88.7 μ mol) were dissolved in 20 ml of CHCl₃. 26.8 mg of NBS (0.15 mmol, 1.7 equiv.) were added and the reaction mixture was heated to reflux at 70 °C for 18 h. Then the solvent was removed *in vacuo*.

The preliminary analysis by mass spectrometry has revealed the presence, even if in trace amounts, of the di-bromo derivative, however from TLC analysis (*n*-hexane/CH₂Cl₂ 7:3) it was noticed that the mono-bromo and the di-bromo derivatives are not easily separable by chromatography, thus the crude product was used for the successive step of the synthesis without other purification.

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 8.83 (7H, m), 8.07 (4H, m), 7.79 (4H, m), 7.34 (8H, m), 3.94 (8H, m), 1.86-0.19 (60H, m), -2.57 (2H, br s).

MS-FAB (+) m/z : calcd for C₇₆H₉₃BrN₄O₄ 1205, found 1205 [M]⁺.

[2-Bromo-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrinate]Zn^{II}

In a 100 ml two-neck round-bottom flask, equipped with an Allihn condenser and a dropping funnel, 107.0 mg of crude 2-bromo-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrin (88.7 μ mol, 1 equiv.) were dissolved in 30 ml of CHCl₃ and heated to reflux. A solution of 48.7 mg of Zn(OAc)₂·2H₂O (0.22 mmol, 2.5 equiv.) in 4 ml of CH₃OH was added dropwise, then the reaction mixture was allowed to reflux for 6 h. The solvents were removed and the crude product was dissolved in CHCl₃, extracted with H₂O (3 \times 50 ml), dried over anhydrous Na₂SO₄ filtered and evaporated *in vacuo* to dryness, obtaining 106.0 mg of product (yield 95%).

¹H-NMR (400.1 MHz, CDCl₃) δ , ppm: 9.03 (1H, m), 8.83 (6H, m), 8.03 (4H, m), 7.76 (4H, m), 7.31 (8H, m), 3.92 (8H, m), 1.35-0.49 (60H, m).

[2-(4'-Carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrinate]Zn^{II}

In an anhydrous Schlenk tube, under nitrogen atmosphere 54.7 mg of 4-ethynylbenzaldehyde (419 μmol , 5 equiv.), 9.7 mg of $\text{Pd}(\text{PPh}_3)_4$ (8.39 μmol , 10 mol-%) and 106.0 mg of [2-bromo-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrinate] Zn^{II} (83.9 μmol , 1 equiv.) were dissolved in 4 ml of DMF anhydrous over molecular sieves and 12 ml Et_3N . The reaction mixture was de-aerated with five freeze-pump-thaw cycles at about $-90\text{ }^\circ\text{C}$, using a bath of liquid nitrogen and acetone. The solution was allowed to warm to room temperature and transferred, under nitrogen flow, into a microwave quartz vessel. 2.4 mg of CuI (12.5 μmol , 15 mol-%) was added and after an additional bubbling of nitrogen for 10 min, the reaction was heated at $120\text{ }^\circ\text{C}$ in a microwave cavity for 1 h. The solvents were removed *in vacuo* and the crude product was purified by flash column chromatography (*n*-hexane/ AcOEt 9:1), obtaining 52.3 mg of product (yield 47%).

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3) δ , *ppm*: 10.03 (1H, s), 9.23 (1H, m), 8.85 (5H, m), 8.77 (1H, m), 8.03 (4H, m), 7.87 (2H, d), 7.77 (2H, m), 7.64 (1H, m), 7.59 (2H, m), 7.38 (8H, m), 7.26 (1H, m), 3.91 (8H, m), 1.09 (8H, m), 0.80-0.52 (52H, m).

MS-FAB (+) *m/z*: calcd for $\text{C}_{85}\text{H}_{96}\text{N}_4\text{O}_5\text{Zn}$ 1317, found 1319 $[\text{M}+\text{H}]^+$.

[2-(4'-((E)-2''-Cyano-3''-acrylic acid)-phenylethynyl)-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrinate]Zn^{II} 3

In a dry Schlenk tube 33.6 mg of [2-(4'-carboxyaldehyde-phenylethynyl)-5,10,15,20-tetrakis(2-octyloxyphenyl)porphyrinate] Zn^{II} (25.4 μmol , 1 equiv.) were dissolved in 5 ml di CHCl_3 . A solution of 21.7 mg of cyanoacetic acid (0.25 mmol, 10 equiv.) in 2 ml of CH_3CN and 2 drops of piperidine were added. Under nitrogen atmosphere the reaction mixture was heated to $85\text{ }^\circ\text{C}$ overnight. The solvents were removed *in vacuo* and the crude product was dissolved in 10 ml di CHCl_3 and washed with 20 ml of brine. The organic phase was dried over anhydrous Na_2SO_4 and then purified by flash column chromatography (CH_2Cl_2 gradient to $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 8:2), obtaining 19.4 mg of product (yield 56%).

$^1\text{H-NMR}$ (400.1 MHz, CDCl_3) δ , *ppm*: 9.19 (1H, m), 8.75 (6H, m), 8.46 (1H, br s), 8.07-7.96 (8H, m), 7.73-7.58 (8H, m), 7.35-7.24 (4H, m), 3.84 (8H, m), 1.86 (8H, m), 1.01-0.40 (52H, m).

Elemental analysis calcd (%) for $\text{C}_{88}\text{H}_{97}\text{N}_5\text{O}_6\text{Zn}$: C 76.25, H 7.05, N 5.05; found C 76.56, H 7.10, N 5.02.

MS-ESI(-) *m/z*: calcd for $\text{C}_{88}\text{H}_{96}\text{N}_5\text{O}_6\text{Zn}$ 1382.66576, found 1382.66536 $[\text{M}-\text{H}]^-$.

Additional electronic absorption data

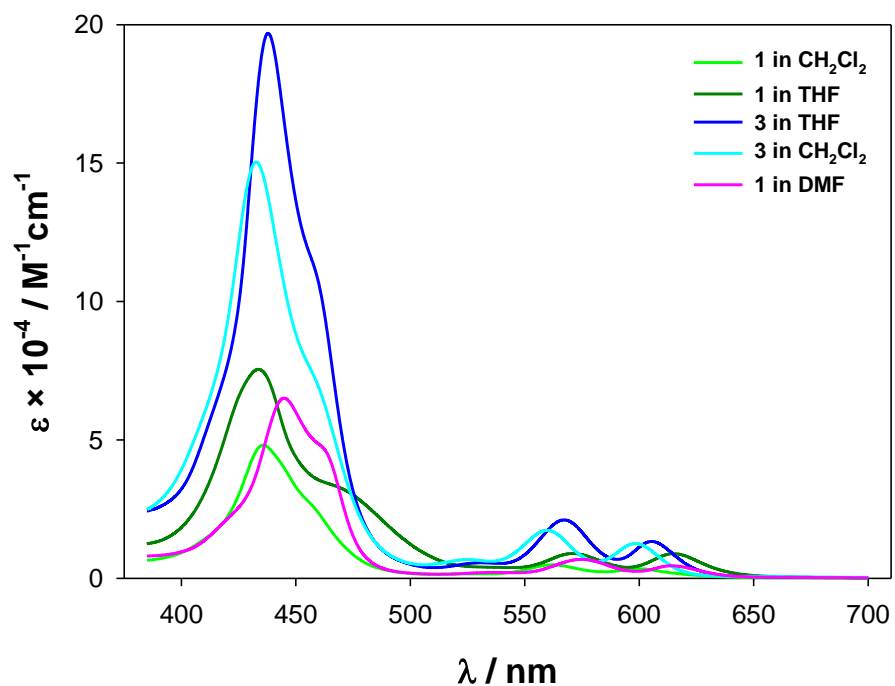


Figure S1. Comparison of UV-vis spectra of dyes **1** and **3** in different solvents.

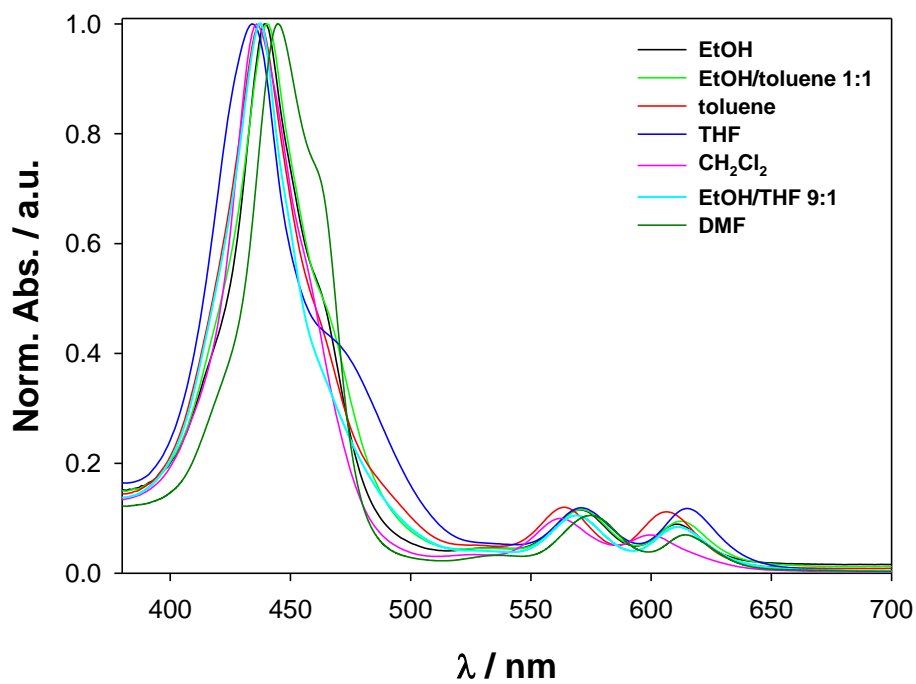


Figure S2. Comparison of UV-vis spectra of dye **1** in different solvents or solvent mixtures for dye loading on TiO_2 photoanode.

Electrochemical data

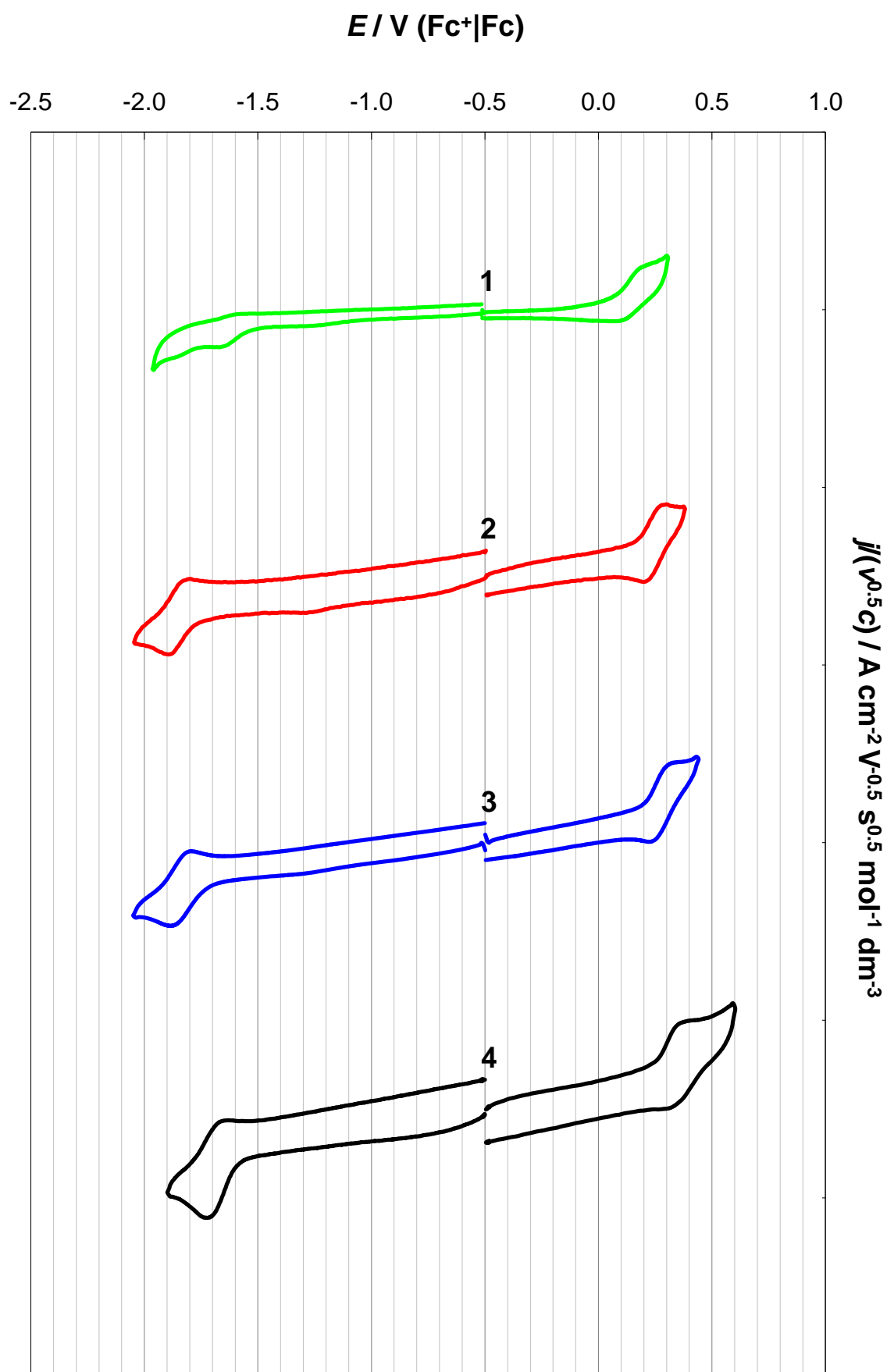


Figure S3. CV pattern of **1-4** on glassy carbon electrode, in DMF + 0.1 M TBAP, at $0.2\,V\,s^{-1}$.

Additional photoelectrochemical data

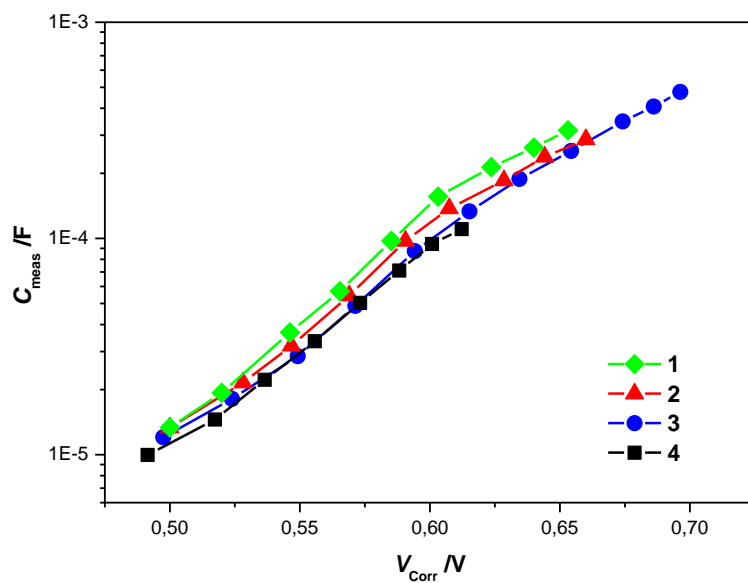


Figure S4. Measured capacitance as a function of the corrected potential for dyes **1-3** under illumination.

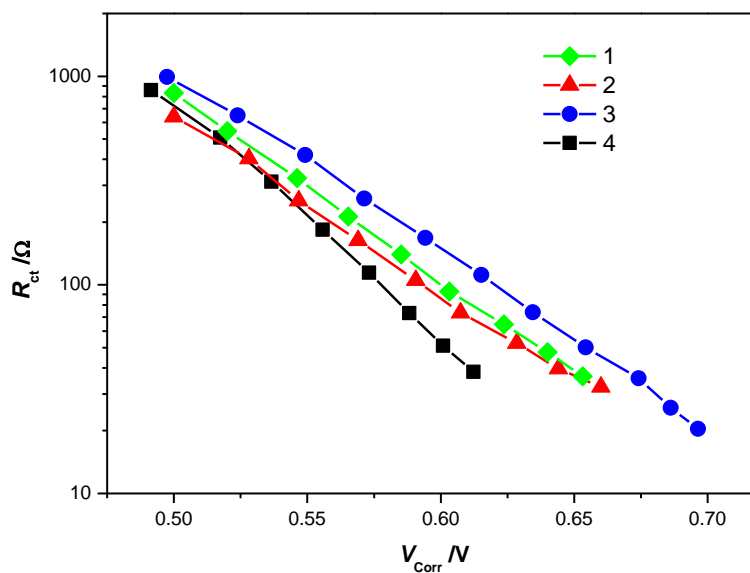


Figure S5. Charge transport resistance as a function of the corrected potential for dyes **1-3** under illumination.

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