Supporting Information

Dithienopyrrole-based oligothiophenes for solution-processed organic solar cells

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General remarks:

NMR spectra were recorded on a Bruker DRX 400 spectrometer (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz). Chemical shift values (δ) are expressed in parts per million using residual solvent protons (¹H NMR, $\delta_{\rm H}$ = 7.26 for CDCl₃; ¹³C NMR, $\delta_{\rm C}$ = 77.0 for CDCl₃) as internal standard. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet) and m (multiplet). Elemental analyses were performed on an Elementar Vario EL. Melting points were determined using a Mettler Toledo DSC 823. Thin layer chromatography was carried out on aluminum plates, precoated with silica gel, Merck Si60 F254. Preparative column chromatography was performed on glass columns packed with silica gel, Merck Silica 60, particle size $40 - 63 \mu m$. High performance liquid chromatography was performed on a Hitachi instrument equipped with a UV-vis detector L-7420, columns (Nucleosil 100-5 NO2 with a pore size of 100 Å) from Machery-Nagel using a dichloromethane/n-hexane mixture (40:60) as eluent. EI mass spectra were recorded on a Varian Saturn 2000 GC-MS, MALDI-MS experiments were performed using a MS Bruker Reflex 2 (Bruker Daltonik GmbH, Bremen, Germany) using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. UV/Vis absorption spectra were recorded in 1 cm cuvettes with Merck Uvasol grade solvents on a Perkin Elmer Lambda 19 spectrometer. Cyclic voltammetry experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell with a platinum working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferrocenium couple. Surface images of the photoactive layers were recorded with the help of a Bruker Nanoscope V AFM at ambient temperature in tapping mode. Tetrahydrofuran and N,N-dimethylformamide (Merck) were absoluted via MB SPS-800 solvent purifying system (MBraun). Diisopropylamine (Merck) was absoluted over calcium hydride. All synthetic steps were carried out under argon atmosphere. n-Butyl lithium (1.6 mol/L in n-hexane) was purchased from Acros, trimethyltin chloride and 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased from Sigma-Aldrich, iodine, ammonium acetate, malononitrile and piperidine was purchased from Merck. Tetrakis(triphenylphosphine)palladium (0) was prepared according to literature.¹

Device fabrication: ITO-coated glass substrates from VisionTec (14 Ohm/sq) were structured and plasma etched (Diener electronic, Pico) with Argon for 120 s at 30W and a base pressure of 0.38 mbar. Then PEDOT:PSS (Clevios P VP.AI 4083 solution from Heraeus) which was diluted with deionized water in a 1:1 ratio was doctor-bladed and ~10 nm thick layers were obtained. Afterwards, the substrates were spin-coated (Laurell CZ-650 series) with chloroform solutions loaded with 12.5 mg/ml of oligomer **1** or **2** and PC₆₁BM ([6,6]-phenyl-C₆₁-butyric acid methyl ester, Solenne) leading to ~70 nm thick photoactive layers. Thin layers of LiF (0.3 nm) and AI (120 nm) were then evaporated at a pressure of 2 x 10⁻⁶ mbar in Univex 450 from Leybold. Current voltage analysis was carried out with a WACOM 2-lamp solar simulator (class AAA, AM 1.5G) and a Keithley 2400 current source measure unit. The quantum efficiency measurements were performed using equipment from Optosolar. As light source we utilized a 100 W xenon lamp and the filtered monochromatic light was monitored with a Si cell. A bias light with 0.1-0.2 sun was used. High resolution field emission scanning electron microscopy was carried out on a Sirion XL30 instrument from FEI.

Synthesis:

The synthesis of dicyanovinylene-capped iodobithiophene **6** is shown in Scheme S1 and starts with the borylation of 2-bromo-3-hexylthiophene² by lithiation at -78 °C using *n*-butyl lithium and subsequent quenching with 2-*iso*-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane resulting in boronic acid ester **8**³ in 66% yield. Pd⁰-catalyzed Suzuki-Miyaura cross-coupling reaction of borylated thiophene **8** and 2-(1,3-dioxolan-2-yl)-5-iodothiophene **9** gave bithiophene **10** in 90% yield. During work up and purification some acetal groups cleaved off to aldehyde **11** which cannot be separated. The follow-up complete deprotection of **10** with hydrochloric acid (25%) led to bithiophene-carbaldehyde **11** in 98% yield. Afterwards, iodination was carried out with mercury caproate and iodine to obtain iodobithiophene carbaldehyde **12** in 91% yield. Knoevenagel condensation of carbaldehyde **12** using malononitrile and ammonium acetate as base gave building block **6** in a yield of 94%. Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013



Scheme S1. Synthesis of building block **6**. (i) n-BuLi, tetrahydrofuran, -78 °C – r.t., 18 h. (ii) **8**, [Pd(PPh₃)₄], K₃PO₄, dimethoxyethane/H₂O, 90 °C, 15 h. (iii) HCl aq. (25%), propanol, 50 °C, 12 h. (iv) Hg(OOCC₅H₁₁)₂, dichloromethane, 25 h, I₂, 4 h, r.t.. (v) CH₂(CN)₂, NH₄OAc, dichloroethane/ethanol, 60 °C, 16h.

Bromo derivative 7 was synthesized according to Scheme S2. Thus, 5'-bromo-3,4'-dihexyl-2,2'-bithiophene³ was formylated by lithiation with lithium diisopropylamide and subsequent quenching with N,N-dimethylformamide resulting in bromo-bithiophene-carbaldehyde **13** in 76% yield. Finally, Knoevenagel condensation of carbaldehyde **13** with malononitrile using piperidine as base gave the corresponding dicyanovinylene derivative **7** in 87% yield.



Scheme S2. Synthesis of building block 7. (i) a) lithium diisopropylamide, tetrahydrofuran, -78 °C, 45 min b) N,N-dimethylformamide, -78 °C – r.t., 20 h. (ii) $CH_2(CN)_2$, piperidine, dichloroethane /ethanol, 60 °C, 18 h.

Experimental:

2-(4,3'-Dihexyl-2,2'-bithien-5-yl)-[1,3]dioxolane (10): To a mixture of 16.15 g (44 mmol) **9**, 14.27 g (48.5 mmol) **8**³ and 2.04 g (1.77 mmol) tetrakis(triphenylphosphine)palladium 105 mL degassed dimethoxyethane was added and purged with argon under stirring. After about 20 min. 67 ml 2 molar aqueous K_3PO_4 solution was added and the heterogeneous mixture was heated to 90 °C under vigorous stirring. Within 15 h the reaction turned darker and was poured on 400 ml water. After phase separation, the aqueous one was extracted three times with diethyl ether and the combined organic solutions were washed twice with water and once with satd. NaHCO₃ solution. After drying over Na₂SO₄, the solvent and volatile materials are removed in vacuum and the residue taken up in pentane. This solution was washed again with 1 molar HCl, water and satd. NaHCO₃ solution, which resulted in a precipitation of the catalyst. The yellow-brown solution was filtered over celite and Na₂SO₄ and the solvent was removed from the filtrate. The residue was purified on a

silica column. Impurities were removed with petrol ether first and the product eluted with diethyl ether. The product consisting of a 1:1 mixture of the acetal **10** and the aldehyde **11** was isolated as a yellow oil in a total yield of 16.09 g (90%). $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.85-0.92 (m, 6H, CH₃), 1.25-1.45 (m, 12H, CH2), 1.55-1.75 (m, 4H, CH2), 2.63 (t, ${}^{3}J = 7.7$ Hz, 2H, CH₂), 2.73 (t, ${}^{3}J = 7.7$ Hz, 2H, CH₂), 3.96-4.06 (m, 2H, OCH₂), 4.11-4.21 (m, 2H, CH₂O), 6.12 (s, 1H, CH), 6.86 (s, 1H, Th-H3), 6.91 (d, ${}^{3}J = 5.2$ Hz, 1H, Th-H4'), 7.13 (d, ${}^{3}J = 5.2$ Hz, 1H, Th-H5'). $\delta_{\rm C}$ (100 MHz, CDCl₃) 14.1, 22.6, 28.4, 29.1, 29.2, 30.6, 30.8, 31.67, 65.3, 99.0, 123.6, 127.9, 129.9, 134.1, 135.6, 139.6, 142.23.

3',4-Dihexyl-2,2'-bithiophen-5-carbaldehyde (11): To a solution of 17.3 g (45 mmol) of acetal **10** (as 50 Mol% mixture with **11**) in 50 mL *n*-propanol were added 58 ml hydrochloric acid (25 w%) and heated to 50-60°C under vigorous stirring for 15 h. The heterogeneous mixture was extracted with pentane twice and the combined organic phases washed two times with water and satd. NaHCO₃ solution. After drying over Na₂SO₄, the solvent was removed and the crude product filtered over silica with dichloromethane -petrol ether (9:1). Pure **11** was isolated in 98% yield (15.96 g, 44.02 mmol) as pale yellow-brown oil. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.88 (t, ${}^{3}J$ = 7.0 Hz, 3H, CH₃), 0.89 (t, ${}^{3}J$ = 7.0 Hz, 3H, CH₃), 1.25-1.45 (m, 12H, CH₂), 1.64 (m, 2H, CH₂), 1.70 (m, 2H, CH₂), 2.81 (t, ${}^{3}J$ = 7.8 Hz, 2H, CH₂), 2.94 (t, ${}^{3}J$ = 7.7 Hz, 2H, CH₂), 6.95 (d, ${}^{3}J$ = 5.1 Hz, 1H, Th-H4'), 7.02 (s, 1H, Th-H3), 7.25 (d, ${}^{3}J$ = 5.2 Hz, 1H, Th-H5'), 10.00 (s, 1H, CHO). $\delta_{\rm C}$ (100 MHz, CDCl₃) 14.1, 22.6, 28.5, 29.0, 29.2, 29.6, 30.4, 31.4, 31.6, 31.7, 125.5, 128.5, 129.8, 130.7, 136.3, 142.0, 145.5, 153.3, 181.7. Elemental analysis calcd for C₂₁H₃₀OS₂: C, 69.56; H, 8.43; S, 17.96%; found: C, 69.45; H, 8.57; S 18.05%.

3',4-Dihexyl-5'-iodo-2,2'-bithiophen-5-carbaldehyde (12): 16.1 g (44.4 mmol) aldehyde **11** was dissolved in 200 mL dichloromethane and 19.5 g (45 mmol) mercury caproate (prepared from mercury oxide and hexanoic acid in chloroform) was added in one portion. After stirring for 25 h at room temperature and exclusion of light, in which a clear solution has formed, iodine (11.5 g, 45.3 mmol) dissolved in 200 mL dichloromethane was added under vigorous stirring. At the end of the addition a red precipitate formed and the mixture became bright yellow. After 4 h the mixture is filtered through celite and the filtrate washed successively with aqueous potassium iodide, sodium carbonate, thiosulfate solution and brine. The organic phase was dried over Na₂SO₄ and the solvent and volatile components removed in vacuum. The dark-brown crude product was purified on a silica column with *n*-hexane-dichloromethane (2:1) furnishing **12** (19.77 g, 40.5 mmol) in yield of 91% as bright yellow oil. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.88 (t, ${}^{3}J$ = 6.6 Hz, 3H, CH₃), 0.89 (t, ${}^{3}J$ = 6.8 Hz, 3H, CH₃), 1.20-1.45 (m, 12H, CH₂), 1.61 (m, 2H, CH₂), 1.68 (m, 2H, CH₂), 2.75 (t, ${}^{3}J$ = 7.8 Hz, 2H, CH₂), 2.93 (t, ${}^{3}J$ = 7.7 Hz, 2H, CH₂), 6.95 (s, 1H, Th-H4'), 7.09 (s, 1H, Th-H3), 7.25 (d, ${}^{3}J$ = 5.2 Hz, 1H, Th-H5'), 10.00 (s, 1H, CHO). $\delta_{\rm C}$ (100 MHz, CDCl₃) 14.1, 22.5, 22.6, 28.4, 29.0, 29.1,

29.2, 30.3, 31.4, 31.5, 31.6, 74.2, 128.7, 135.7, 136.7, 140.3, 143.5, 143.7, 153.2, 181.7. Elemental analysis calcd for C₂₁H₂₉IOS₂: C, 51.63; H, 5.98; S, 13.13%; found: C, 51.74; H, 5.83; S 13.15%.

2-[(3',4-Dihexyl-5'-iodo-2,2'-bithien-5-yl)methylene]malononitrile (6): To a solution of 4.00 g (8.2 mmol) aldehyde **12** in 30 mL 1,2-dichloroethane a solution of 0.81 g (12.3 mmol) malonodinitrile and 0.12 g (1.5 mmol) ammonium acetate in 30 mL ethanol is added and the mixture heated up to 60 °C under stirring. After 15 h the reaction solution was cooled to room temperature and poured onto water. After phase separation the aqueous one was extracted twice with dichloromethane and the combined organic solutions were washed with water and brine. Solvent and volatile components were evaporated in vacuum, during which the product crystallized. The crude product was recrystallized from ethanol and the residue of the filtrate purified on a silica column with dichloromethane-petrol ether (1:1). Compound **6** was obtained in a yield of 94% (4.15 g 7.74 mmol) as a red solid. Mp 95 °C. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.88 (t, ${}^{3}J$ = 6.6 Hz, 3H, CH₃), 0.91 (t, ${}^{3}J$ = 6.8 Hz, 3H, CH₃), 1.20-1.45 (m, 12H, CH₂), 1.61 (m, 2H, CH₂), 1.55-1.70 (m, 4H, CH₂), 2.74 (t, ${}^{3}J$ = 7.8 Hz, 2H, CH₂), 2.78 (t, ${}^{3}J$ = 7.9 Hz, 2H, CH₂), 7.01 (s, 1H, Th-H4'), 7.12 (s, 1H, Th-H3), 7.84 (s, 1H, CH). $\delta_{\rm C}$ (100 MHz, CDCl₃) 14.1, 22.5, 29.0, 29.1, 29.6, 30.3, 31.3, 31.5, 31.6, 74.5, 76.0, 113.7, 115.0, 127.8, 129.5, 135.1, 140.8, 144.9, 145.4, 147.6, 156.2. Elemental analysis calcd for C₂₄H₂₉IN₂S₂: C, 53.73; H, 5.45; N, 5.22; S, 11.95%; found: C, 53.99; H, 5.28; N, 5.19; S, 11.99%.

5'-Bromo-3,4'-dihexyl-2,2'-bithiphene-5-carbaldehyde (13): Diisopropyl amine (245 mg, 2.42 mmol) was added dropwise to a solution of *n*-butyl lithium (1.5 mL, 2.42 mmol) in tetrahydrofuran at -78 °C. the mixture was stirred for 30 min and warmed to 0 °C and stirred for another 30 min. 5'-Bromo-3,4'-dihexyl-2,2'-bithiophene³ (1.00 g, 2.42 mmol) dissolved in tetrahydrofuran was added to the lithium diisopropylamide mixture dropwise. The reaction mixture was stirred for 1 h, then it was quenched with N,N-dimethylformamide and stirred overnight. Then the solvent was removed and the crude compound was purified by column chromatography using petrol ether:dichloromethane (3:2) to yield the pure product **13** (812 mg, 1.84 mmol) as a bright yellow oil in 76% yield. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.89 (t, ${}^{3}J$ = 6.7 Hz, 6H, CH₃) , 1.44-1.26 (m, 12H, CH₂), 1.70-1.56 (m, 4H, CH₂), 2.57 (t, ${}^{3}J$ = 7.8 Hz, 2H, CH₂), 2.74 (t, ${}^{3}J$ = 7.9 Hz, 2H, CH₂), 6.96 (s, 1 H, Th'-H3), 7.57 (s, 1 H, Th-H4), 9.82 (s, 1 H, CHO). $\delta_{\rm C}$ (100 MHz, CDCl₃) 14.1, 14.1, 22.6, 28.9, 29.1, 29.2, 29.5, 29.6, 30.3, 31.6, 111.2, 128.3, 134.3, 138.8, 140.4, 140.5, 143.0, 182.6. Elemental analysis calcd for C₂₁H₂₉BrOS₂ (%): C, 57.13; H, 6.62; S, 14.53; found (%): C, 57.25; H, 6.67; S, 14.45.

2-((5'-Bromo-3,4'-dihexyl-[2,2'-bithien-5-yl)methylene)malononitrile (7): 5'-Bromo-3,4'-dihexyl-2,2'-bithiophene-5-carbaldehyde (800 mg, 1.81 mmol), malononitrile (0.360 g, 5.45 mmol) and 2 drops of piperidine were dissolved in dichloroethane:ethanol (3:1) and heated at 60 °C for 12 h. Then, the solvent was evaporated and dried under vacuum. The crude compound was purified by column chromatography using *n*-hexane:dichloromethane (1:1) followed by recrystallization from

ethanol to obtain **7** as orange solid (771 mg, 1.57 mmol) in 87% yield. Mp 71 °C. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.89 (t, ${}^{3}J = 6.7$ Hz, 6H, CH₃), 1.37-1.28 (m, 12 H, CH₂), 1.63-1.58 (m, 4H, CH₂), 2.57 (t, ${}^{3}J = 7.7$ Hz, 2 H, CH₂), 2.75 (t, ${}^{3}J = 7.9$ Hz, 2 H, CH₂), 7.05 (s, 1 H, Th'-H3), 7.50 (s, 1 H, Th-H4), 7.69 (s, 1 H, CH). $\delta_{\rm C}$ (100 MHz, CDCl₃) 14.0, 14.1, 22.5, 22.6, 28.9, 29.1, 29.5, 29.6, 30.1, 31.5, 31.5, 129.1, 132.2, 133.4, 140.8, 141.6, 143.1, 143.4, 150.1. Elemental analysis calcd for C₂₄H₂₉BrN₂S₂ (%): C, 58.88; H, 5.97; N, 5.72; S, 13.10. Found (%): C, 58.99; H, 6.09; N, 5.60; S, 13.15. MS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₂₄H₂₉BrN₂S₂: 488; found [M]⁺: 488.

2,6-Bis(trimethylstannyl)-*N*-(**2-ethylhexyl)-dithieno**[**3,2-***b***:2'**,**3'-***d***]pyrrole** (**4**): 245 mg (0.84 mmol) N-2-ethylhexyl-dithieno[**3**,2-*b*:2',3'-*d*]**pyrrole** was dissolved in 3.3 mL tetrahydrofuran and cooled to -78 °C. 1.16 mL *n*-butyl lithium (1.6 M, 1.85 mmol) was added dropwise. The reaction mixture was stirred for 1 h at -78 °C and 1 h at 0 °C. After cooling down to -78 °C, 377 mg (1.89 mmol) trimethyltin chloride dissolved in 0.5 mL tetrahydrofuran was added and the reaction mixture was stirred for 2.5 h at that temperature. Subsequently, the reaction mixture was poured into water and extracted with *n*-hexane. After drying over sodium sulfate and removal of the solvents, 511 mg crude product **4** was obtained in >95% purity (determined by ¹H-NMR) as a slightly yellow oil, which was used without any further purification. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.40 (s, 18H, Sn-CH₃), 0.88 (t, ³*J* = 7.2 Hz, 3H, CH₃), 0.92 (t, ³*J* = 7.4 Hz, 3H, CH₃), 1.43-1.26 (m, 8H, CH₂), 2.01-1.94 (m, 1H, CH), 4.10-3.99 (m, 2H, CH₂), 6.96 (s, 2H, DTP-H).

2.2'-[5'.5''-(N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)-bis(3',4-dihexyl-2,2'-bithien-5,5'-diyl)]-bis(methane-1-yl-1-ylidine)dimalononitrile (1): 227 mg (368 µmol) 2,6-Bis(trimethylstannyl)-N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrole, 474 mg (883 µmol) 2-((3',4-dihexyl-5'-iodo-[2.2'-bithiophen]-5-yl)methylene)malononitrile and 17.0 mg (14.7 µmol) tetrakis(triphenylphosphine)palladium(0) were added in a Schlenk-tube and evacuated for 10 min. After adding 23 mL N,N-dimethylformamide, the reaction mixture was carefully degassed and heated to 60 °C for 6 h. Subsequently, the reaction mixture was cooled down to room temperature and poured into satd. ammonium chloride solution. Extraction with dichloromethane followed by drying over sodium sulfate, removal of solvents, digesting in ethyl acetate and succeeding column chromatography using dichloromethane led to oligomer 1 (342 mg, 308 µmol) as a black solid in 84% yield. Mp 264 °C. $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.96-0.88 (m, 18H, CH₃), 1.40-1.27 (m, 28H, CH₂), 1.48-1.42 (m, 4H, CH₂), 1.74-1.60 (m, 8H, CH₂), 1.99-1.93 (m, 1H, CH), 2.74 (t, ${}^{3}J = 7.8$ Hz, 4H, CH₂), 2.83 (t, ${}^{3}J = 7.8$ (t, ${}^{3}J = 7.8$ 7.9 Hz, 4H, CH₂), 4.08-3.98 (m, 2H, CH₂), 7.05 (s, 4H, Th-H), 7.08 (s, 2H, DTP-H), 7.78 (s, 2H, CH). δ_{C} (100 MHz, CDCl₃) 10.7, 14.0, 14.0, 22.5, 22.5, 23.0, 28.4, 29.0, 29.1, 29.2, 30.0, 30.3, 30.5, 31.2, 31.5, 31.6, 73.1, 108.1, 114.0, 115.0, 115.3, 126.6, 126.7, 127.5, 128.9, 134.3, 139.8, 144.9, 145.7, 147.0, 147.0, 156.4. MS (MALDI-TOF) m/z: [M]⁺ calcd for C₆₄H₇₇N₅S₆: 1107; found [M+H]⁺: 1108. Elemental analysis calcd (%) for C₆₄H₇₇N₅S₆: C, 69.33; H, 7.00; N, 6.32; S, 17.35; found: C, 69.03; H, 6.78; N, 6.25; S, 17.17.

2,2'-[5',5''-(N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)-bis(3,4'-dihexyl-2,2'-bithien-5,5'-diyl)]-bis(methane-1-yl-1-ylidine)dimalononitrile (2): 86.4 mg (140 µmol) 2,6-Bis(trimethylstannyl)-N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrole, 166 mg (340 µmol) 2-[(5'-bromo-3,4'dihexyl-[2,2'-bithien-5-yl])methane-1-yl-1-ylidine] malononitrile and 8.1 mg (7.00 µmol) tetrakis-(triphenylphosphine)palladium(0) were added in a Schlenk-tube and evacuated for 10 min. After adding 7 mL N,N-dimethylformamide, the reaction mixture was carefully degassed and heated to 80 °C for 1 d. Subsequently, the reaction mixture was cooled down to room temperature and poured into satd. ammonium chloride solution. Extraction with dichloromethane followed by drying over sodium sulfate, removal of the solvents, digesting in ethyl acetate and subsequent column chromatography using dichloromethane led to oligomer 2 (115 mg, 104 µmol) as a black solid in 74% yield. Mp 214 °C. δ_H (400 MHz, CDCl₃) 0.97-0.87 (m, 18H, CH₃), 1.47-1.29 (m, 32H, CH₂), 1.75-1.65 (m, 8H, CH₂), 2.01-1.94 (m, 1H, CH), 2.87-2.82 (m, 8H, CH₂), 4.14-4.04 (m, 2H, CH₂), 7.07 (s, 2H, DTP-H), 7.23 (s, 2H, Th-H), 7.51 (s, 2H, Th-H), 7.68 (s, 2H, CH). δ_C (100 MHz, CDCl₃) 10.7, 14.0, 14.0, 22.5, 22.6, 22.9, 24.0, 28.6, 29.1, 29.3, 29.3, 29.5, 29.9, 30.6, 30.6, 31.5, 31.6, 40.4, 51.4, 75.4, 109.9, 113.5, 114.4, 115.6, 131.5, 131.9, 132.9, 135.8, 140.3, 140.5, 141.9, 144.0, 145.1, 149.8. MS (MALDI-TOF) m/z: $[M]^+$ calcd for $C_{64}H_{77}N_5S_6$: 1107; found $[M+H]^+$: 1108. Elemental analysis: calcd (%) for C₆₄H₇₇N₅S₆: C, 69.33; H, 7.00; N, 6.32; S, 17.35; found: C, 69.54; H, 6.87; N. 6.27; S, 17.29.

Cyclic voltammetry



Figure S1. Cyclic voltammograms of oligomers 1 and 2 in dry dichloromethane–TBAPF₆ (0.1 M), scan speed 100 mV/s, potentials vs. Fc/Fc^+ .

Photovoltaic behaviour

Table S1. Photovoltaic parameters of solar cells fabricated using the following device structure: ITO| PEDOT:PSS| **Oligomer**: $PC_{61}BM | LiF| Al$, with different oligomer: $PC_{61}BM$ ratios.

Oligomer:PC ₆₁ BM	Oligomer:PC ₆₁ BM ratio	Jsc [mA/cm ²]	Voc [V]	FF	PCE [%]
1:PC ₆₁ BM	1:3	6.8	0.82	0.62	3.5
1 :PC ₆₁ BM	1:1	5.7	0.81	0.46	2.1
1 :PC ₆₁ BM	2:1	1.1	0.39	0.32	0.1
2 :PC ₆₁ BM	1:1	0.2	0.75	0.20	0.03



Figure S2. Power conversion efficiency dependence on active layer thickness for oligomers 1 and 2 blended with $PC_{61}BM$ (ratio 1:2).

SEM characterization



Figure S3. SEM image of the cross section of a representative solar cell demonstrating the active layer thickness and uniformity of 1:PCBM blend.

XRD characterization



Figure S4. XRD diffraction patterns measured for 1:PC₆₁BM (black) and 2:PC₆₁BM (gray) thin films on PEDOT:PSScoated ITO substrates. The measurements were carried using a Bruker D8 diffractometer with a fixed incoming angle of 0.2°. The broad reflection at $2\theta = 12,5^{\circ}$ corresponds to the ITO:PEDOT/PSS substrate.

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NMR spectra



Figure S4. ¹H NMR of oligomer 1 in CDCl₃. (★) water in CDCl₃.



Figure S5. ¹³C NMR of oligomer 1 in CDCl₃.

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Figure S6. MALDI-TOF mass spectrum of oligomer 1.



Figure S7. ¹H NMR of oligomer **2** in CDCl₃. (\bigstar) water in CDCl₃.



Figure S8. ¹³C NMR of oligomer 1 in CDCl₃.



Figure S9. MALDI-TOF mass spectrum of oligomer 2.