Efficient solid-phase synthesis of regioregular head-to-tail-coupled oligo(3-alkylthiophene)s up to a dodecamer

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Solid-phase synthesis of isomerically pure head-to-tail-coupled (HT) oligo(3-hexylthiophene)s on chloromethylated polystyrene resin has been developed. Using novel sequences of iodination and Suzuki cross-coupling reaction, a series up to a dodecamer has been synthesized in high yield and purity. Removal of the conjugated oligomers from solid support as methyl esters, saponification and decarboxylation to the HT-coupled oligo(3-alkylthiophene)s could be effectively achieved.

Due to their well-defined structure α -conjugated oligothiophenes represent the most frequently investigated class of model compounds for conducting polymers.¹ Valuable information can be deduced from structure–property relationships which can normally not be obtained from the corresponding polymers due to their polydisperse nature. Moreover, oligothiophenes proved to be promising new materials for electronic and photonic applications, such as organic light-emitting diodes,² field-effect transistors,³ and photovoltaic cells.⁴ Several series of differently substituted oligothiophenes have been synthesized and characterized; however, their syntheses are notoriously difficult with respect to (isomeric) purity and yield, particularly for longer oligomers.⁵

The emergence of powerful combinatorial synthesis combined with rapid screening methods in pharmaceutical chemistry⁶ and very recently in material science⁷ provides a quickly increasing number of reactions on solid support⁸ on one hand, and the perspective to develop rapid and automated syntheses of organic material libraries on the other hand. In this respect, very few reports have demonstrated that syntheses of conjugated oligomers can successfully be performed on solid support. Using a triazene as linker system, oligo(phenyleneethynylene)s⁹ were built up to a 16-mer via Sonogashira-Hagihara couplings. Very recently, Fréchet et al. reported the first polymer-supported synthesis of asymmetric oligothiophenes using an ester linkage to the Merrifield resin. Via sequential bromination and Stille cross-coupling reactions a quinquethiophene ester was obtained after cleavage from the resin.10

As a result of developments in polythiophene chemistry, several synthetic routes to regioregular HT-coupled oligo-(3-alkylthiophene)s (HT-O3AT)¹¹ were reported representing perfect model compounds for the corresponding HT-poly-(3-alkylthiophene)s which in comparison to the regiorandom polymers exhibit well improved properties.¹² Their synthesis generally faces some inherent problems such as moderate yields in Stille or Suzuki aryl–aryl cross-coupling steps, particularly for longer oligomers and the appearance of homocoupling products which severly impede the purification processes. Herein, we report the first solid-phase synthesis of a series of isomerically pure head-to-tail-coupled oligo(3-hexylthiophene)s. The synthetic strategy first developed in the solution phase ^{11a} has been transferred to the solid phase and perfectly overcomes the inherent problems described above. An efficient

synthesis to a series of oligothiophenes up to a 12-mer in excellent overall yield and purity is provided.

Results and discussion

The synthesis of bithiophenecarboxylic acid $\mathbf{6}$, which is the anchoring group to the solid support, is depicted in Scheme 1.



Scheme 1 Synthesis of bithiophene building blocks 5 and 6.

Palladium-catalyzed cross-coupling of thiopheneboronate **1** which was prepared from 3-hexylthiophene in 40% yield without any 2,3-substituted isomer as a by-product and 2-iodo-3hexylthiophene (**2**) gave isomer-free 3,4'-dihexyl-2,2'-bithiophene (**3**) in 70% yield. Bromination of **3** with one equivalent NBS leads in 96% yield selectively to the 5-bromo-3',4-dihexyl-2,2'-bithiophene (**4**) which was further reacted with magnesium and converted with 2,2'-propane-1,3-diyldioxybis(1,3,2-dioxa-

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J. Chem. Soc., *Perkin Trans.* 1, 2000, 1211–1216 **1211**

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borinane) (trimethyleneborate, TMB) to boronic ester 5 (85% yield). Moreover, the metallated bromobithiophene 4 was quenched with carbon dioxide yielding carboxylic acid 6 (88%) which represents the anchoring group to the solid phase.

The immobilization of bithiophene building block **6** and the sequential solid-phase synthesis (SPS) of the oligothiophene series is depicted in Scheme 2. Using standard Merrifield conditions,¹³ bithiophenecarboxylic acid **6** was nearly quantitatively (98%) attached to chloromethylated polystyrene resin¹⁴ using

caesium carbonate as base. In an iterative process consisting of halogenation and subsequent Suzuki cross-coupling with bithiophene building block **5** longer oligomers **P7**, **P8**, and **P9** were built up and then cleaved off the resin. In comparison to the analogous solution-phase synthesis,^{11a} in SPS time consuming purification processes were shortened by simple resin washing and the yields of the cross-coupling reactions were considerably increased by using excesses of coupling reagents and by the suppressed formation of by-products.



Scheme 2 Solid-phase synthesis of head-to-tail-coupled oligo(3-hexylthiophene)s 7–9.

1212 J. Chem. Soc., Perkin Trans. 1, 2000, 1211–1216

Selective and quantitative α -iodination of the resin-bound bithiophene **P6** and later on of the higher homologues was achieved by adding iodine in the presence of mercuric hexanoate. On account of the higher solubility in dichloromethane– hexanoic acid the use of mercuric hexanoate is advantageous with respect to the usually used mercuric acetate.^{11a} The observed α -selectivity arises from a preceding α -mercuration which is governed by coordination of the mercury atom to the thiophene sulfur atom.¹⁵ Subsequent Suzuki coupling of the resin-bound iodothiophenes with a double excess of bithiophene boronic ester **5** was performed under non-aqueous conditions in THF using caesium fluoride as base with poor nucleophilicity. We found that under these conditions the bithiophene boronic ester **5** which is normally very sensitive to deboronation was sufficiently stable.

Treatment of the resin-bound oligothiophenes **P7**, **P8**, and **P9** with tetrabutylammonium hydroxide (30-hydrate) in refluxing THF followed by the *in situ* conversion of the resulting oligothiophenecarboxylates with iodomethane led to the corresponding methyl esters **7**, **8**, and **9**. HT-coupled tetra(3-hexyl-thiophene) **7** was obtained in an overall yield (relative to carboxylic acid **6**) of 93% over 4 steps, octa(3-hexylthiophene) **8** in 54% over 8 steps, and finally dodeca(3-hexylthiophene) **9** in 15% yield over 12 steps. The oligomers are highly soluble in common organic solvents and were purified by preparative RP chromatography (oligomers **7**, **8**) or HPLC (oligomer **9**). Small amounts of homocoupling products were separated and the oligothiophenes were obtained isomerfree in high purities (HPLC > 99%).

The transformation of the oligothiophene methyl esters 7–9 to the non-functionalized HT-coupled oligo(3-hexylthiophene)s 13–15 is shown in Scheme 3. Saponification of the



Scheme 3 Synthesis of the non-functionalized oligo(3-hexylthiophene)s 13–15.

methyl esters **7–9** with tetrabutylammonium hydroxide results in the corresponding carboxylic acids **10–12** in 88–98% yield. Subsequently, the carboxylic acids were cleanly decarboxylated by means of copper powder in quinoline at 180 °C to yield the desired tetramer 13 in 97% yield, octamer 14 in 95% yield, and dodecamer 15 in 95% yield in high purity.

This SPS protocol clearly demonstrates that very long α -conjugated oligothiophenes can effectively be synthesized on solid support. The improvement of this generally applicable strategy lies in the fact that 1. 2,4-disubstituted boronate 1 is obtained isomer-free; 2. The ester linkage to the resin acts as a protecting group for one a-position providing selective reactions and chain growth on the other α -position of the oligothiophene; 3. The use of the system mercuric hexanoate-iodine in the halogenation step guarantees high selectivities; 4. Nonaqueous conditions in the cross-coupling step lead to maximized resin swelling and effective conversions; 5. Due to the immobilization at the solid support homocoupling by-products are nearly suppressed; 6. The use of excessive reagents and ease of purification on the solid support are clear advantages over the traditional solution-phase purification methods. 7. The use of an ester linkage provides after cleavage from the resin a carboxylic acid group that may be further functionalized or removed. The investigation of the physical and self-organizing properties of oligothiophenes 7-15 is in progress in our laboratory.

Experimental

General methods

Prior to use, solvents and reagents were purified and dried by usual methods. Thin-layer chromatography (TLC) was carried out on plastic plates Polygram SIL from Macherey & Nagel. Preparative column chromatography was performed on glass columns of different sizes packed with Kieselgel 60 (Merck, 0.020-0.200 nm) and a Lobar® LiChroprep® RP₁₈ column (Merck, 40-63 µm). Melting points were determined with a Büchi SMP 20 melting point apparatus and are uncorrected. ¹H NMR spectra were recorded on a Bruker AMX 500 (500 MHz) and a AC 200 (200 MHz) spectrometer (with deuterated solvent as lock-in and tetramethylsilane as internal reference). ¹³C NMR spectra were recorded on a Bruker AMX 500 (126 MHz) and a AC 200 (50 MHz) spectrometer. Elemental analyses were performed with a Elementar Vario EL. HPLC analyses were performed with a Nucleosil 100 nitrophenyl column and *n*-hexane-dichloromethane mixtures as eluent. Mass spectra were recorded with a Varian MAT 711 (70 eV), MALDI-TOF with a Bruker Daltonic Reflex III, GC-MS with a Varian Saturn 2000 spectrometer.

Materials. 3-Bromothiophene (Avocado), 1,2-dimethoxyethane (Merck), hexyl bromide (Fluka), iodine (Merck), lithium diisopropylamide (2.0 M in THF–ethylbenzene–*n*-heptane) (Fluka), iodomethane (Fluka), tetrabutylammonium hydroxide (30-hydrate) (Fluka), and trimethyl borate (Fluka) were purchased. 3-Hexylthiophene,¹⁶ 2-iodo-3-hexylthiophene **2**,¹⁷ and tetrakis(triphenylphosphino)palladium(0),¹⁸ 2,2'-propane-1,3diyldioxybis(1,3,2-dioxaborinane)¹⁹ were prepared following literature procedures. Chloromethylated polystyrene resin was purchased from Novabiochem with a loading capacity of 0.63 mmol g⁻¹ (200–400 mesh, 1% DVB).

Sodium 4-hexylthiophene-2-boronate (1)

Lithium diisopropylamide solution (65 mL, 130 mmol, 2 M in THF–ethylbenzene–*n*-heptane) was added dropwise at -60 °C to a stirred solution of 3-hexylthiophene (20.0 g, 120 mmol) in 200 mL dry THF. The resulting mixture was stirred for one hour and was allowed to warm up to room temperature. After cooling to -60 °C trimethyl borate (30 mL, 240 mmol) was slowly added. The mixture was allowed to come to room temperature overnight and was subsequently hydrolyzed with 1 M HCl and extracted with 150 mL diethyl ether. The organic phase was dried over sodium sulfate, filtered and then stirred

J. Chem. Soc., Perkin Trans. 1, 2000, 1211–1216 1213

with sodium hydroxide. The resulting precipitate was filtered off and washed with cold diethyl ether to yield sodium 4-hexylthiophene-2-boronate (1) as a colorless solid, (12.0 g, 40%). The product was used without further purifications, $\delta_{\rm H}(200 \text{ MHz}; \text{CD}_3\text{OD}; \text{Me}_4\text{Si})$ 6.84 (d, 1H, ${}^4J_{(5,3)} = 1.1 \text{ Hz}$, 5-H), 6.76 (d, 1H, ${}^4J_{(3,5)} = 1.1 \text{ Hz}$, 3-H), 2.59 (t, 2H, ${}^3J_{(\rm H,\rm H)} = 7.3 \text{ Hz}$, α -CH₂), 1.62– 1.53 (m, 2H, β -CH₂), 1.29–1.26 (m, 6H, CH₂), 0.87 (t, 3H, ${}^3J_{(\rm H,\rm H)} = 6.7 \text{ Hz}$, CH₃), OH not resolved; $\delta_{\rm C}(50 \text{ MHz}; \text{CD}_3\text{OD}; \text{Me}_4\text{Si})$ 144.1, 130.7, 119.7, 32.6, 32.5, 31.7, 31.0, 29.7, 29.6, 23.3, 14.1; m/z (EI) 252 [M⁺].

3,4'-Dihexyl-2,2'-bithiophene (3)

Tetrakis(triphenylphosphino)palladium(0)¹⁸ (1.0 g, 0.8 mmol) was added to a solution of 3-hexyl-2-iodothiophene (10.0 g, 33.0 mmol) in 100 mL dimethoxyethane and the mixture was carefully degassed. After addition of sodium 4-hexylthiophene-2-boronate (1) (9.0 g, 36 mmol) the mixture was heated to reflux and a saturated aqueous solution of NaHCO₃ (7.3 g, 100 mmol) was slowly added. After 3 hours the reaction was complete and the mixture diluted with 100 mL diethyl ether, washed with 1 M HCl and with brine. After drying over sodium sulfate the solvent was evaporated and the remaining oil purified by chromatography (SiO₂, cyclohexane) to yield bithiophene 3 (15.2 g, 70%) as a yellow oil (Found: C, 71.78; H, 8.84; S, 18.93. $C_{20}H_{30}S_2$ requires C, 71.80; H, 9.04; S, 19.17%); $\delta_H(200 \text{ MHz};$ CDCl₃; Me₄Si) 7.12 (d, 1H, ${}^{3}J_{(5',4')} = 5.2$ Hz, 5'-H), 6.92 (d, 1H, ${}^{4}J_{(5,3)} = 1.5$ Hz, 5-H), 6.90 (d, 1H, ${}^{3}J_{(4',5')} = 5.2$ Hz, 4'-H), 6.86 (d, 1H, ${}^{4}J_{(3,5)} = 1.5$ Hz, 3-H), 2.72 (t, 2H, ${}^{3}J_{(a',b')} = 7.7$ Hz, α' -CH₂), 2.58 (t, 2H, ${}^{3}J_{(a,b)} = 7.7$ Hz, α -CH₂), 1.60–1.54 (m, 4H, β , β '-CH₂), 1.29–1.25 (m, 12H, CH₂), 0.87 (t, 6H, CH₃); δ _C(50 MHz; CDCl₃; Me₄Si) 143.6, 139.4, 135.9, 131.0, 129.9, 127.3, 123.4, 119.9, 32.0, 31.7, 30.8, 30.6, 30.5, 29.7, 29.6, 29.5, 29.4, 29.2, 22.8, 14.2; *m*/*z* (EI) 334 [M⁺].

5-Bromo-3',4-dihexyl-2,2'-bithiophene (4)

3,4'-Dihexyl-2,2'-bithiophene (3) (28.0 g, 84 mmol) was dissolved in 200 mL DMF and cooled down to 0 °C. Under exclusion of light a solution of NBS (15.5 g, 88 mmol) in 200 mL DMF was slowly added and the solution stirred for six hours. The mixture was allowed to warm up to room temperature and was further stirred for one day. After that the mixture was diluted with 300 mL diethyl ether and poured into water. The organic phase was washed several times with 1 M HCl and water and finally dried over sodium sulfate. After evaporation of the solvents the remaining residue was purified by chromatography (SiO₂, n-hexane) to afford bromobithiophene 4 (34.0 g, 96%) as a yellow liquid (Found: C, 57.69; H, 6.98; S, 15.37. $C_{20}H_{29}BrS_2$ requires C, 58.10; H, 7.07; S, 15.51%); $\delta_H(200 \text{ MHz};$ $CDCl_3; Me_4Si) 7.14 (d, 1H, {}^{3}J_{(5',4')} = 5.2 Hz, 5'-H), 6.89 (d, 1H, {}^{3}J_{(4',5')} = 5.2 Hz, 4'-H), 6.77 (s, 1H, 3-H), 2.69 (t, 2H, 2H)$ ${}^{3}J_{(H,H)} = 7.8$ Hz, α' -CH₂), 2.54 (t, 2H, ${}^{3}J_{(H,H)} = 7.6$ Hz, α -CH₂), 1.62-1.53 (m, 4H, β , β '-CH₂), 1.32-1.25 (m, 12H, CH₂), 0.87 (t, 6H, CH₃); δ_C(50 MHz; CDCl₃; Me₄Si) 142.3, 139.9, 135.7, 130.0, 129.9, 126.8, 123.9, 108.5, 31.6, 30.6, 29.6, 29.5, 29.1, 29.0, 28.9, 22.6, 14.1; m/z (EI) 414 [M⁺].

3',4-Dihexyl-2,2'-bithiophene-5-boronic acid propanediyl ester (5)

A solution of 5-bromo-3,4'-dihexyl-2,2'-bithiophene (4) (6.33 g, 15 mmol) in 100 mL dry THF was mixed with magnesium turnings (0.43 g, 18 mmol) and refluxed until the magnesium had reacted. The mixture was cooled down to -60 °C, mixed with 2,2'-propane-1,3-diyldioxybis(1,3,2-dioxaborinane) (1.83 g, 7.5 mmol) and stirred for two hours. The mixture was allowed to come to room temperature and then cooled again to -60 °C. Boron trifluoride–diethyl ether (1.00 g, 15 mmol, 2 M in diethyl ether) was added dropwise and heated to room temperature. The solvent was evaporated *in vacuo* and the residue

dissolved in 80 mL petroleum ether and filtered over Celite to afford bithiopheneboronic acid propanediyl ester **5** as a yellow oil in 85% purity which was used without further purification, $\delta_{\rm H}(200 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 7.1 (d, 1H, ${}^3J_{(5',4')}$ = 5.2 Hz, 5'-H), 7.0 (s, 1H, 3-H), 6.89 (d, 1H, ${}^3J_{(4',5')}$ = 5.2 Hz, 4'-H), 4.13 (t, 4H, ${}^3J_{(\rm H,\rm H)}$ = 6.6 Hz, -OCH₂CH₂CH₂O-), 2.85 (m, 4H, α, α' -CH₂), 2.05 (q, 2H, ${}^3J_{(\rm H,\rm H)}$ = 5.5 Hz, -OCH₂CH₂CH₂O-), 1.64–1.55 (m, 4H, β,β' -CH₂), 1.31–1.25 (m, 12H, CH₂), 0.87 (t, 6H, CH₃); $\delta_{\rm C}(50 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 153.0, 140.4, 139.4, 131.2, 130.4, 129.9, 123.3, 61.9, 31.9, 31.6, 29.9, 29.7, 29.5, 27.4, 22.7, 14.1; *m/z* (EI) 418 [M⁺].

3',4-Dihexyl-2,2'-bithiophene-5-carboxylic acid (6)

To a solution of 5-bromo-3,4'-dihexyl-2,2'-bithiophene (4) (5.20 g, 12.5 mmol) in dry THF (100 mL) magnesium turnings (0.36 g, 15 mmol) were added and heated under reflux until the magnesium disappeared. The reaction mixture was cooled to 0 °C and excess of solid carbon dioxide was added. After reaching room temperature the mixture was hydrolyzed with 1 M HCl and the organic phase washed several times with water. The organic layer was dried with sodium sulfate and after evaporation of the solvent the residue was purified with column chromatography (SiO₂, dichloromethane-ethyl acetate) to afford bithiophenecarboxylic acid 6 (4.20 g, 88%) as a yellow solid, mp 62 °C (Found: C, 66.47; H, 7.88; S, 16.99. C₂₁H₃₀O₂S₂ requires C, 66.62; H, 7.99; S, 16.91%); $\delta_{\rm H}$ (200 MHz; CDCl₃; Me₄Si) 7.22 (d, 1H, ${}^{3}J_{(5',4')} = 5.2$ Hz, 5'-H), 7.00 (s, 1H, 3-H), 6.93 (d, 1H, ${}^{3}J_{(4',5')} = 5.2$ Hz, 4'-H), 3.00 (t, 2H, ${}^{3}J_{(H,H)} = 7.6$ Hz, α -CH₂), 2.81 (t, 2H, ${}^{3}J_{(H,H)} = 7.8$ Hz, α' -CH₂), 1.71–1.64 (m, 4H, β,β'-CH₂), 1.41–1.21 (m, 12H, CH₂), 0.87 (t, 6 H, CH₃), OH not resolved; δ_c(50 MHz; CDCl₃; Me₄Si) 168.3, 153.3, 142.4, 141.3, 130.4, 129.8, 129.1, 124.9, 31.66, 31.63, 30.4, 30.3, 29.8, 29.4, 29.1, 22.6, 14.1; m/z (EI) 378 [M⁺].

3',4-Dihexyl-2,2'-bithiophene-5-carboxylic acid functionalized polystyrene resin (P6)

To a solution of 3,4'-dihexyl-2,2'-bithiophene-5-carboxylic acid (6) (0.38 g, 1.0 mmol) in 50 mL aqueous ethanol (10% water), caesium carbonate (0.39 g, 1.2 mmol) was added. The mixture was stirred for two hours under reflux. The solvents were evaporated and the resulting salt was dried in vacuo. The caesium salt was dissolved in 100 mL dry DMF and added to chloromethylated polystyrene resin (10.0 g, 0.62 mmol g^{-1} , 6.2 mmol). After addition of catalytic amounts of potassium iodide (10 mg, 0.006 mmol) the mixture was gently stirred for three days at 80 °C. The functionalized resin was washed with DMF, water, ethanol, THF, and finally diethyl ether. The filtrate was evaporated and the residue dissolved in aqueous nitric acid. Then silver nitrate was added in order to quantitatively precipitate chloride ions as silver chloride. The precipitate was washed several times with water and dried in vacuo. The resin loading was determined by weighing the silver precipitate (98%).

General procedure for iodination of resin-bound oligothiophenes

To a suspension of resin-bound oligothiophenes (1.0 equiv.) in a mixture of dichloromethane–hexanoic acid (90:10, 20 mL g⁻¹ of polymer) was added mercury hexanoate (2.0 equiv.) and gently stirred for one hour. To the resulting mixture a solution of iodine (1.3 equiv.) in dichloromethane (50 mL per mmol of iodine) was added dropwise over a period of nine hours. The solvent was removed by filtration and the polymer washed several times with dichloromethane, ethanol, THF, diethyl ether and dried to constant mass *in vacuo*.

General procedure for the Suzuki-coupling reaction of resinbound iodothiophenes

The resin-bound iodinated oligomeric thiophene (1.0 equiv.) was swollen in dry THF (20 mL per g of polymer) and catalytic

tetrakis(triphenylphosphino)palladium(0)¹⁸ (3 mol%) and caesium fluoride (8 equiv.) were added. The mixture was carefully degassed and heated to reflux under an argon atmosphere. To this a solution of bithiopheneboronic acid ester **5** (2 equiv.) in degassed and dry THF (10 mL per mmol of boronic ester **5**) was added dropwise and heated to reflux for five hours. The solvent was removed by filtration and the polymer washed several times with water, methanol, THF, diethyl ether and dried to constant mass *in vacuo*.

General cleavage procedure of resin-bound oligothiophenes P7–P9

The resin-bound oligothiophene P7-P9 (1 equiv.) was swollen in dry THF (30 mL per g of polymer) and after addition of tetrabutylammonium hydroxide (30-hydrate) (2 equiv.) the mixture was refluxed for three days and filtered to remove the polymer. The oligothiophene carboxylate was then converted in situ to the methyl ester with an excess of iodomethane (3 equiv.) at room temperature (one hour). The esterification was controlled by thin layer chromatography (SiO₂, n-hexanedichloromethane). After evaporation of the solvents, the crude product was purified by column chromatography (SiO₂, *n*-hexane-dichloromethane) to separate from homocoupled products. Then, in the case of oligothiophenes 7 and 8 reversed phase chromatography (Lobar[®], RP₁₈-column, acetonitriledichloromethane, 25:75) was used. Dodecamer 9 was purified by HPLC on a nitrophenyl column, *n*-hexane–dichloromethane (90:10) as eluent.

Methyl tetra(3-hexylthiophene-2,5-diyl)-2-carboxylate (7). Yield: 93% (orange solid, HPLC > 99%); mp 54 °C; found: C, 69.58; H, 8.36; S, 17.82. C₄₂H₆₀O₂S₄ requires C, 69.56; H, 8.34; S, 17.69%; $\delta_{\rm H}$ (200 MHz; CDCl₃; Me₄Si) 7.16 (d, 1H, ${}^{3}J_{(5",4")} = 5.2$ Hz, 5‴-H), 6.98 (s, 1H, 4-H), 6.96 (s, 1H, 4'-H), 6.94 (s, 1H, 4"-H), 6.92 (d, 1H, ${}^{3}J_{(4",5")} = 5.2$ Hz, 4‴-H), 3.85 (s, 3H, CH₃O-), 3.01 (t, 2H, ${}^{3}J_{(H,\rm H)} = 7.8$ Hz, α -CH₂), 2.78 (t, 6H, ${}^{3}J_{(\rm H,\rm H)} = 7.8$ Hz, $\alpha',\alpha'',\alpha'''$ -CH₂), 1.65–1.55 (m, 8H, ββ',β'',β'''-CH₂), 1.40–1.25 (m, 24H, -CH₂-), 0.87 (t, 12H, CH₃); $\delta_{\rm C}$ (50 MHz; CDCl₃; Me₄Si) 163.5, 152.0, 141.3, 140.4, 140.1, 139.7, 134.5, 130.1, 128.8, 128.7, 128.6, 123.7, 51.6, 31.6, 30.6, 30.4, 30.37, 30.36, 30.31, 29.7, 29.5, 29.4, 29.28, 29.23, 29.2, 22.6, 14.1; *m*/z (EI) 724 [M⁺].

Methyl octa(3-hexylthiophene-2,5-diyl)-2-carboxylate (8). Yield: 54% (dark red solid, HPLC > 99%); mp 72 °C; found: C, 70.73; H, 8.34; S, 17.88. C₈₂H₁₁₆O₂S₈ requires C, 70.84; H, 8.41; S, 18.45%; $\delta_{\rm H}$ (500 MHz; CDCl₃; Me₄Si) 7.15 (d, 1H, ${}^{3}J_{(5^{mm},4^{mm})} = 5.2 \text{ Hz}, 5^{mm}-\text{H}), 6.99 (s, 1H, 4^{mm}-\text{H}), 6.98 (s, 1H, 4^{mm}-\text{H})$ H), 6.977 (s, 1H, 4""-H), 6.975 (s, 1H, 4"'-H), 6.971 (s, 1H, 4"-H), 6.96 (s, 1H, 4'-H), 6.93 (s, 1H, 3-H), 6.92 (d, 1H, ${}^{3}J_{(4^{mm},5^{mm})} = 5.2$ 1.75–1.62 (m, 16H, β,β',β",β"',β"'',β"''',β"''',β"'''',β"''''',β"''''''-CH₂), 1.45–1.30 (m, 48H, -CH₂-), 0.92–0.87 (m, 24H, CH₃); $\delta_{\rm C}$ (126 MHz; CDCl₃; Me₄Si) 162.8, 152.0, 141.1, 140.3, 140.2, 139.99, 139.92, 139.8, 139.7, 139.6, 134.9, 134.09, 134.08, 133.8, 133.7, 130.4, 130.36, 130.33, 130.06, 130.02, 129.7, 128.7, 128.6, 128.57, 128.55, 124.8, 123.5, 51.6, 31.6, 30.6, 30.5, 30.38, 30.32, 29.7, 29.5, 29.4, 29.3, 29.2, 22.6, 14.0; m/z (MALDI-TOF) 1390.34 $[M^+].$

General procedure for the preparation of oligothiophenecarboxylic acids 10–12

To a solution of oligothiophene methyl ester 7–9 (1.0 equiv.) in dry THF (30 mL per mmol of oligothiophene methyl ester) was added tetrabutylammonium hydroxide (30-hydrate) (2 equiv.) and the resulting mixture was heated under reflux for one hour. After dilution with diethyl ether (100 mL per mmol of oligothiophene methyl ester) the mixture was washed several times with 1 M HCl and finally with water. The organic phase was dried over sodium sulfate and after evaporation of the solvent the residue was purified by column chromatography (SiO₂, dichloromethane) to afford the oligothiophenecarboxylic acids 10–12.

Tetra(3-hexylthiophene-2,5-diyl)-2-carboxylic acid (10). Yield: 88% (orange solid); mp 86 °C; found: C, 69.10; H, 8.35; S, 17.86. C₄₁H₅₈O₂S₄ requires C, 69.25; H, 8.22; S, 18.03%; $\delta_{\rm H}(200$ MHz; CDCl₃; Me₄Si) 7.16 (d, 1H, ${}^{3}J_{(5",4")} = 5.2$ Hz, 5^{*i*''}-H), 7.05 (s, 1H, 3-H), 6.98 (s, 1H, 4"-H), 6.92 (s, 1H, 4'-H), 6.92 (d, 1H, ${}^{3}J_{(4",5")} = 5.2$ Hz, 4^{*i*''}-H), OH not resolved, 3.02 (t, 2H, ${}^{3}J_{(H,H)} = 7.8$ Hz, α -CH₂), 2.75–2.65 (m, 6H, $\alpha', \alpha'', \alpha'''$ -CH₂), 1.65– 1.55 (m, 8H, $\beta_{\beta}\beta', \beta'', \beta'''$ -CH₂), 1.45–1.21 (m, 24H, -CH₂-), 0.87 (t, 12H, CH₃); $\delta_{\rm C}(50$ MHz; CDCl₃; Me₄Si) 168.1, 153.5, 142.1, 141.7, 140.2, 139.7, 135.3, 130.1, 129.5, 128.8, 124.4, 123.7, 31.6, 30.6, 30.4, 30.36, 30.31, 29.8, 29.6, 29.4, 29.3, 29.2, 22.6, 14.1; *m/z* (EI) 710 [M⁺].

Octa(3-hexylthiophene-2,5-diyl)-2-carboxylic acid (11). Yield: 96% (dark red solid); mp 139 °C; found: C, 70.49; H, 8.30; S, 18.29. $C_{s1}H_{114}O_2S_8$ requires C, 70.69; H, 8.35; S, 18.64%; $\delta_H(500 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 7.16 (d, 1H, ${}^{3}J_{(5^{\text{cm}},4^{\text{cm}})} = 5.2 \text{ Hz}$, 5^{mm}-H), 7.03 (s, 1H, 3-H), 6.99 (s, 1H, 4^{mm}-H), 6.98 (s, 1H, 4^{mm}-H), 6.977 (s, 1H, 4^{mm}-H), 6.972 (s, 1H, 4^{mm}-H), 6.96 (s, 1H, 4^{mm}-H), 6.93 (s, 1H, 4'^m-H), 6.92 (d, 1H, ${}^{3}J_{(4^{\text{cm}},5^{\text{cm}})} = 5.2 \text{ Hz}$, 4^{mm}-H), OH not resolved, 3.02 (t, 2H, ${}^{3}J_{(\text{H},\text{H})} = 7.8 \text{ Hz}, a-CH_2$), 2.78 (m, 14 H, $a',a'',a''',a'''',a''''',a''''',c''''-CH_2$), 1.75–1.63 (m, 16H, $\beta,\beta',\beta'',\beta'''$, $\beta'''',\beta''',\beta''',\beta'''',\beta'''',\beta'''',\beta'''',\beta'''',\beta'''',\beta'''',\beta'''',\beta''',\beta'''',\beta''',\beta'''',\beta''',\beta'''',\beta'''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta'',\beta''',\beta''',\beta''',\beta''',\beta''',\beta'',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta''',\beta'',\beta'',\beta'',\beta''',\beta''',\beta''',\beta'',\beta''',\beta$

Dodeca(3-hexylthiophene-2,5-diyl)-2-carboxylic acid (12). Yield: 98% (black solid); mp 173 °C; $\delta_{\rm H}(500$ MHz; CDCl₃; Me₄Si) 7.16 (d, 1H, ${}^{3}J_{(5^{----,4^{----})}} = 5.2$ Hz, $5^{''''''''''}$ -H), 7.03 (s, 1H, 3-H), 6.99 (s, 1H, $4^{''''''}$ -H), 6.98 (s, 1H, $4^{''''''}$ -H), 6.979–6.975 (m, 5H, $4^{'''''''}$, $4^{'''''}$ -H), 6.971 (s, 1H, $4^{'''}$ -H), 6.96 (s, 1H, $4^{'''-H}$), 6.93 (s, 1H, $4^{''''}$ -H), 6.971 (s, 1H, $4^{'''-H}$), 6.96 (s, 1H, $4^{'''-H}$), 6.93 (s, 1H, $4^{'''}$ -H), 6.92 (d, 1H, ${}^{3}J_{(4^{----,5^{---})}} = 5.2$ Hz, $4^{'''''''''}$ -H), OH not resolved, 3.05 (t, 2H, ${}^{3}J_{(H,H)} = 7.8$ Hz, a-CH₂), 2.85–2.79 (m, 22H, a',a'',a''',a'''',a'''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a''''',a'''',a'''',a''''',a'''',a''''',a''',a''',a''',a''',a'''',a'''',a''',a''',a''',a''',a''',a'''',a''',a''',a''',a'''',a''',a''',a'''',a'''',a'',a''',a''',a''',a'',a'',a''',a'',a'',a''',a''',a''',a'''

General decarboxylation procedure for the preparation of oligothiophenes 13–15

To a solution of oligothiophenecarboxylic acid 10-12 (1 equiv.) in dry quinoline (10 mL per mmol of oligothiophenecarboxylic acid) copper powder (15 equiv.) was added and the mixture carefully degassed. Under an argon atmosphere the mixture was heated to 180 °C for one hour and then poured into 1 M HCl. The mixture was extracted several times with diethyl ether (100 mL per mmol of oligothiophenecarboxylic acid) and the combined organic layers were washed with water. The organic phase was dried over sodium sulfate and after evaporation of the solvent the residue was purified by column chromatography (SiO₂, *n*-hexane–dichloromethane) to yield oligothiophenes **13–15**.

Tetra(3-hexylthiophene-2,5-diyl) (13). Yield: 97% (orange oil, HPLC > 99%); found: C, 71.98; H, 8.63; S, 19.02. C₄₀H₅₈S₄ requires C, 72.01; H, 8.76; S, 19.22%; $\delta_{\rm H}(200 \text{ MHz; CDCl}_3;$ Me₄Si) 7.15 (d, 1H, ${}^{3}J_{(5'',4'')} = 5.2 \text{ Hz}, 5'''-\text{H}$), 6.96 (d, 1H, 3-H), 6.95 (s, 1H, 4''-H), 6.92 (s, 1H, 4'-H), 6.90 (d, 1H, ${}^{3}J_{(4''',5''')} = 5.2$ Hz, 4'''-H), 6.87 (d, 1H, ${}^{4}J_{(5,3)} = 1.1 \text{ Hz}, 5-\text{H}$), 2.81–2.71 (m, 6H, $a',a'',a'''-CH_2$), 2.62 (t, 2H, ${}^{3}J_{(\rm H,H)} = 7.8 \text{ Hz}, a-CH_2$), 1.75–1.62 (m, 8H, β,β',β'',β'''-CH₂), 1.45–1.21 (m, 24H, -CH₂-), 0.87 (t, 12H, CH₃); $\delta_{\rm C}(50 \text{ MHz; CDCl}_3; \text{ Me}_4\text{Si})$ 143.5, 139.5, 135.5, 133.9, 133.5, 130.9, 130.5, 130.4, 130.0, 128.6, 128.3, 123.4, 119.9, 31.6, 30.6, 30.4, 30.36, 30.31, 29.8, 29.6, 29.4, 29.3, 29.2, 22.6, 14.1; m/z (EI) 667 [M⁺].

Dodeca(3-hexylthiophene-2,5-diyl) (15). Yield: 97% (black solid, HPLC > 99%); mp 71 °C; found: C, 72.12; H, 8.57. C₁₂₀H₁₇₀S₁₂ requires C, 72.16; H, 8.58%; $\delta_{\rm H}(500 \text{ MHz; CDCl}_3;$ Me₄Si) 7.15 (d, 1H, ${}^{3}J_{(5^{mm}, 4^{mm})} = 5.2 \text{ Hz}, 5^{mmmm}$ -H), 6.97–6.96 (m, 10H, 3-H, 4^{mmmn}, 4^{mmn}, 4^{mmn}, 4^{mm}, 4^{mmn}, 4^{mm}

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