Selective Synthesis of α-Substituted Oligothiophenes

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An improved synthesis of selectively mono- and dibrominated oligothiophenes using the system *N*-bromosuccinimide/dimethylformamide is reported together with the preparation of the corresponding α-alkyl and α,α-dialykl derivatives which represent potent biologically active agents.

Oligothiophenes are among the best investigated model compounds for electrically conducting polymers.[1] The stepwise synthesis using defined key building blocks leads to a well-defined structure. On the contrary, the corresponding polymers involve interruptions of the conjugated system due to mislinkages and other defects. α-Conjugated thiophene oligomers represent not only intriguing model compounds, moreover, they are frequently applied as semiconducting materials in molecular electronic devices[2] or optical devices.[3] Furthermore, the biological activity of bi- and terthiophenes which frequently occurs in plants belonging to the class of *Compositae*,[4] has launched numerous synthetic efforts.[5,6] Many of the isolated and synthesized α-conjugated oligomers exhibit phototoxic activity against nematodes, larvae and eggs of insects, bacteria, algae, and fungi, respectively.[7] Among this class of compounds, e.g. 5-methyl-2,2′:5′,2″-terthiophene was found to be particularly effective.[8]

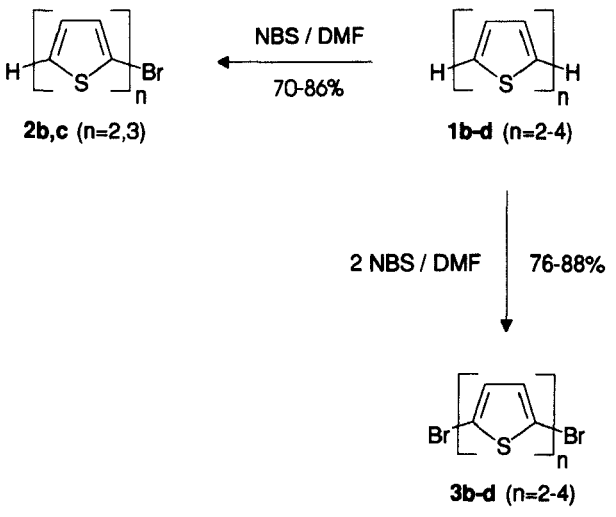
Oligothiophenes monobrominated in α-position represent very valuable key building blocks for the defined synthesis of longer α-conjugated thiophene oligomers[9,10] on one hand, and α-substituted bi- and terthiophenes on the other hand.[6] In general, the preparation of the mono-substituted compounds is rather difficult. Electrophilic substitution[5,6] as well as metalation of the heterocyclic π-system[5,11] lead to α,α-disubstituted products in considerable amounts. In the case of electrophilic formylation,[5] α-functionalized products can be obtained in moderate yields because separation is possible from starting material and the twofold substituted oligothiophene by chromatography.

In this respect, pure α-bromobithiophene and α-bromoterthiophene have been synthesized up to now only by indirect methods and in low yields.[6,12] For example, Rossi et al. obtained 5-bromoterthiophene by palladium-catalyzed cross-coupling of 5-bithienylmagnesium bromide and 2,5-dibromothiophene in 38% yield relative to 5-bromobithiophene, which is produced in 50% yield by analogous coupling of 2-bromothiophene and 2,5-dibromothiophene, respectively.[6] Several research groups therefore investigated the selective monobromination of oligothiophenes using bromine or *N*-bromosuccinimide in various solvents.[5,6,9,10,12,13] Experiments run in our laboratory confirmed that bromination of oligothiophenes with e.g. *N*-bromosuccinimide in chloroform/acetic acid always results in dibrominated products to a larger extent (25%) which cannot be separated even by multiple recrystallization.

Similarly, the synthesis of α-alkyl substituted ter- and quaterthiophenes turns out to be problematic. The direct formation of 5-methyl-2,2′:5′,2″-terthiophene via methylation of α-lithioterthiophene expectantly leads to a mixture of 5-methyl-, 5,5″-dimethylterthiophene, and unreacted starting material. In the series of corresponding quaterthiophenes, 5-methyl-2,2′:5′,2″:5″,2‴-quaterthiophene represents the only derivative reported, synthesis and characterization has not been detailed so far.[14] The preparation of symmetrically α,α-dialkylated oligothiophenes turns out to be somewhat simpler, and higher members of the series up to sexithiophene have been described.[15] Likewise, the series of β-substituted oligothiophenes has recently been extended up to the dodecamer.[16] However, due to the synthetic strategy, isomeric mixtures of the various oligomers have been obtained, and the absolute position of the alkyl substituents remains ambiguous.

We now report on the selective synthesis of monobrominated and dibrominated oligothiophenes in high yield and high purity employing the system *N*-bromosuccinimide/dimethylformamide. The successive reaction of the monobrominated key building blocks with α-alkylated bromothiophene results in a series of novel α-alkylated and α,α-dialkylated oligothiophenes.

N-bromosuccinimide dissolved in dimethylformamide has been successfully used in the monobromination of reactive aromatic hydrocarbons.[17] This method has now been applied to the bromination of oligothiophenes,[18] although these heteroaromatic systems exhibit much lesser selectivities. In the Table the product ratios of equimolar bromination of oligothiophenes **1b–d** with *N*-bromosuccinimide/dimethylformamide are presented (Scheme 1).



Scheme 1

Table. Product Ratio for the Reaction of Oligothiophenes **1** with NBS/DMF (homogeneous solution) to the α-Bromooligothiophenes **2** and Dibromooligothiophenes **3**.

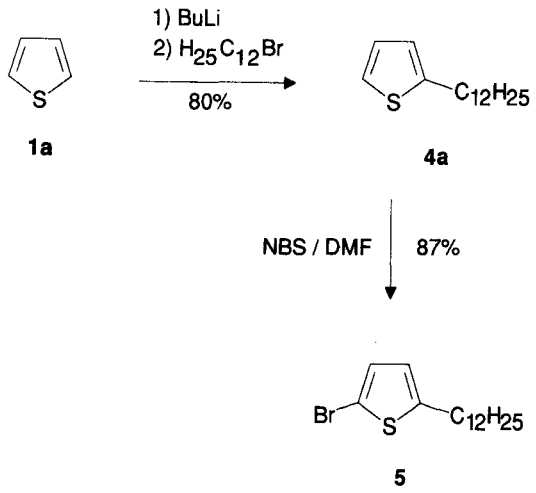
T_n (1)	n	Temp. (°C)	T_n (1) (%)	BrT_n (2) (%)	Br_2T_n (3) (%)
1b[a]	2	−20	9	81	10
1c[b]	3	−20	12	73	15
1c[b]	3	20	13	72	15
1c[a,b,c]	3	−20	12	84	4
1d[b]	4	20	20	60	20

[a] Calibrated by GC.
[b] Calibrated by HPLC.
[c] Concentrated solution from which product **2c** precipitates.

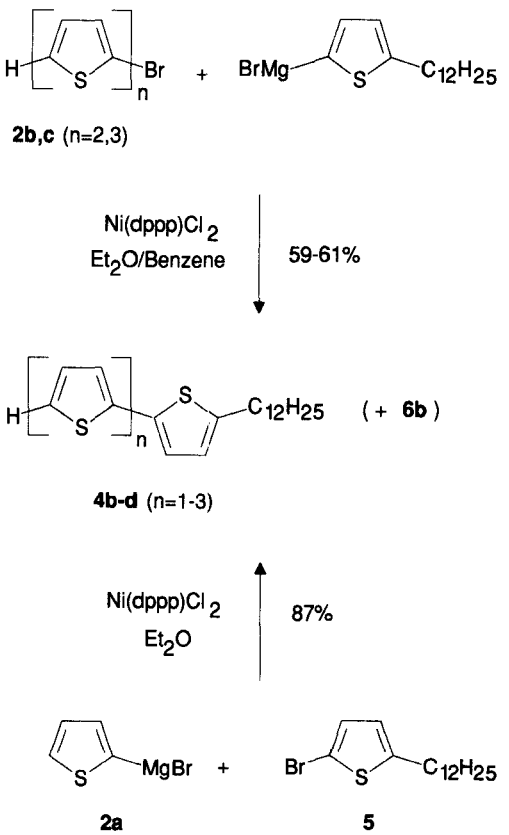
Evidently, the selectivity of the bromination decreases with increasing chain length of the oligothiophenes. Under these conditions, 5-bromobithiophene **(2b)** is formed in 81% yield. Due to the electronic decoupling of the terminal thiophene rings, the portion of 5-bromoterthiophene **(2c)** is reduced to 73%, that of the corresponding quaterthiophene **2d** even to 60%, respectively (Table). Lowering the reaction temperature to −20°C does not improve the selectivity which could be demonstrated in the case of terthiophene **1c**. On a preparative scale, 5-bromobithiophene **(2b)** is obtained in 70% isolated yield after distillation. The highest yields of pure 5-bromoterthiophene **(2c)** (86%) are attained by operating in concentrated solution and by stepwise addition of *N*-bromosuccinimide in a slight deficit. With this, the desired compound **2c** crystallizes from the reaction mixture. In contrast, monobromination of quaterthiophene **1d** is problematic since the dibrominated product is instantaneously formed even at low turnovers.

Dibromination of oligothiophenes **1** with two equivalents *N*-bromosuccinimide in dimethylformamide (Scheme 1) proves less difficult. Pure α,α-dibrominated products are isolated in 76–88% yield employing portionwise addition of *N*-bromosuccinimide and a reaction time of 3 hours at room temperature. Isomeric products which have been found, e.g., for the bromination of terthiophene in the system *N*-bromosuccinimide/tetrachloromethane,[5] do not occur in detectable amounts under the conditions used. The high selectivity of the bromination towards the α-position allows the synthesis of dibromoquaterthiophene **2d** at an elevated temperature which is necessarily due to the low solubility of quaterthiophene **1d**. Ultimately, the melting points of all monobromo- and dibromooligothiophenes synthesized according to our procedure are without exception higher than those reported in literature so far.

Monobromooligothiophenes **2b,c** are ideally suited halogen components in metal-catalyzed Grignard cross-coupling reactions for the assembly of unsymmetrically α-substituted oligothiophenes. Whereas the reaction of α-halothiophenes with alkyl Grignard reagents leads almost exclusively to dehalogenation of the heterocycle, the coupling of aryl or heteroaryl Grignard reagents proceeds smoothly in good yields.[19] In this way, bromooligothiophenes **2b,c** were coupled to the novel α-dodecyloligothiophenes **4c,d** via 'Kumada' coupling reaction using the Grignard reagent of 2-bromo-5-dodecylthiophene **(5)** in 61% and 59% yield, respectively (Scheme 3). Bromoalkylthiophene **5** was obtained very efficiently by *N*-bromosuccinimide bromination of 2-dodecylthiophene **(4a)** in 87% yield (Scheme 2). On the contrary, the homologous 5-dodecyl-2,2′-bithiophene **(4b)** was prepared by coupling of **5** as bromo component and 2-thienylmagnesiumbromide in 87% yield (Scheme 3). The solubilizing dodecyl side groups represented in compounds **4b–d** were chosen in view of their dimerization to higher α,α-dialkylated oligothiophenes.

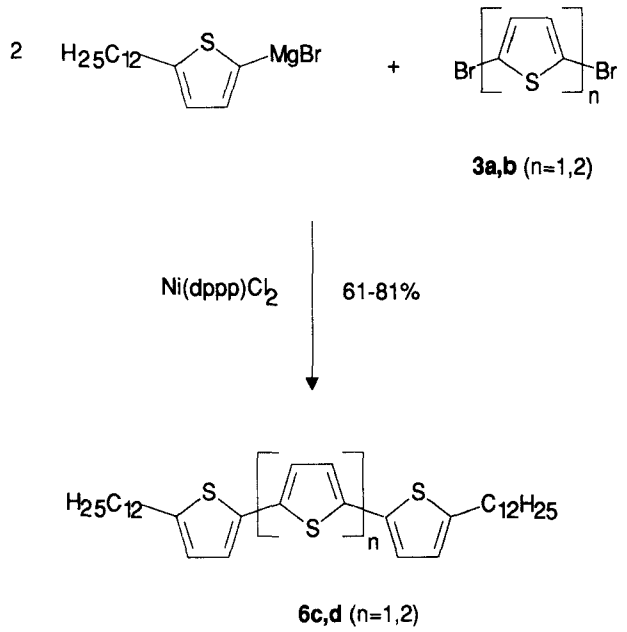


Scheme 2



Scheme 3

The formation of the novel symmetric α,α-didodecyloligothiophenes **6c,d** was likewise realized by the 'Kumada' coupling of two equivalents of Grignard reagent of **5** with dibromothiophenes **3a,b** (81 and 61%, respectively) (Scheme 4). The homologous dialkylbithiophene **6b** was isolated in pure form as byproduct (6%) of the reaction leading to alkylthiophene **4c** (Scheme 3). Homo-coupling products of this type are formed in metal-catalyzed Grignard cross-coupling reactions to a considerable extent by dimerization of the Grignard reagent. This reaction path represents a side reaction in the catalytic cycle. The related chemical constitution renders them often to components which are difficult to separate.



Scheme 4

Following the above mentioned bromination method, we were able to obtain α-bromooligothiophenes **2** and α,α-dibromooligothiophenes **3** in one step and in high yields and purity, respectively. Transition metal catalyzed Grignard coupling reactions of the valuable building blocks lead to novel α-alkylated and α,α-dialkylated oligothiophenes **4** and **6**, respectively. The bromination with the system *N*-bromosuccinimide/dimethylformamide proceeds with unexpected high selectivity also in the case of β-alkylated oligomers allowing the preparation of isomer free dialkylsexithiophene[20] and tetraalkyloctithiophene, respectively.[21]

^{1}H NMR were obtained with a Bruker ACF 250 or a Bruker CXP 300 operating at 250 and 300 MHz, respectively. Chemical shifts are measured relative to TMS in $CDCl_3$ as solvent. Melting points were carried out on Elektrotherm 9100 and Büchi SMP-20 and are not corrected. Preparative column chromatography was performed using glass columns of different size, packed with silica gel A 60, grain size 0.032–0.063 mm (Riedel de Haen). Analytical HPLC was performed with a Shimadzu LC-9A/SPD-M6A instrument fitted with a Nucleosil NO_2 5 μm column (Knauer). GC were taken on Carlo Erba Auto-HRGC, combined with FID detector EL 580, integrator DP 700 (Spectra-Physics), glass column OV 1701 (20 m), and hydrogen as carrier gas. All experiments were performed under N_2 as inert gas with absolute solvents in flame-dried apparatus. Et_2O was distilled from sodium under N_2, DMF from CaH_2 under N_2. NBS was recrystallized from nitromethane prior to use. The known 2-dodecylthiophene (**4a**)[22] (bp 178–182°C/13 Torr, Lit. 181–182°C/13 Torr;[21] GC > 99%) was prepared analogous to 2-butylthiophene in 80% yield.[23] All new compounds gave satisfactory microanalyses: C ± 0.25, H ± 0.15, Br ± 0.23, S ± 0.25.

5-Bromo-2,2′-bithiophene (2b):
In the absence of light, NBS (44.5 g, 0.25 mol) was added portionwise at −20°C to a solution of bithiophene (41.5 g, 0.25 mol) in DMF (150 mL), and stirred for 4 h, poured onto ice, and extracted several times with CH_2Cl_2. The organic phases were combined, washed with water, and dried (Na_2SO_4). Evaporation of the solvent and fractionated distillation under reduced pressure afforded **2b** as yellowish solid; yield: 42.8 g (70%); mp 33–34°C [Lit.[12] mp 30–33°C; (GC > 97%). Subsequent recrystallization from MeOH gave **2b** in pure form; yield: 33.7 g (55%); mp 34°C (GC > 99%).
^{1}H NMR (300 MHz): δ = 6.91 (1 H, d, $^3J_{3,4}$ = 3.9 Hz, 3-H), 6.96 (1 H, d, $^3J_{4,3}$ = 3.9 Hz, 4-H), 7.00 (1 H, dd $^3J_{4',5'}$ = 5.2 Hz, $^3J_{4',3'}$ = 3.6 Hz, 4′-H), 7.10 (1 H, dd, $^3J_{3',5'}$ = 1.1 Hz, $^3J_{3,4'}$ = 3.6 Hz, 3′-H), 7.22 (1 H, dd, $^3J_{5',4'}$ = 5.1 Hz, $^4J_{5',3'}$ = 1.1 Hz, 5′-H).

5-Bromo-2,2′:5′,2″-terthiophene (2c):
In the absence of light, NBS (3.2 g, 18 mmol) was added portionwise over a period of 2 to 3 d at −20°C to a well-stirred solution of terthiophene **1c** (5.0 g, 20 mmol) in DMF (45 mL). Compound **2c** started to precipitate from the reaction mixture after the addition of about 10% NBS. After the last portion of NBS had been added, the suspension was stirred for additional 20 h, poured onto ice, and extracted several times with CH_2Cl_2. The organic phases were combined, washed with water, and dried (Na_2SO_4). Evaporation of the solvent and recrystallization from hexane afforded pure **2c** as yellow solid; yield: 5.06 g (86%); mp 141–142°C [Lit.[5] mp 136–137.5°C]; (HPLC > 96%).
^{1}H NMR (300 MHz): δ = 6.90 (1 H, d, $^3J_{3,4}$ = 3.9 Hz, 3-H), 6.97 (1 H, d, $^3J_{4,3}$ = 3.9 Hz, 4-H), 7.00 (1 H, d, $^3J_{4,3}$ = 3.8 Hz, 3′-H), 7.02 (1 H, dd, $^3J_{4'',5''}$ = 5.1 Hz, $^3J_{4'',3''}$ = 3.6 Hz, 4″-H), 7.06 (1 H, d, $^3J_{3',4'}$ = 3.8 Hz, 4′-H), 7.17 (1 H, dd, $^3J_{3'',4''}$ = 3.6 Hz, $^4J_{3'',5''}$ = 1.1 Hz, 3″-H), 7.23 (1 H, dd, $^3J_{5'',4''}$ = 5.1 Hz, $^4J_{5'',3''}$ = 1.1 Hz, 5″-H).

5,5′-Dibromo-2,2′-bithiophene (3b):
In the absence of light, NBS (26.6 g, 0.15 mol) was added portionwise at 20°C to a solution of bithiophene (12.3 g, 0.074 mmol) in DMF (100 mL), stirred for 3 h, poured onto ice, and the white precipitate was filtered and washed several times with water. Drying over P_2O_5 and recrystallization from abs. EtOH afforded **3b** as white solid; yield: 21.2 g (88%); mp 146°C [Lit.[13] mp 145°C]; (GC > 99%).
^{1}H NMR (300 MHz): δ = 6.84 [2 H, d, $^3J_{3,4(3',4')}$ = 3.9 Hz, 3(3′)-H], 6.98 [2 H, d, $^3J_{4,3(4',3')}$ = 3.8 Hz, 4(4′)-H].

5,5″-Dibromo-2,2′:5′,2″-terthiophene (3c):
NBS (3.74 g, 21 mmol) was added to terthiophene (2.48 g, 10 mmol) dissolved in DMF (130 mL) and reacted under the conditions given for the synthesis of **3b**. After the usual workup 3.96 g (98%, GC > 98%) and subsequent recrystallization from toluene/hexane **3c** was isolated; yield: 3.42 g (84%); mp 159–160°C. [Lit.[5] mp 156–157°C]; GC (> 99%).
^{1}H NMR (300 MHz): δ = 6.91 [2 H, d, $^3J_{3,4(3'',4'')}$ = 3.9 Hz, 3(3″)-H], 6.98 [2 H, d, $^3J_{4,3(4'',3'')}$ = 3.9 Hz, 4(4″)-H], 6.99 [2 H, s, 3′(4′)-H].

5,5‴-Dibromo-2,2′:5′,2″:5″,2‴-quaterthiophene (3d):
NBS (0.356 g, 2 mmol) dissolved in DMF (10 mL) was rapidly dropped to a stirred solution of quaterthiophene (0.330 g, 1 mmol) in DMF (80 mL) at 80°C. After 2 h the solution was cooled to r.t. and poured onto ice. Workup gave **3d** as orange solid; yield: 0.37 g (76%); mp 263–264°C (toluene) [Lit.[9] mp 255–256°C].

^{1}H NMR (300 MHz): δ = 6.92 [2H, d, $^3J_{3,4}$ = 3.9 Hz, 3(3‴)-H], 6.99 [2H, d, $^3J_{4,3}$ = 3.9 Hz, 4(4‴)-H], 7.02 [2H, d, $^3J_{3',4'}$ = 3.8 Hz, 3'(4'')-H], 7.07 [2H, d, $^3J_{4',3'}$ = 3.8 Hz, 4'(3'')-H].

5-Dodecyl-2,2'-bithiophene (4b):
From 2-bromothiophene (2.61 g, 16 mmol) and Mg turnings (0.41 g, 17 mmol) in Et_2O (25 mL), the corresponding Grignard reagent was prepared and coupled with bromide **5** (3.31 g, 10 mmol) and Ni(dppp)Cl_2 (55 mg, 0.1 mmol)[24] in Et_2O (25 mL) and the reaction mixture was refluxed for 6 h. After cooling to r.t., the solution was hydrolyzed with cold 0.5 N HCl and extracted several times with Et_2O. The organic phases were combined, washed successively with $NaHCO_3$ solution and water, and dried (Na_2SO_4). Evaporation of the solvent, chromatography (silica gel, 2:1 hexane/CH_2Cl_2), and recrystallization from MeOH/Et_2O afforded pure **4b** as bright yellow solid; yield: 2.90 g (87%); mp 38°C (HPLC > 99%).

^{1}H NMR (250 MHz): δ = 0.81 (3H, t, ^3J = 6.5 Hz, CH_3), 1.25 (18H, m, alkyl-CH_2), 1.58 (2H, m, β-CH_2), 2.65 (2H, t, 7.8 Hz, α-CH_2), 6.67 (1H, d, $^3J_{4,3}$ = 3.5 Hz, 4-H), 6.97 (1H, d, $^3J_{3,4}$ = 3.7 Hz, 3-H), 6.98 (1H, dd, $^3J_{4',3'}$ = 3.7 Hz, $^3J_{4',5'}$ = 5.0 Hz, 4'-H), 7.09 (1H, dd, $^3J_{3',4'}$ = 3.6 Hz, $^4J_{3',5'}$ = 1.1 Hz, 3'-H), 7.15 (1H, dd, $^3J_{5',4'}$ = 5.1 Hz, $^4J_{5',3'}$ = 1.1 Hz, 5'-H).

5-Dodecyl-2,2':5',2''-terthiophene (4c):
From bromide **5** (7.29 g, 22 mmol) and Mg turnings (0.56 g, 23 mmol) in Et_2O (30 mL), the corresponding Grignard reagent was prepared under heating to reflux for 2 h, and with the aid of an ultrasonic bath and a few drops of dibromoethane as entrainer. The Grignard solution was transferred to the dropping funnel of a second apparatus via cannula and was added dropwise, through a frit, to an ice-cooled suspension of bromobithiophene **2b** (4.90 g, 20 mmol) and Ni(dppp)Cl_2 (110 mg, 0.2 mmol) in Et_2O (30 mL). The mixture was refluxed for 24 h, cooled to r.t., and hydrolyzed with 1 N HCl. The Et_2O phases were separated, neutralized, washed with water, dried over Na_2SO_4, and evaporated. The residue was recrystallized from hexane and was subjected to MPLC (silica gel, hexane). The first fraction afforded pure 5,5'-didodecyl-2,2'-bithiophene (**6b**) as colorless solid; yield: 0.5 g (6%); mp 64–65°C (HPLC > 99%).

^{1}H NMR (250 MHz): δ = 0.88 (6H, t, ^3J = 6.9 Hz, CH_3), 1.26 (36H, m, alkyl-CH_2), 1.66 (4H, m, β-CH_2), 2.76 (4H, t, 7.5 Hz, α-CH_2), 6.64 (2H, d, $^3J_{4(4'),3(3')}$ = 3.6 Hz, 4(4')-H), 6.89 (2H, d, $^3J_{3(3'),4(4')}$ = 3.5 Hz, 3(3')-H).

Pure **4c** as bright yellow solid was isolated a second fraction; yield: 5.07 g (61%); mp 75–76°C (HPLC > 99%).

^{1}H NMR (250 MHz): δ = 0.88 (3H, t, ^3J = 6.8 Hz, CH_3), 1.26 (18H, m, alkyl-CH_2), 1.67 (2H, m, β-CH_2), 2.79 (2H, t, 7.5 Hz, α-CH_2), 6.68 (1H, d, $^3J_{4,3}$ = 3.6 Hz, 4-H), 7.06–6.97 (4H, m, 4'-H, 3'-H, 4''-H, 3-H), 7.15 (1H, dd, $^3J_{3'',4''}$ = 3.6 Hz, $^4J_{3'',5''}$ = 1.1 Hz, 3''-H), 7.20 (1H, dd, $^3J_{5'',4''}$ = 5.1 Hz, $^4J_{5'',3''}$ = 1.1 Hz, 5''-H).

5-Dodecyl-2,2':5',2'':5'',2'''-quaterthiophene (4d):
Following the conditions given for the synthesis of **4c**, the Grignard reagent of **5** (2.83 g, 8.6 mmol) and magnesium turnings (0.22 g, 9 mmol) in Et_2O (15 mL) was coupled with bromoterthiophene **2c** (1.0 g, 3.1 mmol) and Ni(dppp)Cl_2 (16.6 mg, 0.03 mmol) in Et_2O/benzene (2:1, 25 mL). After refluxing for 64 h, workup was performed. Chromatography (silica gel, hexane) of the remaining material gave unreacted **2c** as the first fraction; by further elution with CH_2Cl_2 the orange-red product was obtained which was recrystallized from benzene to give **4d**; yield: 0.91 g (59%); mp 156–158°C (HPLC > 99%).

^{1}H NMR (250 MHz): δ = 0.81 (3H, t, ^3J = 6.3 Hz, CH_3), 1.26 (18H, m, alkyl-CH_2), 1.55 (2H, m, β-CH_2), 2.79 (2H, t, 7.5 Hz, α-CH_2), 6.69 (1H, d, $^3J_{4,3}$ = 3.6 Hz, 4-H), 7.00 1H, d, $^3J_{3,4}$ = 3.6 Hz, 3-H), [6.98 (1H, d, ^3J = 3.4 Hz), 7.05 (2H, d, ^3J = 3.8 Hz), 7.08 (1H, d, ^3J = 3.8 Hz) 3'-H, 4'-H, 3''-H, 4''-H], 7.03 (1H, dd, $^3J_{4''',5'''}$ = 5.1 Hz, $^3J_{4''',3'''}$ = 3.6 Hz, 4'''-H), 7.17 (1H, dd, $^3J_{3''',4'''}$ = 3.6 Hz, $^3J_{3''',5'''}$ = 1.2 Hz, 3'''-H), 7.22 (1H, dd, $^3J_{5''',4'''}$ = 5.1 Hz, $^4J_{5''',3'''}$ = 1.2 Hz, 5'''-H).

2-Bromo-5-dodecylthiophene (5):
In the absence of light, a solution of NBS (8.9 g, 50 mmol) in DMF (30 mL) was slowly added dropwise to an ice-cooled solution of 2-dodecylthiophene **4a** (12.6 g, 50 mmol) in DMF (30 mL), and the mixture was stirred for 4 h at r.t. Workup and fractionated distillation gave **5** as yellowish liquid; yield: 14.5 g (87%); bp 120–125°C/0.001 Torr; (GC > 98%).

^{1}H NMR (250 MHz): δ = 0.88 (3H, t, 6.8 Hz, CH_3), 1.26 (18H, m, alkyl-CH_2), 1.62 (2H, m, β-CH_2), 2.73 (2H, t, $^3J_{1',2'}$ = 7.3 Hz, α-CH_2), 6.52 (1H, dt, $^3J_{4,3}$ = 3.6 Hz, $^4J_{4,\alpha\text{-}CH_2}$ = 0.8–0.9 Hz, 4-H), 6.83 (1H, d, $^3J_{3,4}$ = 3.7 Hz, 3-H).

5,5''-Didodecyl-2,2':5',2''-terthiophene (6c):
The corresponding Grignard reagent prepared from bromide **5** (8.78 g, 26.5 mmol) and Mg turnings (0.73 g, 30 mmol) in Et_2O (30 mL), was coupled with 2,5-dibromothiophene **1b** (1.94 g, 8 mmol) and Ni(dppp)Cl_2 (22.3 mg, 0.04 mmol) according to the procedure described for **4c**. The reaction time was extended to 64 h in this case. After workup and recrystallization from hexane **6c** was isolated as bright yellow solid; yield: 3.87 g (81%); mp 97–98°C (HPLC > 99%).

^{1}H NMR (250 MHz): δ = 0.88 (6H, t, ^3J = 6.8 Hz, CH_3), 1.26 (36H, m, alkyl-CH_2), 1.67 (4H, m, β-CH_2), 2.78 (4H, t, 7.5 Hz, α-CH_2), 6.67 [2H, d, $^3J_{4,3(4'',3'')}$ = 3.6 Hz, 4(4'')-H], 6.96 (4H, m, 3-H, 3'-H, 4'-H, 3''-H).

5,5'''-Didodecyl-2,2':5',2'':2'',5'''-quaterthiophene (6d):
The corresponding Grignard reagent prepared from bromide **5** (3.98 g, 12 mmol) and Mg turnings (0.34 g, 14 mmol) in Et_2O (10 mL), was coupled with 5,5'-dibromobithiophene (**3b**) (1.62 g, 5 mmol) and Ni(dppp)Cl_2 (54 mg, 0.1 mmol) in Et_2O (50 mL) according to the procedure described for **4c**. After workup and recrystallization from hexane/toluene (1:2) **6d** was isolated as an orange solid; yield: 2.35 g (70%); mp 163°C; (HPLC > 99%).

^{1}H NMR (250 MHz): δ = 0.88 (3H, t, ^3J = 6.7 Hz, CH_3), 1.26 (18H, m, alkyl-CH_2), 1.56 (2H, m, β-CH_2), 2.79 (2H, t, 7.4 Hz, α-CH_2), 6.88 [2H, d, $^3J_{4,3(4''',3''')}$ = 3.6 Hz, 4(4''')-H], 6.98–6.99 (4H, ^3J = 3.3 Hz, 3'-H, 4'-H, 3''-H, 4''-H), 7.08 [2H, d, $^3J_{3,4(3''',4''')}$ = 3.7 Hz, 3(3''')-H].

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