Linearly $\pi$-conjugated oligothiophenes as metal-free sensitizers for dye-sensitized solar cells (DSSCs)

**Supporting Information**

**General**

NMR spectra were recorded with a Bruker AVANCE III 300 (1H, 300 MHz and 13C, 75 MHz). Chemical shifts are given in ppm relative to TMS. UV-Vis spectra were recorded with a Perkin Elmer Lambda 19 or 950 spectrometer. Melting points are uncorrected. Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer using dithranol as matrix.

Cyclic voltammetry was performed in dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.10 M as supporting electrolyte) was purchased from Acros and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment. Experiments were carried out in a one-compartment cell equipped with platinum electrodes and saturated calomel reference electrode (SCE) with a Biologic SP-150 potentiostat with positive feedback compensation.

**Synthesis**

5-bromo-3,3''-dioctyl-2,2':5',2''-terthiophene (1b)

N-Bromosuccinimide (0.3 g, 1.75 mmol) is added in small portions to a solution of 1a (1.24 g, 2.62 mmol) in chloroform and acetic acid (50 mL, 1:1) at 0 °C. After being stirred for 3 h at room temperature, the reaction mixture is poured into water and extracted with CH$_2$Cl$_2$. The organic layer is thoroughly washed with water, aqueous sodium bicarbonate, brine and again with water, and then dried over Na$_2$SO$_4$. After removal of solvent it is chromatographed on silica gel using petroleum ether as eluent to afford monobromoterthiophene (0.6 g, 63%) as yellowish oil. $^1$H NMR (300 MHz, CDCl$_3$): 7.16 (d, $J$=5.1 Hz, 1H), 7.04 (s, 2H), 6.95 (s, 1H),
6.95 (d, J=3.0 Hz, 1H), 2.82-2.76 (m, 4H), 1.67-1.54 (m, 10H), 1.39-1.26 (m, 26H), 1.13-1.08 (m, 6H), 0.94-0.84 (m, 15H)

**Tributyl(3,3''-dioctyl-[2,2':5',2''-terthiophen]-5-yl)stannane (1c)**

nBuLi (2.5 M in hexane, 1.27 mmol, 0.51 mL) is added dropwise at 0 °C to a solution containing 1a (0.5 g, 1.06 mmol) dissolved in dry Et₂O under Ar atmosphere. The mixture is stirred for 1/2 h at the addition temperature. Tributyltin chloride (0.33 ml, 1.16 mmol) is then added dropwise at the same temperature. The mixture is allowed to warm slowly to room temperature. After dilution with diethyl ether, a saturated solution of NaF is added and the mixture is stirred for 1 h. The precipitate is filtered off using celite and the filtrate is washed with a saturated solution of NaHCO₃ then with water. After drying over MgSO₄, the solvent is evaporated and the product was used in the next step without further purification.

**1H NMR (300 MHz, CDCl₃):**

7.16 (d, J=5.1 Hz, 1H), 7.04 (s, 2H), 6.95 (s, 1H), 6.95 (d, J=3.0 Hz, 1H), 2.82-2.76 (m, 4H), 1.67-1.54 (m, 10H), 1.39-1.26 (m, 26H), 1.13-1.08 (m, 6H), 0.94-0.84 (m, 15H).

**3''',4'-dioctyl-[2,2':5',2''':5'',2''''-quaterthiophene]-5-carbaldehyde (3)**

A mixture of 2 (0.03 ml, 0.26 mmol), Stille reagent 1c (0.24 g, 0.31 mmol,) and Pd(PPh₃)₄ (61 mg, 20 mol%) in 20 mL of anhydrous toluene is refluxed for 20 h. After concentration, the residue is dissolved in methylene chloride and the organic phase is washed twice with an aqueous solution of NaHCO₃ then with water. After drying over MgSO₄ and solvent removal, the residue is chromatographed on silica gel using a mixture of methylene chloride and petroleum ether (1/1) as eluent to afford a yellowish compound (0.25 g, 92%). **1H NMR (500 MHz, CDCl₃):** 9.85 (s, 1H), 7.67 (d, J=4.2 Hz, 1H), 7.23 (d, J=3.0 Hz, 1H), 7.21 (d, J=5.1 Hz, 1H), 7.20 (s, 1H), 7.12 (d, J=3.6 Hz, 1H), 7.08 (d, J=3.6 Hz, 1H), 6.95 (d, J=5.1 Hz, 1H), 2.78 (t, J=7.8 Hz 4H), 1.70-1.61 (m, 4H), 1.39-1.26 (m, 20H), 0.87 (t, J=7.0 Hz 6H); **13C NMR (75 MHz, CDCl₃):** 182.3, 146.8, 141.4, 140.6, 139.9, 137.3, 136.9, 134.8, 133.3, 132.6; 130.1, 130.0, 129.0, 126.4, 126.0, 123.9, 31.8, 30.6, 30.4, 29.5, 29.4, 29.3, 29.2, 22.6, 14.0; **MALDI:** 582.2; HRMS (ESI): calculated 582.2118; found 582.2133.

**2-cyano-3-(3''',4'-dioctyl-[2,2':5',2''':5'',2''''-quaterthiophene]-5-yl)acrylic acid (4T)**

3 (0.24 g, 0.41 mmol) is mixed with cyanoacetic acid (71 mg, 0.82 mmol), ammonium acetate (0.19 g, 2.47 mmol) in glacial acetic acid (100 mL) and the solution is refluxed for 12 h. After slowly cooling the mixture at room temperature, a dark precipitate is formed, filtered and washed with a diluted solution of sodium hydroxide and then with water to afford a black solid (140 mg, 53%). M.p.: 95-99 °C; **1H NMR (300 MHz, CDCl₃), δ (ppm):** 8.28 (s, 2H), 7.68 (d, J=4.2 Hz, 1H), 7.23 (d, J=4.2 Hz, 1H), 7.20 (d, J=5.1 Hz, 1H), 7.12 (d, J=3.9 Hz, 1H), 7.07 (d, J=3.6 Hz, 1H), 6.95 (d, J=5.4 Hz, 1H), 2.78 (t, J=7.8 Hz 4H), 1.68-1.60 (m, 4H), 1.40-1.27 (m,
20H), 0.87 (m, 6H); $^{13}$C NMR (75MHz, CDCl$_3$), δ (ppm): 167.9, 148.8, 147.6, 141.0, 140.6, 140.0, 137.2, 134.7, 133.8, 133.7, 132.7, 130.2, 130.0, 126.6, 126.1, 124.2, 124.0, 115.6, 95.6, 31.8, 30.6, 30.4, 29.6, 29.5, 29.4, 29.3, 29.2, 22.6, 14.1; MS MALDI: 649.3; HRMS (MALDI): calculated 649.2177; found 649.2159.

2,5-bis(tributylstannyl)thiophene (6). n-BuLi (2.5 M in hexane, 26 mmol, 10.4 mL) is added dropwise at -78 °C to a solution containing the 2,5-dibromothiophene (2.42 g, 10 mmol) dissolved in dry THF under Ar atmosphere. The mixture is stirred for 1 h at the addition temperature. Tributyltin chloride (8.6 ml, 30 mmol) is then added dropwise at the same temperature. The mixture is stirred at -20°C for 1/2h and then allowed to warm slowly to room temperature. After dilution with diethyl ether, a saturated solution of NaF is added and the mixture is stirred for 1 h. The precipitate is filtered off using celite and the filtrate is washed with a saturated solution of NaHCO$_3$ then with water. After drying over MgSO$_4$, the solvent is evaporated and the product was used in the next step without further purification.

$^1$H NMR (300 MHz, CDCl$_3$): 7.34 (s, 2H), 1.62 - 1.53 (m, 12 H), 1.38 - 1.29 (m, 12 H), 1.13 - 1.08 (m, 12 H), 0.94 - 0.84 (m, 18 H)

3,3'',3''''',4'''''-tetraoctyl-2,2':5',2''':5'',2'''':5'''':2''''':5'''''':2''''''':5''''''':2'''''''-septithiophene (7a). A mixture of 1b (0.5 g, 0.9 mmol), Stille reagent 6 (0.27 g, 0.41 mmol,) and Pd(PPh$_3$)$_4$ (100 mg, 10 mol %) in 100 mL of anhydrous toluene is refluxed overnight. After concentration, the residue is taken in CH$_2$Cl$_2$ and the organic phase is washed twice with an aqueous solution of NaHCO$_3$ then with water. After drying over MgSO$_4$, the solvent is removed and the residue is chromographed on silica gel using a mixture of dichloromethane and petroleum ether (1:3) as eluent to afford a reddish oil (0.42 g, 47%).

$^1$H NMR (300 MHz, CDCl$_3$): 7.19 (d, J=5.1 Hz, 2H), 7.08-7.04 (m, 6H) 7.01 (s, 2H), 6.95 (d, J=5.1 Hz, 2H), 2.81-2.74 (m, 8H), 1.73-1.60 (m, 8H), 1.39-1.23 (m, 40), 0.90-0.82 (m, 12 H).

3,3'',3''''''''''-tetraoctyl-[2,2':5',2''':5'',2'''':5'''':2''''':5'''''':2''''''':5'''''''':2'''''''''-septithiophene]-5-carbaldehyde (7b). A Vilsmeier reagent, which is prepared with POCl$_3$ (0.05 mL, 0.49 mmol) in dry DMF (0.04 mL, 0.49 mmol), is added to a cold solution of 7a (0.36 g, 0.35 mmol) in 1,2-dichloroethane (20 mL) at 0 °C under Ar. After being stirred at 70 °C for 20 h, the solution is cooled to room temperature, diluted with CH$_2$Cl$_2$ and stirred with a solution of NaCOOCH$_3$ for 2 h. The organic layer is washed with water and brine, dried over MgSO$_4$. After removal of solvent the residue is chromographed on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluent to afford a reddish solid (0.12 g, 34%).

$^1$H NMR (300 MHz, CDCl$_3$): 9.83 (s, 1H), 7.59 (s, 1H), 7.25 (d, J=3.9 Hz, 1H), 7.19 (d, J=5.1 Hz, 1H), 7.12 (d, J=3.9 Hz, 1H), 7.08-7.05 (m, 3H), 7.02-7.01 (m, 2H), 6.95 (d, J=5.1 Hz, 1H),
2-cyano-3-(3,3''',3''''',4''''''-tetraoctyl)[2,2':5',2''':5'',2''':5'',2''''':5'''',2''''''':5''''','2'''''''':5''''''',2'''''''''':5''''''''']-5-yl)acrylic acid (7Ti). 7b (100 mg, 0.09 mmol) is mixed with cyanoacetic acid (40 mg, 0.19 mmol), ammonium acetate (80 mg, 0.47 mmol) in glacial acetic acid (40 mL) and the solution is refluxed for 12 h. After slowly cooling the mixture at room temperature, a dark precipitate is formed, filtered and washed with a diluted solution of sodium hydroxide and water to afford a black solid (70 mg, 66%). M.p.: 70-72°C; ¹H NMR (500 MHz, THF-d8), δ (ppm): 10.85 (s, 1H), 8.30 (s, 1H) 7.77 (s, 1H), 7.14 (d, J=4.0 Hz, 1H), 7.30 (d, J=5.0 Hz, 1H), 7.25 (d, J=3.5 Hz, 1H), 7.21-7.19 (m, 3H), 7.17 (s, 1H), 7.15 (d, J=4.0 Hz, 1H), 7.11 (d, J=3.3 Hz, 1H) 6.98 (d, J=3.3 Hz, 1H), 2.84-2.74 (m, 8H), 1.7-1.60 (m, 8H), 1.14-1.12 (m, 40H), 0.90-0.85 (m, 12H); ¹³C NMR (75 MHz, THF-d8), δ (ppm): 163.7, 146.0, 142.0, 141.7, 141.2, 141.0, 140.4, 139.7, 138.6, 137.0, 136.8, 136.3, 136.1, 136.0, 135.4, 135.0, 134.3, 130.7, 130.3, 129.6, 129.0, 127.6, 127.5, 127.1, 126.8, 125.4, 125.2, 124.8, 116.2, 115.0, 99.8, 85.1, 32.7, 31.5, 31.2, 31.1, 30.9, 30.3, 30.2, 30.0, 29.8, 23.4, 14.2; HRMS (MALDI): calculated 1119.4312; found 1119.4323.

3,3''',3''''',4'-tetraoctyl-[2,2':5',2''':5'',2''':5'',2''''':5'''',2''''''':5''''''',2'''''''''':5'''''''''',2''''''''''':5'''''''''']-5-carbaldehyde (4b). A Vilsmeier reagent, which is prepared with POCl₃ (0.16 mL, 1.74 mmol) in dry DMF (0.13 mL, 1.74 mmol), is added to a cold solution of 4a (1 g, 1.16 mmol) in 1,2-dichloroethane (25 mL) at 0 °C under Ar. After being stirred at 60 °C for 12 h, the solution was cooled to room temperature, diluted with CH₂Cl₂ and stirred with a solution of NaCOOCH₃ for 2 h. The organic layer is then washed with water and brine, dried over MgSO₄. After removal of solvent it is chromatographed on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluent to afford reddish oil (0.33 g, 32%). ¹H NMR (300 MHz, CDCl₃): 9.82 (s, 1H), 7.58 (s, 1H), 7.18 (d, 1H), 7.13 (s, 1H), 7.12 (d, 1H), 7.10 (d, 1H), 6.95 (s, 1H), 6.94 (d, 1H), 2.85-2.75 (m, 8H), 1.74-1.62 (m, 8H), 1.41-1.27 (m, 40H), 0.89-0.85 (m, 12H)

2-cyano-3-(3,3''',3''''',4'-tetraoctyl)[2,2':5',2''':5'',2''':5'',2''''':5'''',2''''''':5''''''',2'''''''''':5'''''''''',2''''''''''':5'''''''''']-5-yl)acrylic acid (5T). 4b (0.32 g, 0.36 mmol) is mixed with cyanoacetic acid (47 mg, 0.54 mmol), ammonium acetate (57.2 mg, 0.72 mmol) in glacial acetic acid (50 mL) and the solution is refluxed for 12 h. After cooling at room temperature, the mixture is poured into water, extracted with CH₂Cl₂, dried over MgSO₄. The obtained residue is precipitated from acetic acid
and reprecipitated from MeOH to afford a dark shiny precipitate (0.2 g, 59%). M.p.: 120-123 °C; 1H NMR (500 MHz, THF-d6), δ (ppm): 10.85 (s, 1H), 8.29 (s, 1H), 7.74 (s, 1H), 7.31 (s, 1H), 7.28 (d, J=5.0 Hz, 1H), 7.23 (d, J=4.0 Hz, 1H), 7.18 (d, J=4.0 Hz, 1H), 7.02 (s, 1H), 6.96 (d, J=5.0 Hz, 1H), 2.90-2.79 (m, 8H), 1.48-1.41 (m, 8H), 1.40-1.29 (m, 40H), 0.89-0.86 (m, 12H); 13C NMR (75 MHz, THF-d6), δ (ppm): 163.7, 146.0, 141.9, 141.8, 141.3, 140.9, 140.4, 137.1, 135.6, 135.4, 134.2, 133.4, 133.3, 131.5, 130.8, 130.6, 130.5, 129.4, 127.4, 126.9, 124.7, 116.3, 99.7, 32.7, 31.4, 31.3, 30.8, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.7, 23.4, 14.2; MS MALDI: 955.4; HRMS (MALDI): calculated 955.4558, found 955.4557.

3,3'''',3''''',3'''''''-hexaoctyl-[2,2':5',2''':5'',2''''':5''''',2'''''':5''''''',2'''''''''-septithiophene]-5-carbaldehyde (5b). A Vilsmeier reagent, which is prepared with POCl₃ (0.09 mL, 0.99 mmol) in dry DMF (0.07 mL, 0.99 mmol), is added to a cold solution of 5a (1.04 g, 0.83 mmol) in 1,2-dichloroethane (15 mL) at 0 °C under Ar. After being stirred at 60 °C for 12 h, the solution is cooled to room temperature, diluted with CH₂Cl₂ and stirred with a solution of NaCOOCH₃ for 2 h. The organic layer is washed with water and brine, dried over MgSO₄. After removal of solvent the residue is chromatographed on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluent to afford a reddish solid (0.3 g, 30%).

1H NMR (300 MHz, CDCl₃): 9.82 (s, 1H), 7.58 (s, 1H), 7.17 (d, J=5.0 Hz, 1H), 7.13 (s, 1H), 7.11 (s, 2H), 7.01 (s, 1H), 6.98 (s, 1H), 6.94 (s, 1H), 6.94 (d, J=5.0 Hz, 1H), 2.85-2.76 (m, 12H), 1.72-1.68 (m, 12H), 1.39-1.28 (m, 60H), 0.90-0.86 (m, 18H).

2-cyano-3-(3,3'''',3''''',3'''''''-hexaoctyl-[2,2':5',2''':5'',2''''':5''''',2'''''':5'''''''''-septithiophen]-5-yl)acrylic acid (7Tr). 5b (0.61 g, 0.47 mmol) is mixed with cyanoacetic acid (41 mg, 0.47 mmol), ammonium acetate (55.15 mg, 0.71 mmol) in glacial acetic acid (50 mL) and the solution is refluxed for 12 h. After cooling at room temperature, the mixture is poured into water, extracted with CH₂Cl₂, dried over MgSO₄. The obtained residue is solved in minimum of CH₂Cl₂ and reprecipitated from MeOH. The dark precipitate is chromatographed on silica gel using first dichloromethane and then methanol as eluent to afford reddish oil 9 (0.35 g, 57%). M.p.: 48-52 °C; 1H NMR (500 MHz, THF-d8), δ (ppm): 8.29 (s, 1H), 7.74 (s, 1H), 7.31 (s, 1H), 7.28 (d, J=5.0 Hz, 1H), 7.20 (d, J=4.0 Hz, 1H), 7.18 (d, J=4.0 Hz, 1H), 7.15 (s, 1H), 7.07 (s, 1H), 7.01 (s, 1H), 6.96 (d, J=5.0 Hz, 1H), 2.90-2.79 (m, 12H), 1.47-1.42 (m, 12H), 1.38-1.27 (m, 60H), 0.89-0.87 (m, 18H); 13C NMR (75 MHz, THF-d8), δ (ppm): 163.8, 145.9, 141.6, 141.1, 140.8, 140.3, 139.3, 139.2, 139.0, 136.6, 134.6, 134.2, 134.0, 133.2, 130.8, 130.6, 129.7, 129.0, 126.8, 126.6, 126.4, 126.3, 124.7, 116.3, 99.7, 32.6, 31.4, 31.2, 30.9, 30.3, 30.2, 30.0, 29.8, 23.3, 14.2; MALDI: 1343.6; HRMS (ESI): calculated 1342.6743, found 1342.6742.
Fabrication and evaluation of solar cells

TiO$_2$ electrodes were prepared by spreading (doctor blading) a colloidal TiO$_2$ paste (20 nm sized; “Dyesol” DSL 18NR-T) onto a conducting glass slide (FTO, Hartford glass company, TEC 8, having a thickness of 2.3 mm and a sheet resistance in the range 6–9 $\Omega/\text{cm}^2$) that had been cleaned with water and EtOH, treated with a plasma cleaner at 100W for 10 min, dipped in a freshly prepared aqueous TiCl$_4$ solution (4.5x10$^{-2}$ M), at 70 °C, for 30 min, and finally washed with ethanol. After a first drying at 125 °C for 15 min, a reflecting scattering layer containing >100 nm sized TiO$_2$ (“Solaronix” Ti-Nanoxide R/SP) was bladed over the first TiO$_2$ coat and sintered till 500 °C for 30 min. Then the glass coated TiO$_2$ was dipped again into a freshly prepared aqueous TiCl$_4$ solution (4.5x10$^{-2}$ M), at 70 °C for 30 min, washed with ethanol and heated once more at 500 °C for 15 min. At the end of these operations the final thickness of the TiO$_2$ electrode was in the range 8–12 µm, as determined by SEM analysis. After the second sintering, the FTO glass coated TiO$_2$ was cooled at about 80 °C and immediately dipped into a dichloromethane solution [5x10$^{-3}$ M] of the selected dye at r.t. for 24 h. The dyed titania-glasses were washed with EtOH and dried at r.t. under a N$_2$ flux. Finally the excess of TiO$_2$ was removed with a sharp Teflon penknife and the exact active area of the dyed TiO$_0$ was calculated by means of a microphotography. A 50 µm thick Surlyn spacer (TPS 065093-50 from Dyesol) was used to seal the photoanode and a platinized FTO counter electrode. Then the cell was filled up with an electrolytic solution of the following composition: N-methyl-N-butylimidazolium iodide (0.6 M) + I$_2$ (0.04 M) + LiI (0.025 M) + guanidinium thiocyanate (0.05 M) + t-butylpyridine (0.28 M) in valeronitrile/acetonitrile 15:85 (v/v).

The photovoltaic performances of the cells were measured with a solar simulator (Abet 2000) equipped with a 300W Xenon light source; the light intensity was adjusted with a standard calibrated Si solar cell (“VLSI Standard” SRC-1000-RTD-KG5); the current–voltage characteristics were acquired by applying an external voltage to the cell and measuring the generated photocurrent with a “Keithley 2602A” (3A DC, 10A Pulse) digital source meter.
**Fig. S1.** $^1$H and $^{13}$C NMR spectra of 4T.
Fig. S2. $^1$H and $^{13}$C NMR spectra of 5T.
Fig. S3. $^1$H and $^{13}$C NMR spectra of 7Tr.
Fig. S4. $^1$H and $^{13}$C NMR spectra of 7Ti.
Theoretical calculations

Fig. S5. Optimized geometries for various conformations and calculated absorption spectra for 7Ti
Fig. S6. Optimized geometries for various conformations and calculated absorption spectra for 7Tr.