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SUPPLEMENTARY INFORMATION

Dye-sensitized solar cells using cobalt electrolytes: The influence of porosity and pore size to achieve high-efficiency

Aswani Yella†,||,*, Simon Mathew‡, Sadig Aghazada,§ Pascal Comte||, Michael Grätzel||, Mohammad Khaja Nazeeruddin§*

§ Group for Molecular Engineering of Functional Materials (GMF), Ecole Polytechnique Federale de Lausanne Valais Wallis, Rue de l'Industrie 17, CH-1950, Sion, Switzerland.

*Corresponding Author: aswani.yella@iitb.ac.in, mdkhaja.nazeeruddin@epfl.ch

||Laboratory of Photonics and Interfaces (LPI), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015, Lausanne, Switzerland.

† Current Address: Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology-Bombay, Powai, Mumbai-400076, India.

‡ Current Address: van 't Hoff Institute for Molecular Sciences, Universiteit van Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands. Email: s.mathew@uva.nl.

Materials and methods

Device fabrication

All materials were purchased from commercial suppliers and used as received, unless stated otherwise. Synthesis of $Co(bpy)_3(TFSI)_2$ and $Co(bpy)_3(TFSI)_3$ was performed by a literature method.[1] The working electrodes and the corresponding devices were prepared according to literature procedures.[2,3]

Working Electrode: The working electrode was composed of a 7 μm thick TiO_2 film (active area 0.28 cm^2), composed of a 3.5 μm transparent layer with a TiO_2 particle size of 32 nm and a 3.5 μm scattering layer composed of 400 nm sized TiO_2 particles. The paste was screen printed onto a pre-cleaned TCO glass (NSG 10, Nippon sheet glass, Japan) and pre-treated with $TiCl_4$ (twice, 60 mM, 1hr at 80°C), followed by a series of sintering steps (from ambient temperature, ramping over 5 min at 25°C min^{-1} to 125°C then holding for 10 min, ramping over 15 min at 13.3°C min^{-1} to 325°C then holding for 5 min, ramping over 5 min at 10°C min^{-1} to 375°C then holding for 5 min, ramping over 5 min at 15°C min^{-1} to 450°C then holding for 15 min and finally ramping over 5 mins at 10°C min^{-1} to 500°C and holding for 15 min). The thickness of the printed film after the sintering process was measured using a KLA Tencor alpha-step 500 surface profilometer and was found to be around 7 μm. The mesoporous TiO_2 photoanodes were post-treated with freshly prepared $TiCl_4$ solutions by immersing the substrates into a $TiCl_4$ bath at 70 °C for 30 min. The dye solutions were 0.2 mM in THF/Ethanol (1:4) and contained a twofold excess of chenodeoxycholic acid (CDCA) as an additive. The photoanodes underwent dipping for 6 h to complete the loading with sensitizer. The mesoporous titania employed in this study possessed a porosity of ~70% and a pore diameter of ~20 nm, elucidated from Brunauer–Emmett–Teller (BET) measurements.

Counter Electrode: The counter electrode was prepared by drop casting a suspension of graphene nanoplatelets (ABCR, Karlsruhe, 6-8 nm thick × 15 μm wide, 0.1 mg/mL in acetone) onto FTO glass (Nippon Sheet Glass, NSG, 10 □/□) and drying at ambient temperature.

Electrolyte preparation: Two different electrolytes were used in this study, either an iodide/triiodide redox mediator or Co(II)/Co(III) redox mediator. The cobalt electrolyte contained 0.25 M $Co(bpy)_3(TFSI)_2$, 0.06 M $Co(bpy)_3(TFSI)_3$, 0.1 M LiTFSI, and 0.5 M 4-*tert*-butylpyridine in acetonitrile.

Cell Assembly: Fabrication of sealed cell was performed by using a 15 μm thick hot-melt ionomer (Surlyn, DuPont) and heating at 120°C. The electrolyte was introduced through pre-drilled holes in the counter electrode, which were sealed with a Surlyn sheet and a thin glass cover by heating (120°C). A black mask (0.159 cm^2) which is smaller than the active area (0.280 cm^2) was used in the subsequent photovoltaic studies to ensure an accurate measure of the incident light.

Device characterization

***J-V* Characterization:** A 450 W xenon light source (Oriel, USA) was used to characterize the solar cells. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra to less than 2%. The current–voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA).

IPCE: A similar data acquisition system (used in *J-V* characterization) was used to control the incident photon-to-collected electron conversion efficiency measurement. Under computer control, light from a 300W xenon lamp (ILC Technology, U.S.A.) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE (λ). The photovoltaic parameters are average values with statistical error less than 2% based on 3 devices for each tested electrolyte.

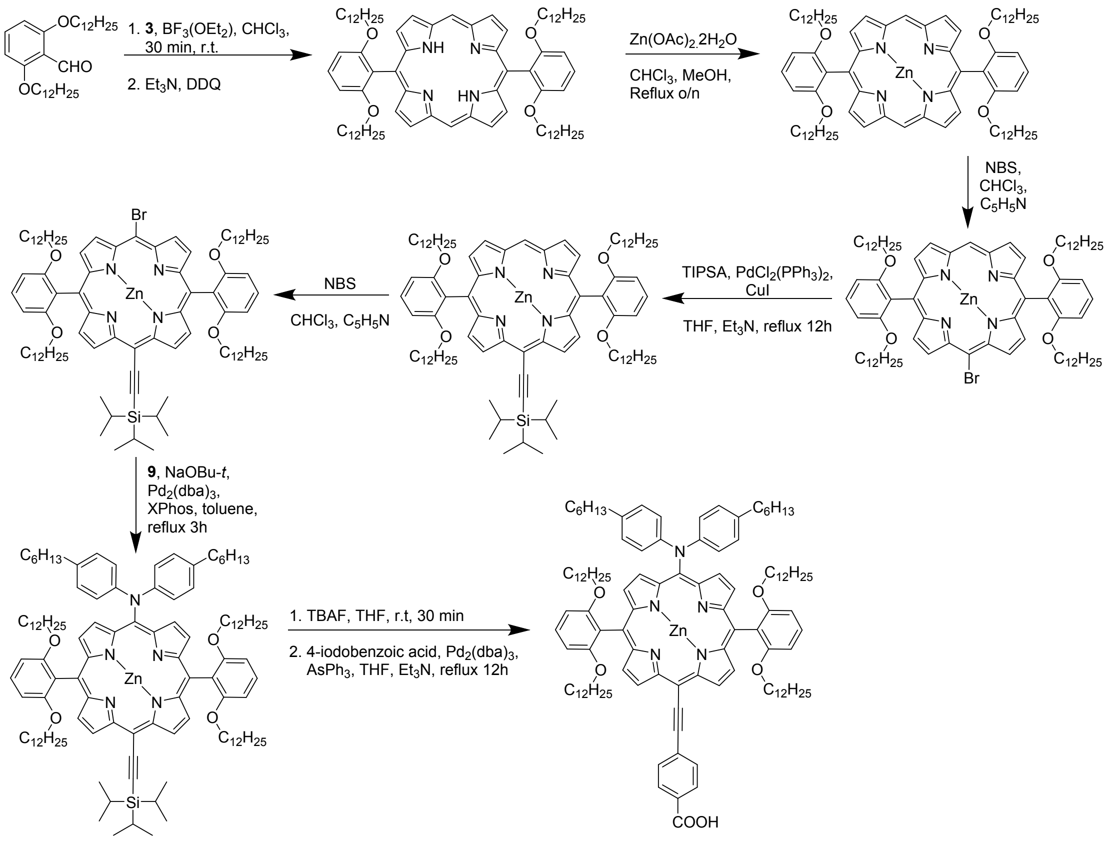
Photovoltage/Photocurrent Decay Measurements: For the transient photovoltage/photocurrent decay measurements, a white light bias was generated from an array of diodes. Red light pulse diodes (with a square pulse width, 100 ns rise and fall time) controlled by a fast solid-state switch were used as the perturbation source. The voltage dynamics were recorded on a PC-interfaced Keithley 2602 source meter with a 500 μs response time. The perturbation light source was set to a suitably low level in order for the voltage decay kinetics to be mono-exponential. By varying the white light bias intensity, the electron recombination lifetime could be estimated over a range of applied biases. Before the LEDs switched to the next light intensity, a charge extraction routine was executed to measure the electron density in the film. In the charge extraction techniques, the LED illumination source was turned off in <1 μs, while simultaneously, the cell was switched from open to short circuit. The resulting current, as the cell returns to V=0 and J=0, was integrated to give a direct measurement of the excess charge in the film at that V_{OC}.

Experimental Section

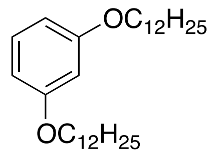
General information

All commercially available reagents were used as received. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Thin-Layer Chromatography (TLC) was performed with Merck KGaA pre-coated TLC silica gel 60 F254 aluminum sheets, visualizing with UV (254 nm) light where required. Flash column chromatography was performed using Merck Silica gel 60 (0.015-0.040 mm). 1H NMR spectra were recorded on a Bruker Avance-400 (400 MHz), BrukerAvance III-400 (400 MHz) or Bruker DPX-400 (400 MHz) spectrometer and are reported in ppm using a solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Peaks are reported as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet/quintet, m = multiplet, br s = broad singlet; coupling constant (Hz); integration. UV-vis spectra were measured with a Hewlett-Packard 8453 UV-vis spectrophotometer. Emission spectra were recorded with a Fluorolog Horiba Jobin Yvon Model FL-1065.

Synthetic Route to SM342

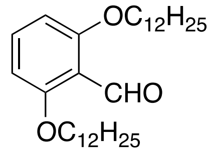


Synthesis



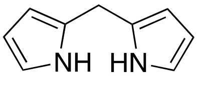
1,3-bis(dodecyloxy)benzene (1): Resorcinol (1.48 g, 13.4 mmol) and K_2CO_3 (5.58 g, 40.3 mmol) were combined in dry DMF (25 mL) under an inert atmosphere and heated to 80°C. 1-bromododecane (8.11 mL, 33.5 mmol) was added via syringe and the reaction mixture stirred at 80°C for 15 hours. After cooling to room temperature, the reaction mixture was poured into H_2O (100 mL) and stirred for 3 hours before filtering and washing with MeOH. Recrystallization from EtOH afforded the pure product (5.02 g, 84%) as a white solid.

^{1}H NMR(400 MHz, $CDCl_3$): δ 7.14 (t, *J* = 8 Hz, 1H), 6.49 (s, 1H), 6.46 (m, 2H), 3.93 (t, *J* = 6.6 Hz, 4H), 1.80-1.73 (m, 4H), 1.48-1.39 (m, 4H), 1.38-1.22 (m, 32H), 0.88 (t, *J* = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 129.7, 106.6, 101.3, 67.9, 31.9, 29.7, 29.64, 29.60, 29.58, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; ESI-ToF-HRMS ($M+H^+$), calc. 447.4202, obs. 447.4204.



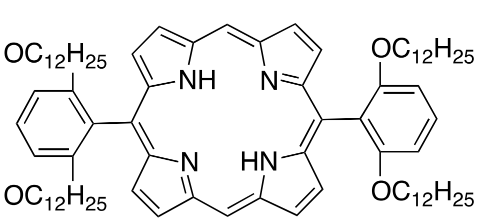
2,6-bis(dodecyloxy)benzaldehyde (2): using a modified procedure,[1] dry Et_2O (9 mL) and TMEDA (0.6 mL, 6.7 mmol) were added to **1** (1.79 g, 4 mmol) under an inert atmosphere and the solution was cooled to 0°C. *n*-BuLi (2.5 M in hexane, 2.4 mL, 6 mmol, 1.5 equiv.) was added dropwise and the resulting solution was stirred at 25°C for 3 hours. Dry DMF (0.4 mL, 5.8 mmol) was added and the solution stirred for 2 hours before pouring the reaction mixture into ice water (50 mL). The organics were extracted with DCM (2 × 50 mL), the organics dried (Na_2SO_4), filtered and evaporated to give the crude product which was precipitated from hexane (using $N_{2(l)}$ to cool) to afford the desired product (1.6 g, 84%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.53 (s, 1H), 7.37 (t, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 2H), 4.02 (t, *J* = 6.4 Hz, 4H), 1.87-1.75 (m, 4H), 1.51-1.40 (m, 4H), 1.35-1.21 (m, 32H), 0.876 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 161.7, 135.5, 114.7, 104.4, 68.9, 31.9, 29.65, 29.62, 29.59, 29.54, 29.3, 29.0, 26.0, 22.7, 14.1; ESI-ToF-HRMS ($M+H^+$), calc. 475.4151, obs. 475.4154.



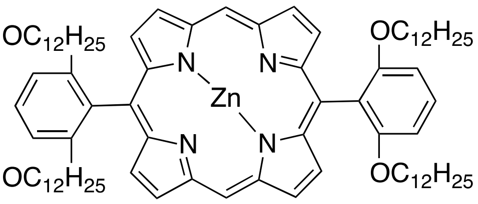
Dipyrromethane (3): Using a modified procedure,[2] pyrrole (700 mL, 10.86 mol 54 equiv, passed through an alumina column) was combined with paraformaldehyde (6 g, 0.2 mol). The suspension was degassed by bubbling N_2 and heating at 55°C until solution was achieved. $InCl_3$ (3.08 g, 13.93 mmol, 7mol% w.r.t paraformaldehyde) was added and the reaction stirred for 2 hours at 55°C. Powdered NaOH (24 g) was added and the reaction mixture filtered through Celite, washing with pyrrole (50 mL). The excess pyrrole was removed by distillation at reduced pressure (maintaining < 55°C) and the trace pyrrole was removed by high vacuum. The resulting solid was purified by column chromatography (silica, 1%$Et_3N/CHCl_3$) to afford the pure product (12.3g, 42%) as an off white solid.

^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (br s, 2H), 6.66 (dd, *J* = 1.6, 2.8 Hz), 6.16 (q, *J* = 2.8 Hz, 2H), 6.06-6.02 (m, 2H), 3.98, (s, 2H);^{13}C NMR (100 MHz, $CDCl_3$): δ 129.0, 117.3, 108.3, 106.4, 26.4.



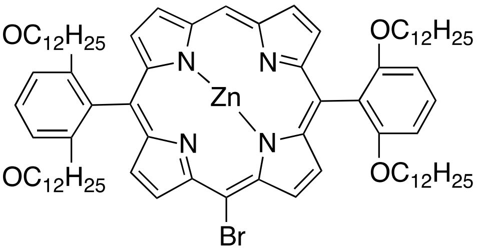
5,15-bis(2,6-bis(dodecyloxy)phenyl)porphyrin (4): Compound **2** (1.215 g, 2.56 mmol) and **3** (374 mg, 2.56 mmol) were combined in $CHCl_3$ (1% EtOH stabilized, 213 mL) and degassed by bubbling the solution with N_2. $BF_3.OEt_2$ (neat, 182 □L, 1.44 □mol) was added and the resulting dark solution stirred for 30 minutes. DDQ (873 mg, 3.85 mmol, 1.5 equiv) was added and the solution stirred for an additional hour. The reaction mixture was neutralized by the addition of Et_3N (0.2 mL) and the reaction mixture passed through a plug of silica, eluting with DCM to collect the purple porphyrin band. The solvents were evaporated and the remaining solid recrystallized from DCM/MeOH to afford the product (530 mg, 35%) as a purple crystals.

^1H NMR (400 MHz, $CDCl_3$): δ 10.13 (s, 2H), 9.26 (d, *J* = 4.4 Hz, 4H), 8.98 (d, *J* = 4.4 Hz, 4H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 4H), 3.83 (t, *J* = 6.4 Hz, 8H), 1.30-1.21 (m, 8H), 1.19-1.08 (m, 16H), 1.05-0.97 (m, 8H), 0.96-0.83 (m, 16H), 0.86 (t, *J* = 7.2 Hz, 12H), 0.75-0.68 (m, 8H), 0.61-0.51 (m, 16H), 0.49-0.42 (m, 8H), -3.00 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 147.6, 144.8, 130.7, 130.4, 129.9, 119.9, 11.5, 105.2, 103.9, 68.6, 31.9, 29.5, 29.4, 29.3, 29.2, 29.0, 28.7, 28.5, 25.2, 22.7, 14.1; ESI-ToF-HRMS ($M+H^+$), calc. 1199.9231, obs. 1199.9208.



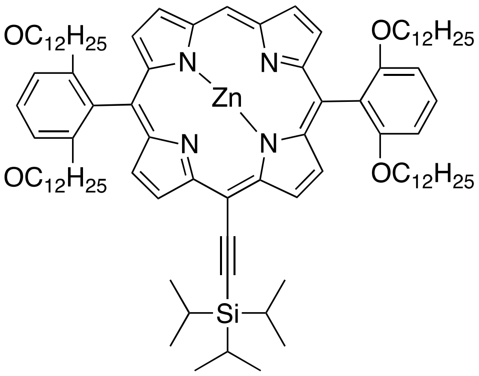
(5,15-bis(2,6-bis(dodecyloxy)phenyl)porphyrinato) zinc(II) (5): Porphyrin **4** (400 mg, 0.333 mmol) was dissolved in $CHCl_3$ (33 mL) and combined with a solution of $Zn(OAc)_2.2H_2O$ (366 mg, 1.67 mmol, 5 equiv) prior to heating at reflux overnight. The solvents were evaporated, dissolved in DCM and the mixture filtered through a plug of silica, eluting with DCM. The eluent was evaporated and the solid recrystallized from DCM/MeOH to afford the title compound (410 mg, 97%) as purple-pink crystals.

^1H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 2H), 9.32 (d, *J* = 4.4 Hz, 4H), 9.06 (d, *J* = 4.4 Hz, 4H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 4H), 3.83 (t, *J* = 6.4 Hz, 8H), 1.29-1.20 (m, 8H), 1.19-1.17 (m, 16H), 1.01-0.87 (m, 16H), 0.86 (t, *J* = 7.2 Hz, 12H), 0.84-0.75 (m, 8H), 0.67-0.56 (m, 8H), 0.54-0.38 (m, 16H), 0.35-0.27 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 150.5, 149.1, 131.6, 131.2, 129.6, 121.4, 112.3, 105.4, 104.9, 68.6, 31.9, 29.5, 29.3, 29.2, 29.1, 29.0, 28.6, 28.5, 25.1, 22.7, 14.1; ESI-ToF-HRMS ($M+H^+$), calc. 1260.8289, obs. 1260.8262.



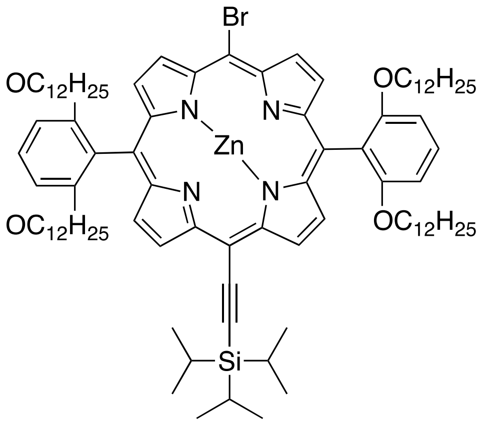
(5-bromo-10,20-bis(2,6-bis(dodecyloxy)phenyl)porphyrinato) zinc(II) (6): Porphyrin **5** (336 mg, 0.263 mmol) was dissolved in $CHCl_3$ (26 mL) and pyridine (0.26 mL) and stirred vigorously under N_2. *N*-bromosuccinimide (61 mg, 0.342 mmol, 1.3 equiv) was added and the solution stirred for 30 minutes. The reaction was quenched with acetone (5 mL) and the solvents evaporated. The remaining solid was purified by column chromatography (silica, 1:1 $CHCl_3$/hexane then 2:1 $CHCl_3$/hexane) to afford the desired product (210 mg, 59%) as a purple solid.

^1H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 9.70 (d, *J* = 4.8 Hz, 2H), 9.25 (d, *J* = 4.4 Hz, 2H), 8.98 (d, *J* = 4.4 Hz, 2H), 8.97 (d, *J* = 4.8 Hz, 2H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 4H), 3.84 (t, *J* = 6.6 Hz), 1.29-1.19 (m, 8H), 1.18-1.05 (m, 16H), 0.99-0.89 (m, 16H), 0.86 (t, *J* = 7.2 Hz, 12H), 0.85-0.77 (m, 8H), 0.68-0.59 (m, 8H), 0.55-0.39 (m, 16H), 0.38-0.29 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 151.0, 150.9, 149.9, 148.8, 132.3, 132.2, 132.1, 131.5, 129.8, 121.1, 113.5, 105.3, 68.6, 31.9, 29.4, 29.34, 29.26, 29.16, 29.0, 28.63, 28.56, 25.2, 22.7, 14.1; ESI-ToF-HRMS (M+H$^+$), calc. 1338.7393, obs. 1338.7405.



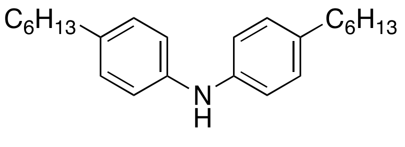
(5,15-bis(2,6-bis(dodecyloxy)phenyl)-10-(2-(triisopropylsilyl)ethynyl)-porphyrinato) Zinc(II) (7): Using an established method,[3] Porphyrin **6** (190 mg, 0.140 mmol), $PdCl_2(PPh_3)_2$ (4.9 mg, 0.007 mmol, 5mol%) and CuI (2.7 mg, 0.014 mmol, 10mol%) were combined under and inert atmosphere to which THF (5.5 mL) and Et_3N (1.1 mL) were added. Triisopropylsilylacetylene (63 mL, 0.28 mmol, 2 equiv) was added and the solution heated at reflux for 12 hours. The solvent was evaporated and the residue subjected to column chromatography (silica, 1:2 DCM/hexane) to afford the desired compound (191 mg, 95%) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 9.81 (d, *J* = 4.8 Hz, 2H), 9.27 (d, *J* = 4.4 Hz, 2H), 9.01 (d, *J* = 4.4 Hz, 2H), 8.99 (d, *J* = 4.8 Hz, 2H), 7.73 (t, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 4H), 3.87 (t, *J* = 6.4 Hz, 8H), 1.57-1.48 (m, 22H), 1.34-1.22 (m, 8H), 1.21-1.08 (m, 16H), 1.02-0.92 (m, 16H), 0.90-0.81 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 12H), 0.75-0.65 (m, 8H), 0.62-0.50 (m, 16H), 0.49-0.40 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 152.0, 150.9, 150.3, 149.1, 131.9, 131.5, 131.3, 130.6, 129.7, 121.3, 113.7, 110.5, 106.2, 105.3, 98.8, 95.8, 68.7, 64.1, 31.9, 29.5, 29.33, 29.26, 29.17, 29.0, 28.7, 28.6, 25.2, 22.8, 22.7, 19.2, 14.1, 12.0, ; ESI-ToF-HRMS (M+H$^+$), calc.1440.9623 , obs. 1440.9622.



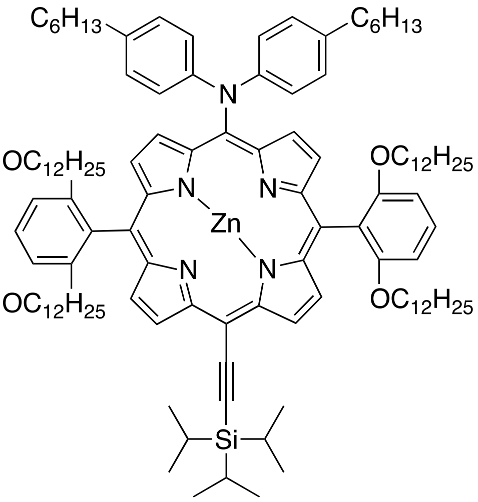
(5-bromo-15-(2-(triisopropylsilyl)ethynyl)-10,20-bis(2,6-bis(dodecyloxy)phenyl)-porphyrinato) zinc(II) (8): Using an established method,[3] porphyrin **7** (183 mg, 0.125 mmol) in $CHCl_3$ (12.5 mL) and pyridine (125 □L) were stirred vigorously under N_2. *N*-bromosuccinimide (25 mg, 0.138 mmol, 1.1 equiv) was added and stirred under an inert atmosphere for 30 minutes upon which the solution turned a darker purple color. The reaction was quenched by the addition of acetone (10 mL) the solvents evaporated. The residue was subjected to purification through a plug of silica, eluting with 1:2 DCM/hexane. The solvents were evaporated to afford the desired product (181 mg, 95%) as a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (d, J = 4.4 Hz, 2H), 9.60 (d, J = 4.4 Hz, 2H), 8.88 (d, J = 4.4 Hz, 2H), 8.85 (d, J = 4.4 Hz, 2H), 7.69 (t, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 4H), 3.84 (t, J = 6.4 Hz, 8H), 1.51-1.40 (m, 22H), 1.27-.1.17 (m, 8H), 1.15-1.02 (m, 16H), 1.15-1.02 (m, 16H) 0.98-0.89 (m, 16H), 0.87-0.76 (m, 8H), 0.84 (t, J = 7.2 Hz, 12H), 0.68 (m, 8H), 0.57-0.44 (m, 16H), 0.43-0.33 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 152.8, 151.4, 150.6, 148.8, 143.7, 132.5, 132.4, 132.0, 130.9, 129.8, 114.9, 109.9, 105.2, 105.0, 99.3, 96.4, 68.6, 29.4, 29.3, 29.24, 29.17, 29.0, 28.6, 28.6, 25.2, 22.7, 19.1, 14.1, 11.9; ESI-ToF-HRMS ($M+H^+$), calc. 1518.8728, obs. 1518.8820.



Bis(4-hexylphenyl)amine (9): using a method adapted from Buchwald *et al.*,[4] 1-bromo-4-hexylbenzene (1.00 g 4.15 mmol), $Pd_2(dba)_3$ (30 mg, 0.041 mmol, 1mol%), NaOBu-*t* (558 mg, 5.81 mmol, 1.4 equiv) and XPhos (99 mg, 0.207 mmol, 5mol%) were combined under an inert atmosphere and a solution of NH_3 (0.5 M in dioxane, 24.9 mL, 12.44 mmol, 3 equiv) and dry 1,4-dioxane (41 mL) was added. The resulting solution was heated at 80°C for 16 hours, after which the reaction mixture was diluted with EtOAc, filtered through silica and the solvents evaporated. The resulting solid was purified through column chromatography (silica, 1:4 EtOAc/hexane) to afford the desired product (479 mg, 68%) as a colorless oil.

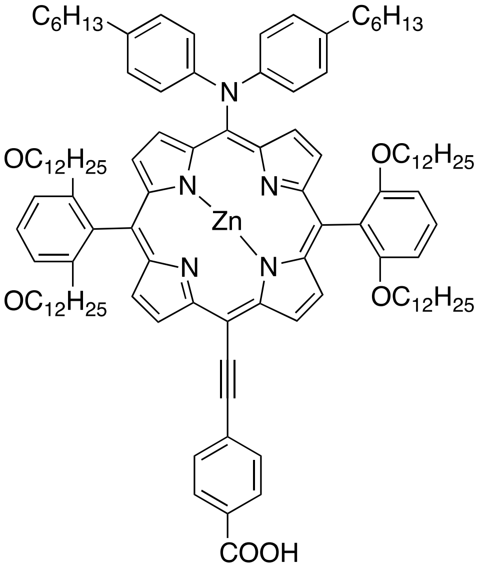
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 8.4 Hz, 4H), 7.00 (d, J = 8.4 Hz, 4H), 5.55 (br s, 1H), 2.58 (t, J = 7.6 Hz, 4H), 1.67-1.57 (m, 4H), 1.43-1.29 (m, 12H), 0.94 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 135.3, 129.1, 117.8, 35.2, 31.8, 31.7, 29.0, 22.6, 14.1; ESI-ToF-HRMS ($M+H^+$), calc. 338.2848, obs. 338.2836.



(5-bis(4-hexylphenyl)amino-15-(2-(triisopropylsilyl)ethynyl)-10,20-bis(2,6-bis(dodecyloxy)phenyl)-porphyrinato) zinc(II) (10): Porphyrin **8** (164 mg, 0.107 mmol) was combined with amine **9** (90 mg, 0.266 mmol, 2.5 equiv), NaOBu-*t* (51 mg, 0.533 mmol, 5 equiv), $Pd_2(dba)_3$ (9.8 mg, 0.0107 mmol, 10mol%) and XPhos (10.2 mg, 0.0213 mmol, 20mol%) under an inert atmosphere prior to the introduction of dry toluene (21.5 mL) and the resulting solution was heated at reflux for 3 hours. After cooling the solution to ambient temperature, H_2O (50 mL) was added and the aqueous washed with EtOAc (50 mL). The organics were combined, dried (Na_2SO_4), filtered and evaporated. Purification via column chromatography (silica, 1:3 DCM/hexane) afforded the desired product (178 mg, 94%) as a green solid.

^{1}H NMR (400 MHz, $CDCl_3$ + 1 drop C_5D_5N): δ 9.57 (d, J = 4.4 Hz, 2H), 9.01 (d, J = 4.4 Hz, 2H), 8.78 (d, J = 4.4 Hz, 2H), 8.60 (d, J = 4.4 Hz, 2H), 7.62 (t, J = 8.4 Hz, 2H), 6.99 (d, J = 8.8 Hz, 4H), 6.94 (d, J = 8.8 Hz, 4H), 6.79 (d, 8.4 Hz, 4H), 3.80 (t, J = 6.6

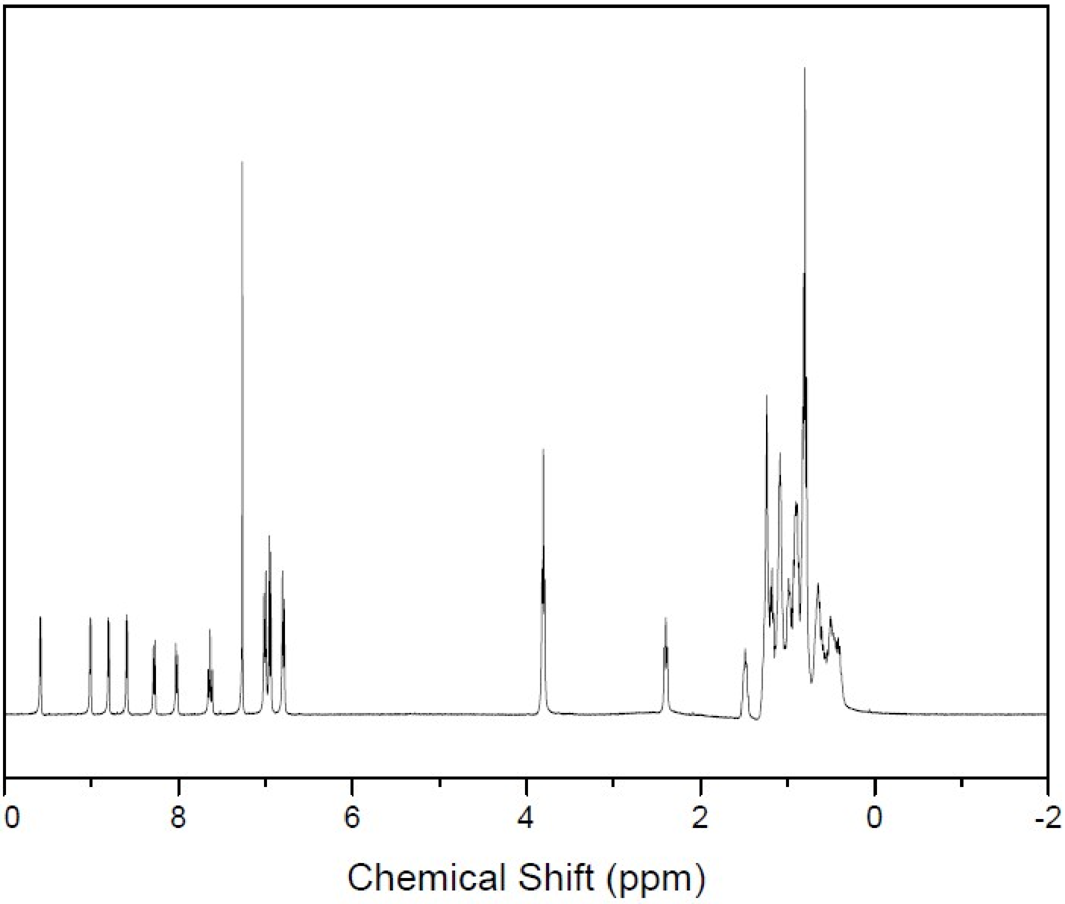
Hz, 8H), 2.41 (t, *J* = 7.8 Hz, 4H), 1.56-1.46 (m, 4H), 1.45-1.38 (m, 22H), 1.32-1.18 (m, 20H), 1.16-1.06 (m, 16H), 1.04-0.95 (m, 8H), 0.95-0.87 (m, 16H), 0.86-0.75 (m, 14H), 0.82 (t, *J* = 7.2 Hz, 12H), 0.75-0.39 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$ + 1 drop C_5D_5N): δ 159.9, 152.4, 151.3, 150.44, 150.42, 149.9, 133.9, 131.51, 131.49, 130.2, 130.1, 129.3, 128.3, 122.2, 121.5, 121.4, 113.4, 111.2, 105.1, 98.2, 94.7, 68.5, 35.2, 31.8, 31.7, 31.5, 29.5, 29.34, 29.32, 29.2, 29.1, 29.0, 28.6, 28.5, 25.0, 22.6, 22.5, 19.1, 14.0, 11.9; ESI-ToF-HRMS (M+H$^+$), calc. 1776.2235, obs. 1776.2358.



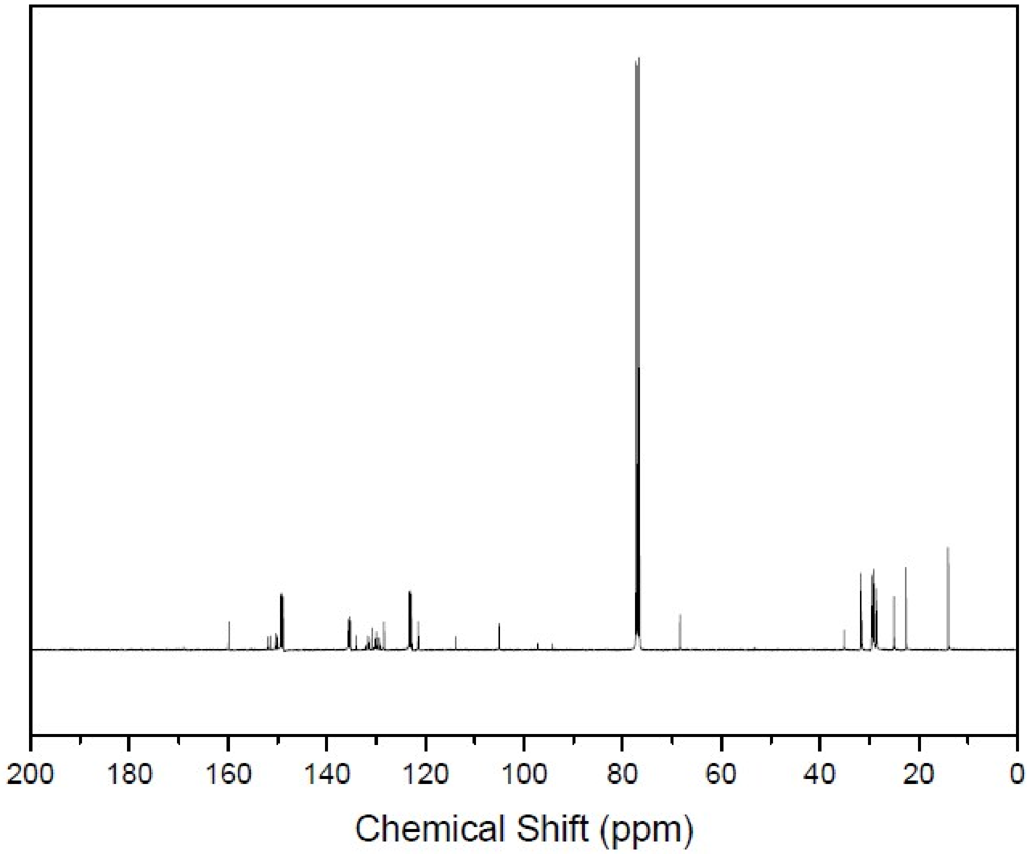
(5,15-bis(2,6-bis(dodecyloxy)phenyl)-10-bis(4-hexylphenyl)amino-20-(4-carboxyphenylethynyl)porphyrinato) Zinc(II) (7): Using an established method,[3] Porphyrin **10**(51 mg, 0.0284 mmol) was dissolved in THF (5.6 mL) under a N_2 atmosphere, and TBAF (1M in THF, 57 □L, 0.0568 mmol, 2 equiv) was added. After stirring at ambient temperature for 30 minutes, the reaction mixture was partitioned between H_2O (50 mL) and Et_2O (50 mL) the organic dried (Na_2SO_4), filtered and evaporated. To the deprotected porphyrin was added 4-iodobenzoic acid (35 mg, 0.1421 mmol, 5 equiv), $Pd_2(dba)_3$ (2.6 mg, 0.0028 mmol, 10mol%), $AsPh_3$ (17.3 mg, 0.057 mmol, 2 equiv), THF (5.6 mL) and Et_3N (1.1 mL) and the resulting mixture stirred at reflux for 12 hours. Evaporation of the solvent and purification by column chromatography (silica, DCM then 1:9 MeOH/DCM) afforded the pure product, which was recrystallized from DCM/MeOH to give the product (35 mg, 71%) as a green solid.

^{1}H NMR (400 MHz, $CDCl_3$ + 1 drop C_5D_5N): δ 9.58 (d, *J* = 4.8 Hz, 2H), 9.01 (d, *J* = 4.8 Hz, 2H), 8.80 (d, *J* = 4.4 Hz, 2H), 8.59 (d, *J* = 4.4 Hz, 2H), 8.27 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 8.4 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 4H), 3.80 (t, *J* = 6.4 Hz, 8H), 2.34 (t, *J* = 7.6 Hz, 4H), 1.53-1.43 (m, 4H), 1.32-1.14 (m, 20H), 1.13-1.03 (m, 16H), 1.02-0.95 (m, 8H), 0.94-0.86 (m, 16H), 0.85-0.74 (m, 14H), 0.80 (t, *J* = 7.2 Hz, 12H), 0.71-0.34 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$ + 1 drop C_5D_5N): δ 168.9, 159.4, 151.9, 151.4, 150.42, 150.37, 150.0, 134.0, 132.1, 131.7, 131.6, 131.4, 130.8, 130.1, 129.9, 129.8, 129.4, 129.3, 129.0, 128.3, 122.6, 121.5, 121.4, 113.8, 105.1, 97.2,5, 97.20, 94.3, 68.4, 35.2, 31.8, 31.7, 31.5, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.6, 28.5, 25.0, 22.6, 22.5, 14.0; MALDI-ToF-MS(CHCA) (M^+), calc. 1740.1112, obs. 1740.0651.

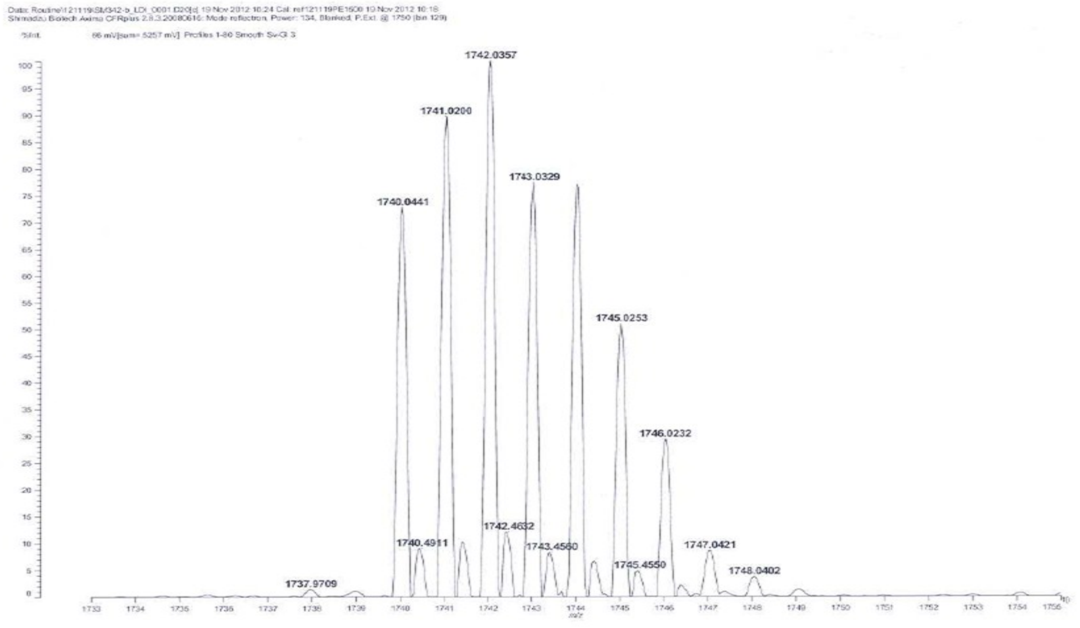
^{1}H NMR of SM342



^{13}C NMR of SM342



MS of SM342



the lower intensity peaks approximately 0.5 a.m.u greater than observed peaks are an electronic artifact.

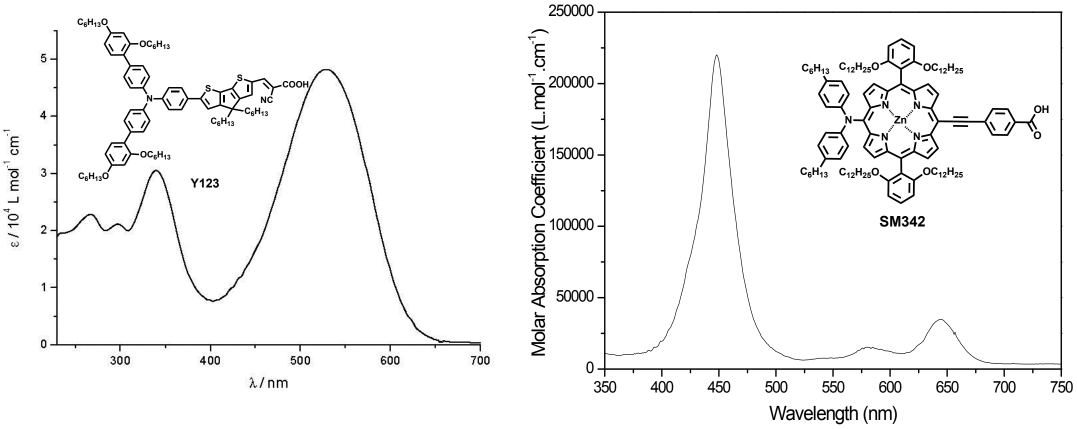


Figure S1. Absorption spectra of the two dyes used in this study (a) Y123 dye and (b) SM342 dye in THF solution.

Paste	TiCl4	Particle size	Porosity	Pore size	Surface area
18NR-T	-	17.7 nm	65%	22 nm	88 m2/g
18NR-T	40 mM	21.6 nm	55%	17 nm	72 m2/g
18NR-T	27 mM	21.3 nm	59%	20 nm	73 m2/g

Table S1. Comparision of the BET data obtained with the mesoporous films made with and without TiCl4 post treatment

Dye	TiCl$_4$	Intensity	J_{SC} (mA cm^{-2})	V_{OC} (mV)	*FF*	PCE (%)
Y123	13 mM	100%	14.24	853	0.77	9.5
		10%	1.39	770	0.80	9.27
Y123	20 mM	100%	14.12	875	0.78	9.79
		10%	1.41	799	0.80	9.66
Y123	27 mM	100%	14.13	877	0.76	9.66
		10%	1.45	801	0.79	9.79
Y123	40 mM	100%	11.21	892	0.80	8.1
		10%	1.46	821	0.80	10.15

Table S2. The short circuit current density (J_{SC}), open circuit potential (V_{OC}), fill factor (*FF*) and power conversion efficiency (PCE) with different concentrations of TiCl$_4$ post-treatments with the Y123 dye, and an electrolyte containing 4-*tert*-butylpyridine.

Dye	$TiCl_4$	Intensity	J_{SC} (mA cm^{-2})	V_{OC} (mV)	*FF*	PCE (%)
Y123	13 mM	100%	13.61	892	0.78	9.47
		10%	1.41	827	0.81	10.00
Y123	20 mM	100%	12.96	903	0.79	9.44
		10%	1.43	840	0.81	10.24
Y123	27 mM	100%	11.64	899	0.79	8.5
		10%	1.41	839	0.81	10.09
Y123	40 mM	100%	8.38	909	0.80	6.1
		10%	1.46	849	0.80	10.51

Table S3. The short circuit current density (J_{SC}), open circuit potential (V_{OC}), fill factor (*FF*) and power conversion efficiency (PCE) with different concentrations of $TiCl_4$ post-treatments with the Y123 dye and an electrolyte containing 0.5 M 4-(5-nonyl)-pyridine.

Dye	Conc. $TiCl_4$	Intensity	J_{SC}, (mA cm^{-2})	V_{OC}, (mV)	*FF*	PCE, %
SM342 + Y123 (7:1)	13 mM	100%	16.76	944	0.74	11.57
		10%	1.69	863	0.78	11.68
	20 mM	100%	15.61	952	0.76	11.15
		10%	1.70	878	0.78	11.88
	27 mM	100%	14.99	942	0.77	10.78
		10%	1.72	866	0.78	11.82
	40 mM	100%	12.57	938	0.80	9.34
		10%	1.72	866	0.78	11.82

Table S4. The short circuit current density (J_{SC}), open circuit potential (V_{OC}), fill factor (*FF*) and power conversion efficiency (PCE) for cells using photoanodes utilizing different concentrations of $TiCl_4$ during post-treatment and sensitized with a cocktail solution of 0.2 M SM342/Y123 (7:1).

Dye	Conc. $TiCl_4$	Intensity	J_{SC}, mA cm^{-2}	V_{OC}, mV	*FF*	PCE, %
SM342 + Y123 (7:1)	13 mM	100%	17.39	937	0.78	12.55
		10%	1.72	855	0.80	12.12
	20 mM	100%	17.76	941	0.77	12.76
		10%	1.77	857	0.80	12.34
	27 mM	100%	17.04	859	0.77	11.21
		10%	1.72	778	0.80	11.17
	40 mM	100%	16.09	830	0.76	10.12
		10%	1.68	752	0.80	10.59

Table S5. The short circuit current density (J_{SC}), open circuit potential (V_{OC}), fill factor (*FF*) and power conversion efficiency (PCE) with different concentrations of $TiCl_4$ during post-treatment of photoanodes fabricated with modified 18NR-T TiO_2 paste, sensitizing with a 0.2 mM cocktail dye solution of SM342/Y123 (7:1) and an electrolyte containing 0.5 M 4-(5-nonyl)-pyridine

Paste	$TiCl_4$, mM	Particle size, nm	Porosity	Pore size, nm	Surface area, $m^2\ g^{-1}$
18NR-T	0	17.7	65%	22	88
18NR-T	40	21.6	55%	17	72
18NR-T	27	21.3	59%	20	73
Modified 18NR-T	0	19.3	69%	28	82
Modified 18NR-T	20	21.0	62%	23	74
Modified 18NR-T	40	21.6	55%	17	72

Table S6. Comparison of the BET data for the mesoporous TiO_2 films made using the commercially available Dyesol 18NR-T and the modified 18NR-T paste with different concentrations of the $TiCl_4$ post treatment.

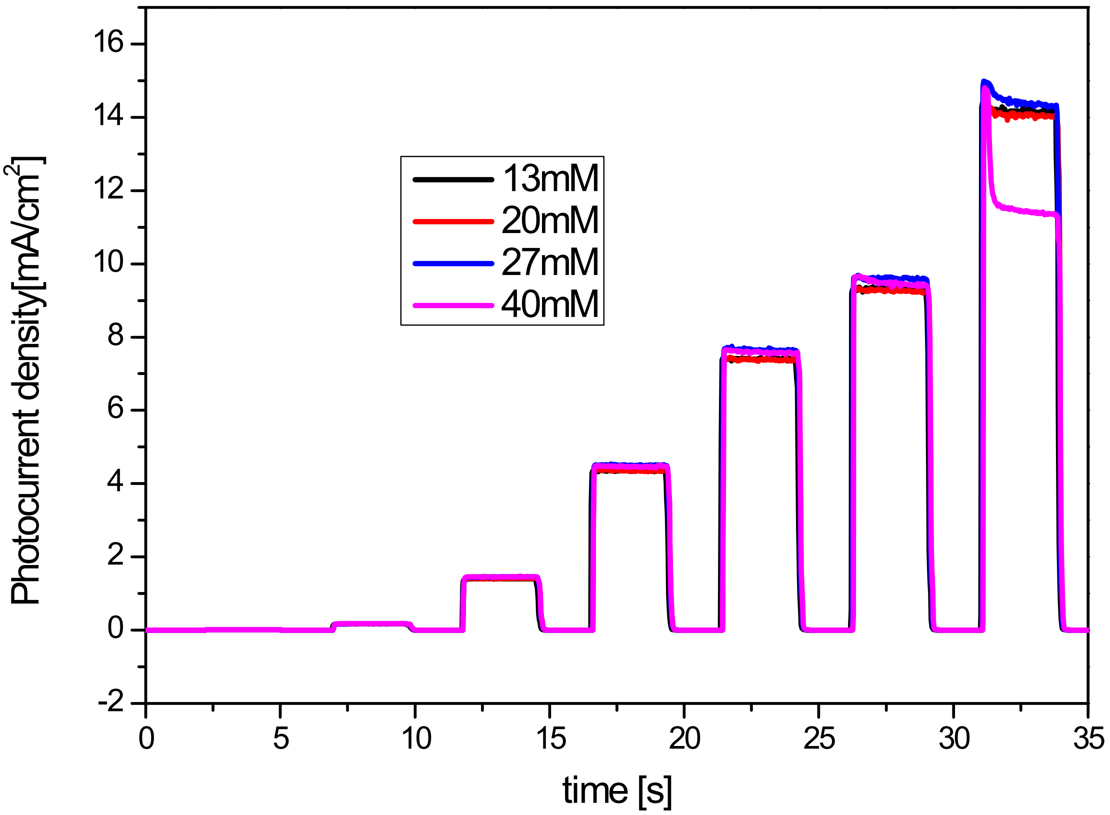


Figure S2. The photocurrent dynamics obtained from devices using mesoporous TiO2 films fabricated with commercially available 18NR-T paste, post-treated with different concentrations of $TiCl_4$, sensitization with the dye Y123 and an electrolyte containing 0.25 M of the pyridine derivative.

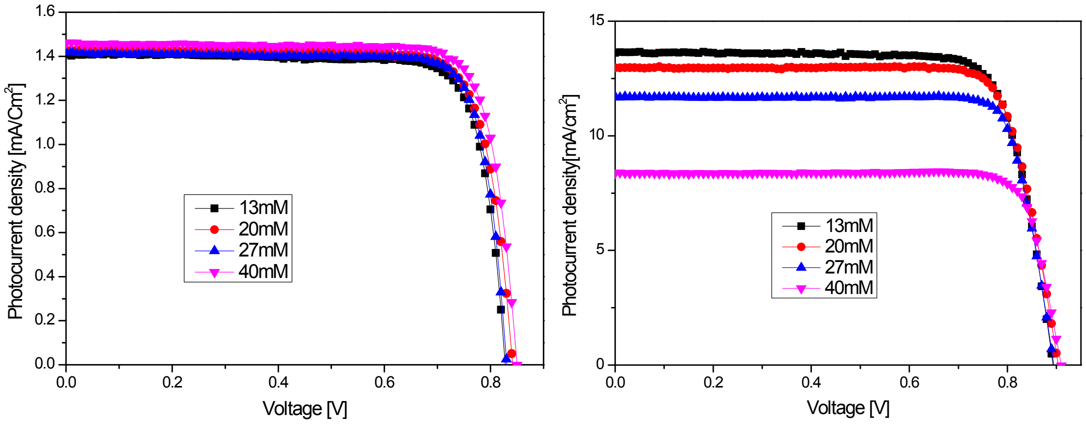


Figure S3. The current-voltage (J-V) characteristics of the DSC made with dye Y123 and different concentrations of $TiCl_4$ during post-treatment at 10% sun (a) and full sun intensity (b) using the electrolyte containing 0.5 M pyridine.

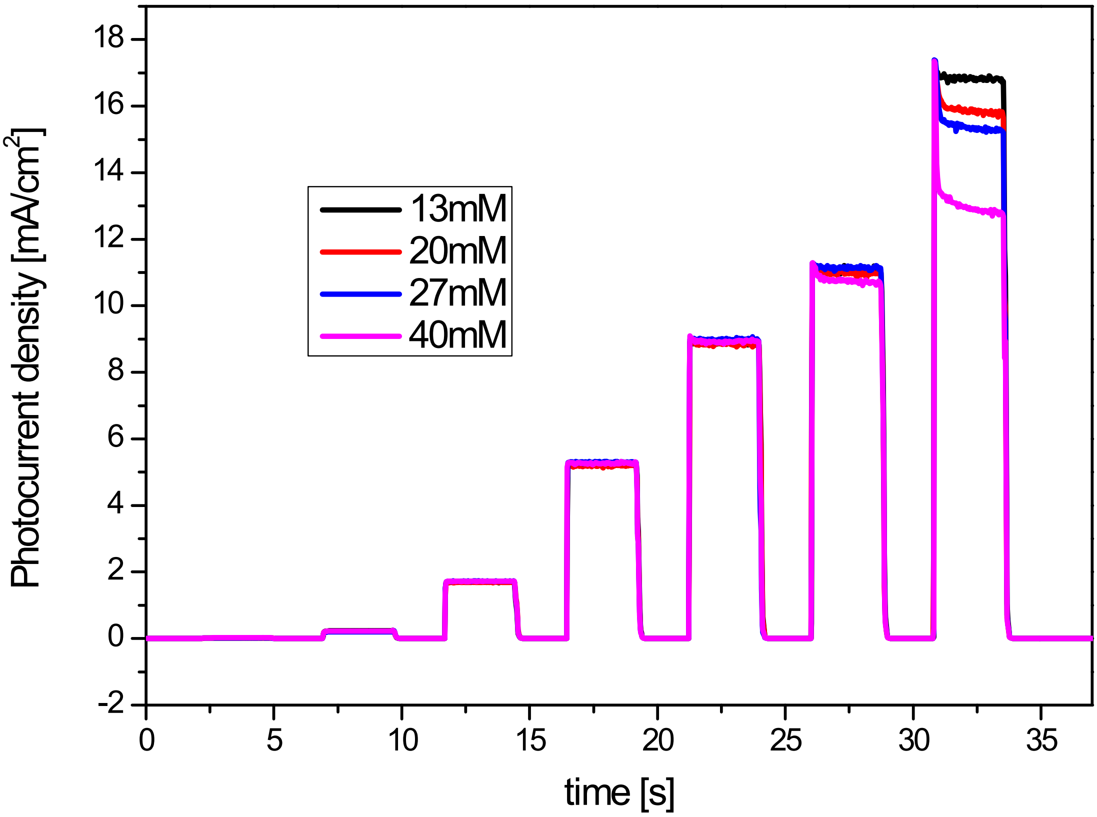


Figure S4. The photocurrent dynamics obtained with a cocktail dye solution of SM342/Y123 (7:1) using mesoporous TiO_2 films fabricated with 18NR-T paste, post-treated with different concentrations of $TiCl_4$.

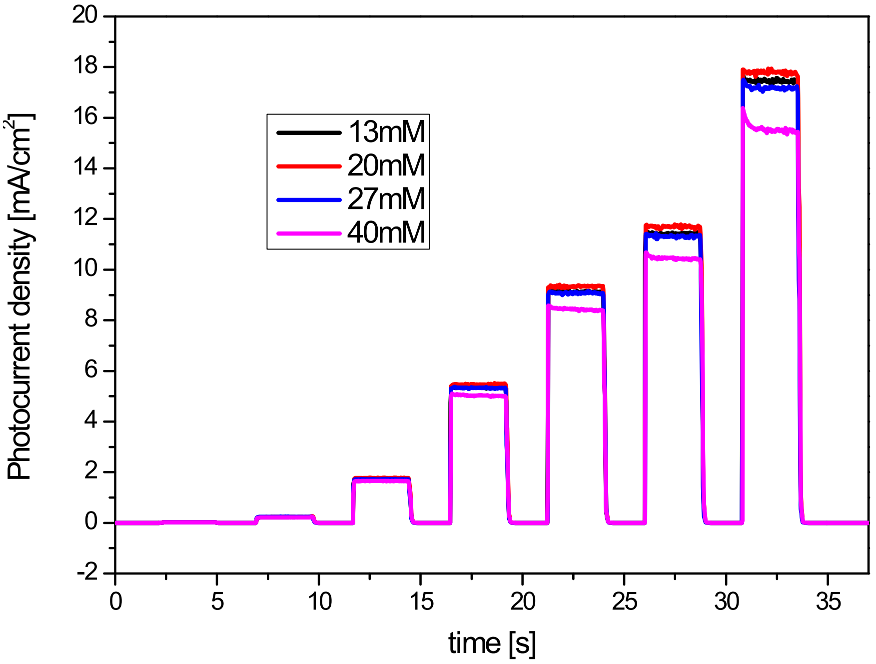


Figure S5. The photocurrent dynamics obtained with a cocktail dye solution of SM342/Y123 (7:1) using mesoporous TiO_2 films fabricated with modified18NR-T paste, post-treated with different concentrations of $TiCl_4$

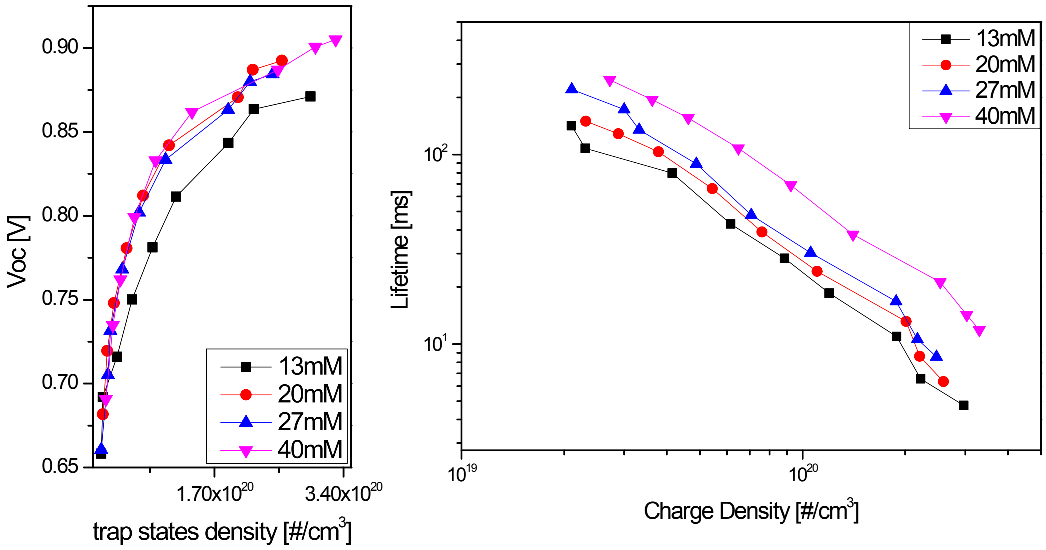


Figure S6. Trap state distribution as a function of Voc and the lifetime as a function of charge density in the case of Y123 dye and 18NRT paste.

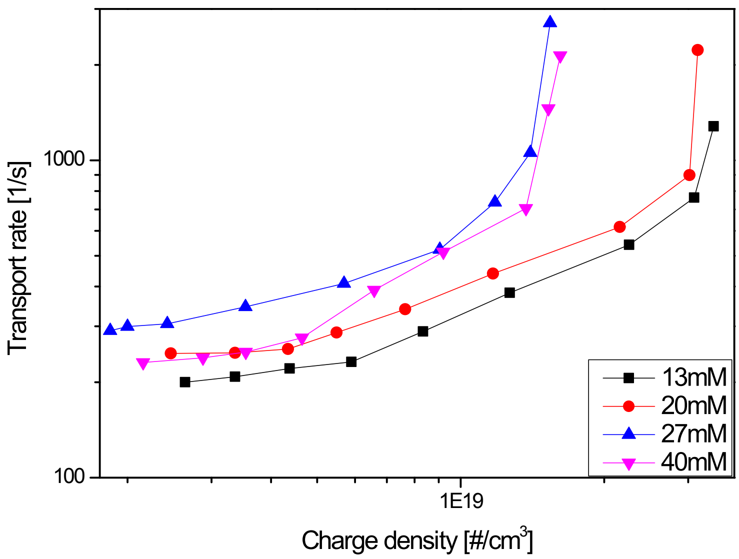


Figure S7. The transport rate of the photogenerated electrons as a function of the charge density.

References

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